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## EDITORIALS

### CHEMICAL ENGINEERING IN THE UNIVERSITY AND ITS RELATION TO THE INDUSTRIES

The functions of many of the departments of a university are capable of being extended to the fields of pure scientific training and research without regard to the direct applicability of the results to the industries and arts. A department of Chemical Engineering is, however, necessarily so intimately related to industrial work that it is dependent upon the industries for its guidance and development, and its success is measured solely by its achievements in furthering industrial progress.

It is believed that one of the most important functions of a course in chemical engineering is to train men who will ultimately be able, after the proper post-school experience, to take an important part in developing, designing, erecting and directing manufacturing plants and processes along sound scientific and economic lines. Engineers and works managers are produced from suitably trained graduates only through an additional process of evolution in which judgment matures, resourcefulness develops, efficiency improves, and that as yet undefined sense is acquired which seems to result from the accumulation of experience, preferably gained at considerable cost and expenditure of time. The schools make no pretense of being able to turn out finished engineers or works managers, but try to develop a good prospect from which engineers and managers may be evolved by proper and careful treatment. Obviously the making of a finished industrial man is a work of considerable magnitude, and, when it is well done, may be regarded, with pardonable pride, as a work of art.

The problem appears in its two phases to show an apparent line of cleavage between that portion of the work to be done by the schools and that portion to be done by the industries. The development of these men for positions of responsibility thus becomes a duty which is shared jointly by the school and the industry. The school is responsible for the fundamental training, for the man's general knowledge and for workable methods of its application to typical, but by no means all, industrial problems. The industry, on the other hand, is responsible to the graduates it employs for an opportunity to use their training to advantage, to exercise such natural or acquired talent as they may have, and to gain the essential experience with its resultant maturity of judgment. If a prospect has it in him this two-stage treatment is bound to produce a man who will advance industrial development and render valuable services to his employers.

It goes without saying that the combined efforts of the school and the industry sometimes fail to accomplish highly satisfactory results. In other words, we do not get a 100 per cent yield from our coöperative "captain of industry factory." If this failure is chargeable to the school it is not surprising when we consider that an educational plant is the only pro-

ductive institution in the world which is not permitted to select and classify the raw materials from which its finished product is to be made. It is well known that the most effective way of controlling the quality of the product of any other plant is by the rigid inspection and selection of raw materials. The material from which engineers are to be made is put through an examination of one dimension, which usually shows how well memory has been developed and nothing more, while physical fitness, temperament, instinctive ability and sense of proportion—all so essential in engineering work—are left out of the consideration. This lack of control over our raw materials accounts in a large measure for the misfits among technical graduates. The industries appear at times to fail to appreciate this difficulty inherent in present-day educational work, and expect too much. On the other hand, industrial managers sometimes contribute to failures among good men by not accepting their full responsibility for the development of the men they employ, and by not offering graduates suitable opportunity for the use and exercise of their natural ability as well as their training.

The technical schools have undertaken to provide that portion of the training which they are best able, from the nature of their environment, to give: (1) the development of general knowledge and the fundamental sciences which underly the profession; (2) illustrations of the use of scientific knowledge as applied to specific industrial problems; and (3) practice in the methods of applying such training and knowledge to productive work.

Courses of instruction should be planned partly upon the instructors' experience and knowledge of industrial conditions and requirements and partly upon the suggestions and advice of experienced industrial managers. Only in this way can the school work be coordinated, from the beginning, with that of the industrial manager.

An important part of the university's work is to coöperate with industrial managers in the selection from among its graduates of the men most suitable for their organizations. In making recommendations, all the requirements of a position should be carefully considered and those men selected who are nearest fitted by temperament, talent and training to offer good prospects of success. It is not the case, as is sometimes assumed, that endorsement is governed entirely by a student's ability to pass examinations—this is often the least important of qualifications—not that the value of good scholarship should be depreciated, but it simply should take its place along with such other equally important qualities as judgment, self-reliance, dependability, tact, a sense of proportion, etc.

The university is not always effectively assisted in matching men to the opportunity by the employers, because their inquiries often lack definiteness and directness of statement as to the nature and scope

of the work required. Furthermore, some managers do not appear to understand the functions of the chemist or the chemical engineer, while still others fail to recognize the laws of supply and demand among young technical graduates and completely undo all good intentions of the educational institution by arbitrarily establishing a salary schedule and other conditions which result in their getting the culls of the classes.

The acceptance of a position by a young graduate is a matter of serious consequence to him, to the school which sends him out and a matter of first importance to an employer who is desirous of making a real addition to his organization. Graduates should be advised, especially in their first jobs, and directed into the particular positions for which they are best fitted by training and personality to succeed, and where the opportunities for success are promising. To that end the school needs to enjoy the confidence of the employers in order that the conditions surrounding the position and its future prospects, so far as they are developed, may be mutually understood. With such coöperation men would be selected with better judgment, and much of the criticism which now arises in regard to misfits would be eliminated.

Graduates frequently return for advice in regard to making a new start on account of real or imaginary conditions which exist in connection with their positions. Here is a chance to render real service, but it is impossible to advise correctly and justly without a full understanding of the relation of the employer to the grievance of the employee. Sometimes personal acquaintanceship and a willingness on the part of the employer to coöperate clear up the situation, but at other times such an understanding appears to be difficult or impossible of attainment, with the result that dissatisfaction develops on both sides.

Probably the most important function of the educational institution directly available to the industries, to-day, is the offering of facilities for productive research.

It seems to be necessary now to be more specific when we are discussing research. First of all, we have the self-styled "Pure Research" which we shall not attempt to define because its chief charm seems to lie in its vagueness, lack of direction or purpose and its undefinability. Then we have industrial research, the disclosed motive of which is productive results, and from these, profits. Again we have research for political purposes in which the investigations and reputations of modest and hard-working scientific men are blatantly flaunted throughout the country for the admitted purpose of creating political favor for some department or bureau of the government. *Research* is becoming a well-known word in our daily language, due largely to the activity of the press agents and, like the word *conservation*, it will be made to serve many masters.

The one point upon which industrial and educational men seem to agree is that research, both pure and for direct application to productive work, is essential to industrial progress, but we do not always

agree upon the amount of time which should be spent and the kind of talent which should be devoted to fishing in the open sea of knowledge with all kinds of bait, nor what type of men should be put to work in known fishing grounds with approved bait. Much of such discussion is academic and would seem to call for reconsideration in view of world conditions as they exist to-day.

The average manufacturing concern cannot afford the organization and equipment necessary for carrying out real research. The usual environment of the factory is not favorable to good research work. The slow progress and deliberate methods of research have been found to be out of keeping with the bustling activity of men whose slogan is, "the production of a product at a profit," and whose constant concern is to fill the orders when and as promised. Research under such conditions soon makes way for the more pressing, more important work of production, and thus the researcher joins the procession engaged in making goods, testing raw materials or analyzing the last delivery of coal. Constant interruptions, lack of ample library facilities, the absence of sympathetic surroundings and the encouragement, stimulation and inspiration of fellow-workers, constitute the natural conditions surrounding research in the ordinary factory—and we could not expect it to be otherwise in an organization where *capacity* and *output* are the only achievements recognized.

The exceptional resources of some of our larger corporations have made it possible to create and maintain highly efficient research organizations within the plant, as an independent body. Such research laboratories when surrounded with the proper conditions and safeguarded from the encroachments of the manufacturing departments have done wonderful work, but this solution of the industrial research problem is expensive and one not within the reach of the great majority of our industries.

The facilities of the technical schools would appear to offer the simplest and promptest solution of the problem of industrial research. Besides the fully equipped laboratories and libraries, they have, ready made, those other important considerations: the atmosphere of research, the interested and helpful associates, the counsel and advice of specialists in a wide variety of fields and other advantages too numerous to mention. Furthermore, the educational institutions have at their command a large body of graduates from which to pick those likely researchers who have the natural instinct, enthusiasm and ambition to undertake the task of putting science to work for industry. Such men as these, armed with a real problem of industrial importance, availing themselves of all the facilities and favorable conditions of an institutional research laboratory, can and do get results. Their researches serve to broaden the training and usefulness of the investigators and sharpen their appetite for productive results.

The laboratories of a number of universities and technical schools meet the manufacturer and the consulting chemical engineers more than half way



by furnishing a place to serve the needs of industry and render service in the solution of its real problems. Chemical laboratory reactions may be taken into such chemical engineering laboratories and developed in commercial sized apparatus, on a scale sufficiently large to enable the investigators to establish dependable chemical engineering data on which to base plant or process design and cost estimates. The purchase of such facilities for a particular investigation would require weeks or months of valuable time and a prohibitive outlay of money, while in such a place the use of such apparatus may be obtained for as long or short a time as may be necessary and without delay.

There comes a time in every business when it is either necessary or desirable, for sound business or economic reasons, to convert the marketable resources of the institution into cash. Later, when the crisis is over, the balance may be readjusted to its normal conditions. In certain games of chance, with which you are doubtless all familiar, the process is known as "cashing in."

To-day we are witnessing the most appalling crisis in the world's history, when culture, however you may elect to spell the word, is literally being shot to pieces in Europe, when whole nations are being wiped off the map, when this country is dangerously near and obviously will sooner or later be involved, and when the *application* of every known fact and principle of science is the only hope of self-preservation. Is this not the time to think seriously of "cashing in" our scientific knowledge and converting it from resources of doubtful value into real tangible assets? Is this not a crisis in which it is not so much a matter of increasing the general stock of useful knowledge as it is of preserving and making available for immediate use what we have?

The development of applications of science requires ability and talent of the highest order. More Ph.D.'s are *earned* every year in the applications of science to industry than are conferred in all the institutions of the land. Arguments as to the relative merits of pure and applied research are beside the mark even in ordinary times; to-day such discussions are footless. American industry must now *mobilize* her scientific resources for national defense, for self-preservation and for future growth, and we believe every technical laboratory in America is ready and every qualified man of research ability is anxious to be shown a research problem, the solution of which will advance industrial progress.

#### THE ORIGIN OF PETROLEUM AND ASPHALT<sup>1</sup>

Of the many theories proposed to explain the origin of petroleum none appears to the writer as being in any way satisfactory or sustained by the evidence offered in support of them. For this reason he has not accepted any of them as tenable nor taken part

in any way in the discussion of this question. With the recent extension of our comprehension of the relation and behavior of surfaces and films as the result of studies involving the principles of colloidal chemistry and the phenomena of adsorption connected with surfaces, a new theory has been opened for the interpretation of the question of the origin of the liquid and solid forms of native bitumen. In the study of the behavior of surfaces and films, bitumen and colloidal matter, meaning thereby matter which is sufficiently subdivided to produce distinct and easily recognized phenomena as they are exhibited in the Island of Trinidad, it was recognized that the origin of the more or less solid bitumen, which forms the well-known asphalt found there, was to be attributed to the conversion, by surface phenomena, of a heavy petroleum into the asphalt by the surface action of a colloidal clay upon the soft bitumen, as described in previous papers [*J. Phys. Chem.*, **19** (1915), 241 *THIS JOURNAL*, **7** (1915)]. It was shown that the heavy petroleum rising from the oil sands through a paste of colloidal clay and water, was emulsified therewith by the violent action of escaping natural gas and that this emulsion of oil and colloidal material was converted, after reaching the surface, into a solid asphalt.

In view of this phenomenon, in which the action of colloidal material on petroleum is so plainly demonstrated, it seems to the writer that the origin of all forms of petroleum must be attributed to similar surface action between a natural gas and the "sands," using this term in a general sense, with which it comes in contact.

The character of petroleum formed in this way will be dependent on two conditions: (1) the nature of the gas itself; and (2) that of the "sand." If the gas contains sulfur, a sulfur petroleum will be formed, but otherwise one free from it. If the "sands" contain sulfur a type of petroleum will result which may be quite different from that originating from a gas containing sulfur. This might explain the difference between a Trinidad and a Mexican petroleum in which the sulfur is present in quite different forms. If the sand is of a colloidal nature and consequently much more active, the asphaltic petroleum will be originated, whereas if it is more of a true sand, with much less surface action, oil of a paraffin nature may result.

It seems that the phenomena of surfaces and films, as demonstrated by the recent developments of colloidal chemistry, open up an entirely new point of view for the interpretation of the origin of petroleum and asphalt and one which will be, no doubt, widely developed in the future.

In presenting this theory of the formation of petroleum in its different types, it is unnecessary to carry the theory further back than the change which takes place in a natural gas, as to the origin of which, while there are many theories, it is, perhaps, unnecessary to speculate at present.

<sup>1</sup> Presented before the American Petroleum Congress, San Francisco, October 25, 1915.

WOOLWORTH BUILDING  
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CLIFFORD RICHARDSON

## ORIGINAL PAPERS

POLYMERIZATION OF CHINESE WOOD OIL<sup>1</sup>By CARL LOUIS SCHUMANN<sup>2</sup>

Received October 21, 1915

## PRODUCTION OF CHINESE WOOD OIL

Chinese wood oil or tung oil is derived from the seeds of the trees, *Aleurites Montana*<sup>3</sup> and the *Aleurites Fordii*,<sup>4</sup> each species occupying for the most part distinct geographical areas. The former is a native of the southeastern parts of China, and is also cultivated there; the latter, the more hardy relative of the *Aleurites Montana*, is a native of the central and northern parts of China, and is also cultivated in Algiers. The *Aleurites Fordii* yields fully nine-tenths of the tung oil exported from China. The *Aleurites Cordata*<sup>5</sup> occurs in Southern Japan: the oil from this tree, however, is used locally and does not at present figure as an article of exportation. These three distinct species of trees are plants belonging to the family of Euphorbiaceae.

A great deal of confusion has arisen through the indiscriminate use of various names for the *Aleurites Montana* and the *Aleurites Fordii*, some being provincial localisms of China and some being botanical synonyms.<sup>3</sup>

The tung oil tree grows luxuriantly in the warmer parts of China, thriving upon the poorest of soils, such as the rocky and stony portions. The banks of the rivers afford very favorable conditions for this quick-growing and short-lived tree. It usually attains a height of six or seven meters and rarely a height of ten. The tree is highly ornamental, especially while in bloom; it is then covered with small white flowers stained with pink. The leaves are long-pointed, heart-shaped at the base, and dark shining green in color. The fruit, which ripens in September or October, changes from an apple-like green to a dull brown color. It contains from three to five light brown seeds, which are enclosed in a fibrous flesh. The seeds consist of about 49 per cent shells and 51 per cent meat. The kernels contain from 50 to 53 per cent oil, of which 40 to 42 per cent can be extracted by pressing. This oil is of an exceedingly poisonous character.

The cold drawn oil obtained by pressing is pale yellow in color, and is termed white tung oil; it has a peculiar and characteristic nutty odor and unpleasant taste. The oil obtained by hot pressing is dark brown in color and is termed black tung oil. It has a stronger smell than the light pressed oil, which precludes its use for many purposes, and it is therefore largely consumed in China.

Due to the lack of efficient means of transporta-

tion throughout China the individual grower of the tung oil tree presses the oil from the seeds, and uses the presscake as a fertilizer or for making lampblack. This presscake, on account of its poisonous qualities, cannot be used as a fodder. He then carries the oil to market in bamboo baskets lined with oiled paper. From these local markets the excess oil gradually finds its way to the ports of Hankow and Wuchow, from whence the chief shipments are made to other countries.

When we take into consideration the crude methods employed in pressing out the oil and the opportunities offered for adulteration, as well as possible variations in analytical procedure, it is not to be wondered that there has been a lack of concordant results obtained upon the several analytical constants of commercial samples of chinawood oil.

Recent investigators working upon authentic samples of this oil have been able to check much closer in the determination of these constants. This would indicate that adulteration may have been a decided factor in the variation first observed. Wilson<sup>1</sup> believes that soya bean and sesame oils are chiefly used as adulterants.

In 1900, 21,960 tons of the white drawn oil were exported from Hankow, and 1627 tons from Wuchow; in 1910, 50,338 tons were exported from Hankow and 3,465 tons from Wuchow. A few years ago comparatively little Chinese wood oil was imported into the United States, the bulk of the oil going to Europe. Recently, however, the consumption in the United States has increased enormously. This decided increase has induced the United States Department of Agriculture to investigate the possibilities of starting a tung oil industry in the United States.

In 1905 a quantity of Chinese wood oil nuts was imported from Hankow by the United States Department of Agriculture. They were planted in California and a year later were sent out as one-year-old trees. The trees proved easy to cultivate, doing especially well in the states of Georgia, Louisiana, South Carolina, Alabama, Florida and Mississippi. The first fruits were collected five years later in such quantities as to demonstrate that the tung oil industry is feasible in the Southern states. The trees require little attention and but little labor is involved in gathering and husking the fruits. Although the freight rate from the Southern states to New York is somewhat higher than the rate by water from Hankow to New York the cheap lands and the use of team labor here may offset this handicap, and that of the difference in price of labor.<sup>2</sup>

We can gather some idea as to the valuable qualities of Chinese wood oil from the variety of uses to which the Chinese have put the oil. The Occidental nations are just beginning to realize the possibilities of this wonderful natural varnish. In China it serves primarily as a natural varnish for their boats, houses, furniture, and as a waterproofing material for their

<sup>1</sup> A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

<sup>2</sup> Holder of the Acme White Lead & Color Works Fellowship, 1915.

<sup>3</sup> Wilson, *Bull. Imp. Inst.*, London, England, 2, No. 3 (1913), 441 to 461.

<sup>4</sup> Hemsley, *Hooker's Icon.*, xxix ff., 2801, 2802 (1906); Fairchild in the *U. S. Dept. Agr. Circ.*, 108 (1913).

<sup>5</sup> R. Brown, *apud Steudel, Nomend. Bot.*, 1821, 286; Mueller, *Arg. in DeCandolle, Prodr.* xv., Pt. II, 724 (quoad specimina Japon.) (1966); Hayata, *Jour. Coll. Sci. Tokio*, 20 (1904), art. 3, 55 (Rev. Euphorb. Jap.) (quoad plantam Japon.); Hemsley, *Kew Bull. Misc. Inform.*, 1906, 120 (quoad specimina Japon.); Matsumura, *Ind. P. Jap.*, ii, 300 (exclud. synon. Vernicia Montana) (1912).

<sup>1</sup> Loc. cit.

<sup>2</sup> Fairchild, *Oil, Paint and Drug Reporter*, Nov. 18, 1912, p. 36.



paper umbrellas. It is likewise used as an illuminant, as a medicine, in the manufacture of silk, and as a building material when mixed with sand, clay and lime. In the United States and the European countries its main use is in the manufacture of paint driers and rosin-china-wood oil varnishes. A large number of patents have been taken out in Germany and the United States for the utilization of this oil in the manufacture of linoleum, rubber substitutes and waterproof paper, but the extent to which it is being used cannot be stated because of the reticence of manufacturers to expose the details of their business. At present its chief importance is as a varnish material, for it is a recognized fact that with rosin it makes a varnish superior to any linseed-rosin varnish on the market.

The varnish manufacturer, upon the introduction of Chinese wood oil as a varnish material, soon observed peculiar variations in the products he obtained upon heat-treating tung oil, especially marked with different oils. This lack of uniformity was thought to be due to excessive adulteration, and many attempts have been made to find a standard method of analysis for this oil.

In spite of the number of investigators interested in finding a suitable method for testing the purity of the oil little actual progress had been made up to the last year or so. The efforts of the "Oil Committee" of the American Society for Testing Materials<sup>1</sup> have been instrumental in standardizing the methods of analysis to a point where they are much more reliable in the hands of different operators.

The constants for the oil were found by the Committee to agree remarkably closely for authentic samples of tung oil, which had not been the case with the oils previously examined.

In testing out in this laboratory the several proposed methods, interesting results were obtained, particularly when working with the "iodine-jelly" test. The samples sent out by the Committee were tested by this method and it was found that both the pure oil and the adulterated samples jellied in less time than we had been led to expect from work previously reported from other laboratories. This acceleration of the jelling was probably due to differences in choroform used, as it was found that certain substances act very decidedly in catalyzing the reaction. For instance, by the addition of a very small quantity of alcohol the jelly formation is retarded several hours, while a slightly larger amount of alcohol will entirely prevent it. Following the regular procedure it was possible to retard the jelly formation to the time specified only by diluting the iodine solution to considerably below the strength specified for the method. The above phenomenon is thus analogous to the jelling of heat-treated oils and is subject to the same retardation and prevention as is exhibited by them.

#### CONSTITUTION OF CHINESE WOOD OIL

Chinese wood oil is composed mainly of the glycerides of oleic and elaeomargaric acids.<sup>2</sup> Lewko-

<sup>1</sup> Reprint of Report of Committee D-1, American Society for Testing Materials (1915).

<sup>2</sup> Lewkowitsch, "Chemical Technology of Oils, Fats and Waxes," 1909.

witsch prefers the use of the name "elaecomargaric" acid to that of "elaostearic" acid used by many investigators, and states that it is an isomer of linolic acid.

In this paper the term elaeomargaric acid will be used for the acid of the fresh glyceride, and the term  $\beta$ -elaostearic acid for the acid of the stereoisomeride of elaeomargaric acid, formed under the influence of light rays.

Cloez<sup>1</sup> reported 24 per cent oleic acid and 72 per cent elaeomargaric acid in Chinese wood oil. The elaeomargaric acid he found to have a melting point of 48° C., it being a crystalline solid. When this acid was exposed to the light or to the action of carbon bisulfide it was transformed into what he called a "polymer,"  $\beta$ -elaostearic, melting at 72° C. He also mentioned that the same transformation occurred with the glyceride of elaeomargaric acid into  $\beta$ -elaostearic acid glyceride. He assigned the formula  $C_{17}H_{30}O_2$  to elaeomargaric acid.

Later Maquenne<sup>2</sup> repeated the experiments of Cloez: he declared the formula to be  $C_{18}H_{30}O_2$  instead of  $C_{17}H_{30}O_2$ , as given by Cloez, and named it elaeostearic acid. Upon oxidation with potassium permanganate he obtained *n*-valeric and azelaic acids; the question of the number and position of the double bonds he left open. He disagreed with Cloez that  $\beta$ -elaostearic acid is a polymer of elaeomargaric acid as he believed it to be an isomer instead.

Moritz Kitt<sup>3</sup> subjected the acid to oxidation with alkaline potassium permanganate, and observed that a part remained unchanged and also that small amounts of dioxystearic acid, a water-soluble acid, some lower fatty acids, and carbonic acid were formed. Kitt likewise mentions the formation of the isomer of elaeomargaric acid through the action of light rays, and ascertained that this isomer could be distilled under a vacuum without decomposition.

Norman<sup>4</sup> and Morrel<sup>5</sup> both mention the fact that the rate of change of elaeomargaric acid glyceride into its stereoisomeride, under the influence of light, is very slow. Morrel noted that this change was accelerated by the removal of the quantity first formed and by treatment with acetone. Meister believes that the quick formation of a film, when Chinese wood oil dries, is due to this transformation of elaeomargarine into elaeostearine.

Kametaka<sup>6</sup> repeated the oxidation experiments of Kitt with alkaline potassium permanganate and obtained sativic and dioxystearic acids. On bromination he obtained the tetrabromide and not the hexabromide, as might have been expected from the work previously done on this acid. This indicated the presence of only two double bonds, a conclusion likewise drawn by Walker and Warburton.<sup>7</sup>

Majima,<sup>8</sup> using the ozone method, worked out by

<sup>1</sup> *Compt. rend.*, **81** (1875), 469; **82** (1876), 501; **83** (1876), 943.

<sup>2</sup> *Ibid.*, **135** (1903), 686; *Jour. Chem. Soc.*, **83** (1903), 1042.

<sup>3</sup> *Chem. Ztg.*, **23** (1899), 23 and 38.

<sup>4</sup> *Chem. Zentr.-Blatt*, **1** (1907), 1207.

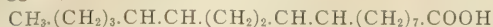
<sup>5</sup> *Transactions Chem. Soc.*, **101** (1912), 2082.

<sup>6</sup> *Jour. Coll. Sci. Tokio*, **25** (1908), Art. 3, p. 1-8.

<sup>7</sup> *Analyst*, **27** (1902), 238.

<sup>8</sup> *Ber.*, **24** (1909), 674.

Harries,<sup>1</sup> identified the cleavage products, azelaic and *n*-valeric acids. He was not able, however, to prove the presence of succinic acid, which should be also formed if the formula he gave for elaeomargaric acid was correct. This acid was later found by Schapringer,<sup>2</sup> using the same ozone method of Harries, thus establishing with certainty the following formula suggested by Majima:



Schapringer stated that this acid is a stereoisomeride of linolic acid. Fahrion,<sup>3</sup> however, pointed out that the formula worked out by Goldsobel<sup>4</sup> is distinguished from the elaeomargaric acid formula in the position of the double bonds and is thus not a stereoisomeride but an isomer of linolic acid.

Fahrion<sup>5</sup> concluded from his work upon tung oil that the main constituent of the fatty acids of wood oil is elaeomargaric acid, besides about 10 per cent of oleic acid and from 2 to 3 per cent of saturated fatty acids. This percentage of elaeomargaric acid is just a little higher than that calculated by Kame-taka,<sup>6</sup> who gave 86 per cent of this glyceride and 14 per cent olein.

From the results obtained in this laboratory by crystallizing out the elaeomargaric acid according to the procedure as outlined in the experimental part, as well as from the potassium soap and light break methods,<sup>7</sup> the writer should judge that the percentage of elaeomargaric acid tri-glyceride present in raw Chinese wood oil is still higher than reported by Fahrion, varying from 90 per cent for the darker to 94 per cent for the light colored cold pressed oil.

#### GELATINATION OF CHINESE WOOD OIL

The most striking characteristic of Chinese wood oil is the property of being transformed by heat into a transparent, solid mass possessing considerable elasticity in the softer condition, and then becoming more brittle as further heat is applied. Throughout the literature upon tung oil we find a large number of statements regarding this ability to polymerize to a solid product when heated to certain temperatures for definite periods of time, yet a satisfactory explanation of the causes for this transformation has not been given, although several investigators have advanced theories to account for the phenomenon.

Cloez,<sup>8</sup> Zucker<sup>8</sup> and Norman<sup>9</sup> observed that there is a decrease in the iodine number from 163, for the original oil, to an iodine number of 107.7 of the polymerized Chinese wood oil, and that the saponification value is subject to a slight increase.

Jean<sup>10</sup> assumed that the gelatination is due to a sudden, unusual oxygen absorption. Moritz Kitt,<sup>11</sup>

however, opposed the views held by Jean, maintaining that the oxygen could hardly penetrate to the lower part of the oil, as would have to be the case in order to explain uniform gelatination. This theory of Jean was further disproved by Jenkins,<sup>1</sup> who found that tung oil polymerizes to a clear, elastic solid out of air when heated to 180° C. and finally to 250° C.

This gelatination Kitt<sup>2</sup> believed to be due to polymerization through the formation of intramolecular anhydrides of the nature of lactones, these being subsequently formed from the fatty acids freed by a partial cleavage of the tung oil with liberation of glycerine.

Schapringer<sup>3</sup> assumed that gelatination of Chinese wood oil is somewhat different from the bodying of linseed oil. From his experiments he concluded that the gelatination proceeded in two distinct stages, the former as a progressive change and the latter as an instantaneous one. He declared it to be a "mesomorphic polymerization,"<sup>4</sup> since there is formed during the first stage an intermediate product, soluble in benzol, while in the second stage an insoluble final product is formed with an evolution of heat. He did not find the decrease in glycerine content observed by Moritz Kitt, nor that decomposition products appeared during polymerization.

Since the saponification value remains practically constant and the small acid number decreased to a fraction of one per cent, Schapringer thinks that these fatty acids alone form anhydrides, and that the union takes place between the double bonds, as stated by Fahrion.<sup>5</sup>

Schapringer based his conclusion that mesomorphic polymerization takes place, mainly upon the comparative solubilities of the intermediate and final product. He was confronted with the fact that the changes of the constants of wood oil are different on heating to different temperatures, and to explain this he assumed that at various temperatures the reaction proceeds differently, and consequently at each of these temperatures, different intermediate products are formed.

Fahrion, in this earlier paper, stated that the polymerization of Chinese wood oil is analogous to the thickening of linseed oil,<sup>6</sup> taking place through dissolution of the double bonds. This agrees with the molecular weight determinations of Norman,<sup>7</sup> who found a molecular weight of about 440 for the fatty acids from the raw oil and around 800 for the fatty acids from the heated oil.

The next paper by Fahrion appeared shortly after the dissertation of Schapringer had been completed. He then goes into greater detail upon the phenomena of gelatination, and points out that the conclusion of Schapringer, that "mesomorphic polymerization" takes place, can hardly be correct.

<sup>1</sup> *J. Soc. Chem. Ind.*, **16** (1897), 194.

<sup>2</sup> *Chem. Zentr.-Blatt*, **2** (1905), 1469.

<sup>3</sup> *Loc. cit.*

<sup>4</sup> Kronstein, *Ber.*, **35** (1902), 4150-4153.

<sup>5</sup> *Farben-Ztg.*, **17** (1912), 2583-2584.

<sup>6</sup> *Z. für angew. Chem.*, **5** (1892), 174; Leeds, *J. Soc. Chem. Ind.*, **13** (1894), 203.

<sup>7</sup> *Loc. cit.*

<sup>1</sup> *Ber.*, **39** (1906), 2844, 3728; **40** (1907), 4154, 4905; **41** (1908), 1227.

<sup>2</sup> Dissertation, Karlsruhe, 1912.

<sup>3</sup> *Farben-Ztg.*, **18** (1913), 2418-2420.

<sup>4</sup> *Chem. Ztg.*, **30** (1906), 825; *Chem. Zentr.-Blatt*, **1** (1910), 1231.

<sup>5</sup> *Loc. cit.*

<sup>6</sup> *Jour. Coll. Sci. Tokio*, **25** (1908), Art. 4, 1-4.

<sup>7</sup> *This Journal*, **6** (1914), 806.

<sup>8</sup> *Pharm. Ztg.*, **43** (1898), 628.

<sup>9</sup> *Chem. Ztg.*, **31** (1907), 188.

<sup>10</sup> *Ibid.*, **21** (1898), 183.

<sup>11</sup> *Ibid.*, **23** (1899), 38.



Fahrion gives several reasons why he does not believe the polymerization of Chinese wood oil to be analogous to the polymerization of styrolene, cited as a typical mesomorphic polymerization by Kronstein and Seeligman.<sup>1</sup>

One reason he gives is that it is impossible to isolate the intermediate product as has been done with styrolene. He further states that proportions between the changes of the constants of Chinese wood oil are different on heating to different temperatures, and that to explain this Schapringer must not only assume the existence of a special intermediate product for each temperature, but also of several of these intermediate products when he presumes that at different temperatures the reaction proceeds differently. Another reason he gives for not accepting the views of Schapringer is that on heating polymerized styrolene a decomposition takes place with a reformation of the initial product, while such a reformation is not possible with wood oil. He further states that the product of the polymerization of linseed oil does not necessarily have to be the same as that from tung oil, although polymerization in both cases occurs through dissolution of a part of the double bonds. Fahrion is inclined to believe that a transformation product, soluble in the oil up to a certain per cent, is formed. If this per cent be exceeded, gelatination, or colloidal gel formation takes place on cooling. He goes on to say that this polymerization product is insoluble in benzol alone, but dissolves in this medium up to a certain per cent if an excess of the unchanged oil be present. He also mentions the extraction experiments of Schapringer, who found 17.0, 13.7 and 7.4 per cent, respectively, of benzol-soluble matter, while Wolff<sup>2</sup> found up to 80 per cent ether-soluble matter. Wolff, however, triturerated solidified product with sand, which Schapringer did not do.

Chinese wood oil has come to be an important factor in the varnish industry of the world, and it is essential, in order to maintain a more perfect control of the operations of cooking it with other varnish materials, that there shall exist a thorough understanding of its properties and of the change it undergoes in its manipulation by the varnish maker.

In view of the differences in opinion as to the reaction occurring on the solidification of Chinese wood oil, as well as the fact that the data presented is not entirely in harmony with these theories, it was decided to make a study of the polymerization of this oil, and the part polymerization plays in inducing solidification, and to determine, if possible, the influence of other materials in preventing this solidification.

#### EXPERIMENTAL

##### I—PHYSICAL AND CHEMICAL CONSTANTS FOR TUNG OIL

In the following experiments Chinese wood oil was used which gave the following constants:

Acid number.....	4.7
Saponification value.....	190.9
Iodine number (Wijs).....	167.7
Refractive index 20° C.....	1.5182
Specific gravity 15.5° C.....	0.9402
Fatty acids.....	95.1 per cent
Oxyacids.....	1.7 per cent

<sup>1</sup> Dissertation, Karlsruhe, 1906.

<sup>2</sup> *Farben-Ztg.*, **18**, 1171 (1913).

In making saponification determinations on the solidified Chinese wood oil it was observed that the rate of saponification is slow, requiring several days for the hard, solid product formed by continuing the heat treatment for some time after gelatination has taken place. This slow rate of saponification is probably due to the insolubility of the colloid rather than to the difficulty in the saponification of the polymerized material. The soft gels saponified in a comparatively short time, which may be due to the fact that the unchanged oil saponified readily, permitting a larger surface contact of the saponifying solution with the polymerized tri-glyceride. In all cases complete saponification takes place according to the regular procedure, except that the rate is slower.

Norman<sup>1</sup> recommends the evaporation of the alcoholic soap solution to dryness at least once, while determining the saponification value of tung oil, as it saponified with difficulty. Meister<sup>2</sup> followed the above suggestion of Norman but did not state whether he found it necessary to do so. This difficulty of obtaining complete saponification is not confirmed by Fahrion,<sup>3</sup> however, and he does not recommend making the change in the ordinary procedure as suggested by Norman.

In the determination of the iodine numbers of Chinese wood oil in this laboratory no difficulty was experienced in obtaining concordant results by the Wijs method, when following the suggestions of Chapman,<sup>4</sup> who likewise prefers the Wijs method to that of Hübl.

It has been shown by Kreikenbaum<sup>5</sup> and in the Contracts Laboratory<sup>6</sup> of the U. S. Bureau of Chemistry that in the determination of the iodine number the Hanus solution gives abnormally high results on tung oil, and that the Wijs solution gives concordant results only when all the conditions of time, temperature and proportionate amounts of the weight of tung oil to the quantity of solution are identical.

The determination of oxyacids was made according to the method used by Fahrion,<sup>7</sup> which is based on the insolubility of the oxyacids in very light petroleum ether, while the unoxidized acids and the polymerized acid are quite soluble in that solvent. The writer likewise observed that the oxyacids determined in this manner gave a small iodine number, as earlier reported by Fahrion.

##### II—METHOD TO DETERMINE PERCENTAGE OF ELAEO-MARGARIC ACID

The method used in determining the percentage of elaeomargaric acid present in the liberated fatty acids of Chinese wood oil is based upon the property of elaeomargaric acid to crystallize from a dilute alcohol solution at 0° C., while the polymerized, *i. e.*, the dimolecular acid formed by the union of two molecules of elaeomargaric acid through the loss of a double bond in each chain, remains in solution under these

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Chem. Rev. Fett. u. Harz-Ind.*, **1912**, p. 159.

<sup>3</sup> *Chemisch-Technisches Repertorium*, **36** (1912), 672.

<sup>4</sup> *Analyst*, **37** (1912), 543.

<sup>5</sup> *THIS JOURNAL*, **2** (1910), 205.

<sup>6</sup> *Proceedings 7th Intern. Congr. Appl. Chem.*, **1909**, Sect. 1, p. 89.

<sup>7</sup> *Farben-Ztg.*, **17** (1912), 2635, 2636.

conditions. At 0° C. the elaeomargaric acid is comparatively insoluble while the polymerized and oleic acids are quite soluble in the above solvent and do not crystallize from any organic solvent.

**PROCEDURE**—Five grams of chinawood oil, raw or heat-treated, are saponified and the fatty acids liberated. These mixed fatty acids, amounting to approximately 4.760 g., are then dissolved in 40 cc. absolute alcohol and the solution is cooled to 0° C. From 14 to 14.5 cc. water are added, drop by drop, shaking continuously. The amount of water used is dependent upon the relative concentrations of the polymerized and unpolymerized fatty acids present. This solution is then warmed to about 5° C., and allowed to cool slowly and to stand over night at 0° C. The elaeomargaric acid crystallizes out in rhombic flakes, which may be filtered out upon paper held in a specially constructed, ice-cooled copper Buchner funnel. The alcohol is then distilled from the filtrate under reduced pressure at the temperature of a steam bath. The remaining fatty acids may be dried by the addition of absolute alcohol and redistilling the alcohol, after which they may be weighed, and the elaeomargaric acid computed by difference. The amount of elaeomargaric acid remaining soluble in the filtrate under these conditions is about 0.132 g., a correction for which is applied to the weight of elaeomargaric acid as computed. When the percentage of elaeomargaric acid present in the sample under analysis is less than 0.132 g., 0.5 g. of raw tung oil, which is known to be pure, may be added before saponification. This procedure permits the estimation of smaller amounts of elaeomargaric acid in a mixture.

This method was also found to give excellent results in determining the purity of samples of chinawood oil. It has a decided advantage over the methods not founded upon a distinct property of elaeomargaric acid. It further allows examination of the fatty acids from the adulterated oil, contaminated by only a small percentage of oleic and elaeomargaric acids, and is not subject to the extreme precautions necessary in working with the insoluble potassium soap method.<sup>1</sup>

### III—EFFECT OF OXIDATION AND CATALYZERS

The avidity with which tung oil takes up oxygen from the air is striking, our finding being in contrast to the results of Schapringer,<sup>1</sup> who reports that the oxygen merely induces polymerization and does not produce oxidation products during the gelatination experiments. In all cases studied in this laboratory, as has been reported,<sup>2</sup> there have been formed progressively increasing amounts of oxidized products, whenever Chinese wood oil or wood oil mixtures have been heated in air (see Fig. II).

**OXIDATION**—It has been further observed that the oxygen does not act directly as a catalyzer on the rate of polymerization, as stated by Schapringer, but indirectly in the formation of oxidation products which then act as positive catalyzers. Blowing air through heated wood oil had a decided effect upon the time required for gelatination to take place. Without a doubt the products formed by autooxidation had some bodying effect upon the wood oil, but not in proportion to the actual quantity present, as indicated by the consistency of the mixture in the second of the following experiments. It was evident that there was a decided

catalyzing influence, however, on the rate of polymerization.

Chinawood oil solidified when blown at 150° C. in 2½ hours, and at 200° C. in less than 1 hour. Heated in an open dish at 150° C., but not blown, it did not gelatinize before the end of 30 hours. The following experiments were carried out to determine whether the oxygen or oxidation products were responsible for the catalyzing influence.

1—200 grams of Chinese wood oil were heated at 235° C. under an atmosphere of nitrogen, in a glass container, connected to a mercury seal to permit volatile products to escape. A transparent, solid gel was formed at the end of 5½ hours; no gases were given off except at the moment of gel formation.

2—200 grams of a mixture of chinawood oil, containing 15 per cent blown wood oil, were heated under the same conditions as in the above experiment. Identical results took place at the end of 1½ hours.

3—200 grams of Chinese wood oil were heated at the above temperature, open to the air. The same result took place at the end of 4½ hours.

It is apparent from these experiments that the oxidation products, and not the oxygen itself, cause the increased rate of polymerization.

**REDUCING METALS**—Several experiments were carried out in this laboratory to observe the influence of the presence of a quantity of strongly reducing powdered metal in Chinese wood oil upon heat treatment.

Five 200 gram masses of tung oil were mixed with 1 per cent finely powdered zinc, 1 per cent magnesium, 1 per cent lead, and 5 per cent zinc, respectively, and heated under an atmosphere of nitrogen at 235° C. Gelatination took place in every case within 2 hours compared to 5½ hours for the wood oil heated alone. Two like quantities of wood oil were then taken; to the first 2 per cent sodium amalgam was added, and to the second 2 per cent litharge, and heated under the same conditions given above. Again gelatination took place at the end of 2 hours.

The results in the first series of experiments with the powdered metal are hardly what we should expect from the process for gel prevention, as given by Weinschenk.<sup>1</sup>

### IV—CONSTITUTION OF POLYMER

The explanation for the gelatination of chinawood oil is that there are formed molecular complexes of the dimolecular tri-glyceride, through the dissolution of one-half the unsaturated linkages in the tri-glyceride of elaeomargaric acid, while the insolubility of this jellied product is largely due to its colloidal condition.

Several patents have been taken out for processes to prevent the gelatination of wood oil, incorrectly called polymerization prevention. The German Patent No. 211,405 is of particular interest from a theoretical standpoint. The claim of this patent is the formation of hard-drying product obtained by heating the raw chinawood oil alone, for a short time, above the "polymerizing" temperature, while keeping the oil in constant motion.

The inventor of this process recognizes that the gel formation is also dependent upon the inertness of the separate mass particles, and that with the help of purely

<sup>1</sup> Loc. cit.

<sup>2</sup> THIS JOURNAL, 7 (1915), 572.

<sup>1</sup> German Patent No. 219,715.



physical means gel formation may be prevented without the addition of a resin. He does not, however, distinguish between polymerization and gelatination, and makes an error when he states that the Chinese wood oil can be heated above the polymerizing temperature, and that since a certain length of time is required for the polymerizing reaction to go to completion by rapid heating, this condition can be eliminated. Had he determined the iodine number of the superheated product, he would have noticed his error.

The constants upon several superheated Chinese wood oils are as follows:

Acid number.....	12.5 to 16.1
Iodine number.....	80.0 to 84.6
Saponification value.....	187 to 194
Unsaturation.....	8.2 to 11.9 per cent

With the exception of the saponification value a pronounced change has taken place in the constants.

The glycerides were separated from the superheated oil by repeated extraction with hot absolute alcohol and finally with extra light petroleum ether. A glyceride to the extent of about 75 per cent of the original oil was found to be insoluble in the latter solvent under these conditions, while the ordinary elaeomargaric acid tri-glyceride is quite soluble in that solvent. The constants and molecular weight for this separated tri-glyceride were as follows:

		MOLECULAR WEIGHT
Acid number.....	0.0 (a)	1692 and 1730
Iodine number.....	85.8 (b)	1752 and 1814
Saponification value.....	190.1	

(a) Freezing-point method using benzol as the solvent.

(b) Freezing-point method using naphthalene as the solvent.

These results show the tri-glyceride has double the molecular weight of the original elaeomargaric acid tri-glyceride and that one-half of the unsaturated linkages have disappeared.

The fatty acids were then liberated and their molecular weight and iodine number determined. The freezing- and boiling-point methods were used in the determination of the former, and were found to be 570 and 558, respectively, using benzol as the solvent. The iodine number was found to be 89.8.

Upon heating a portion of the di-molecular tri-glyceride separated from the superheated oil by the above process gelatination resulted almost immediately. Further portions were then dissolved in chloroform and benzol and allowed to stand for 24 hours out of contact with air. A gel formed more readily with the former solvent; this gel did not redissolve upon the addition of further solvent, nor upon heating the solution. These gels were then saponified, the acids liberated, and the molecular weight as well as iodine number determined. The molecular weight by the freezing-point method with benzol as the solvent was found to be 550 and 570, and the iodine number 90.1.

A residue benzol solution of the di-molecular tri-glyceride remaining from a molecular weight determination was allowed to stand over night, stoppered tightly. The molecular lowering was then again determined and it was found to be but a fraction of the original lowering.

It is evident that the above gel product is not the same as the intermediate product, but must consist of complexes formed from the intermediate product. Since the iodine number and molecular weight of the fatty acids from this gel remain the same, and the re-formation of the dimolecular tri-glyceride, *i. e.*, the intermediate product, is possible by heating with rosin or oleic acid, the writer is inclined to believe that this

formation of complexes is not accompanied by a decided change in the molecule.

The absence of gelatination in the superheated product upon heating at polymerizing temperatures must be due to the presence of decomposition products formed during this superheating process, for the polymerization to the intermediate product is complete. Upon the addition of 25 per cent raw tung oil to a superheated oil, the mass will readily gelatinize at polymerizing temperatures. It is thus apparent that there is a minimum amount of decomposition products that must be present to prevent gel formation, *i. e.*, to prevent the formation of complexes of the di-molecular tri-glyceride.

An experiment was carried out to see if the polymerized tri-glyceride of elaeomargaric acid formed as readily when the raw Chinese wood oil was dissolved in a solvent such as naphthalene.

150 grams of Chinese wood oil were heated with 50 grams of naphthalene at 200° C., out of air for 24 hours under a reflux condenser. Gelatination took place, forming an insoluble colloidal gel, similar to that formed when the oil is heated alone. Equal quantities of Chinese wood oil and naphthalene were then heated under the conditions as outlined above; gelatination did not take place and the mass remained soluble in the ordinary organic solvents. From the latter mixture 100 grams were taken and an attempt made to distill off the naphthalene. Upon the removal of about 15 per cent of the naphthalene gelatination took place. This gel product was apparently as difficultly soluble in the ordinary organic solvents as that influenced by a solvent.

From the above experiments it is shown that the action of the naphthalene must be that of a diluent, and that the minimum percentage which must be present to prevent gel formation is exceedingly large.

A further quantity of this heat-treated mixture of 50 per cent tung oil and 50 per cent naphthalene was taken and the polymerized tri-glyceride separated from the mass by extraction with hot absolute alcohol and finally with petroleum ether, boiling point of 55° C. The molecular weight of this insoluble glyceride was found to be 1711 and 1755, by the freezing-point method with benzol as the solvent. The iodine number was found to be 86.0.

The iodine number of the fatty acids liberated from this glyceride was found to be 90.1 and the molecular weight 544 and 560, determined by the boiling-point method with acetone as the solvent.

Two samples of Chinese wood oil were then heated out of air at 150° C. and 225° C., respectively, the heating being discontinued immediately upon solidification. The gelatinized products were then saponified, the fatty acids liberated and their molecular weights determined by the freezing-point method, using benzol as the solvent, and were found to be 483 and 495 for the former and 452 and 460 for the latter fatty acids. The iodine numbers were found to be 114 and 128. A superheated tung oil that had gelatinized, due to an insufficient amount of decomposition products being formed, was then saponified and the fatty acids liberated. The molecular weight upon two samples by the above method was found to be 533 and 553, and the iodine number 87.3.

The percentage of elaeomargaric acid glyceride remaining unpolymersized was then determined in the above three samples of heat-treated, gelatinized wood oils, and assuming 10 per cent olein present in the oil used the amount was calculated to be

20 per cent, 28 per cent, and 4 per cent, respectively, of the total amount present in the original oil.

Complete polymerization to the intermediate product takes place in 15 minutes at 350° C., while at 150° C. it requires at least 30 hours to solidify when heated out of air.

#### ACTION OF HEAT ON CHINESE WOOD OIL

What actually occurs on the transformation of Chinese wood oil by heat from the raw state to the solid product is as follows: Upon heating at sufficiently high temperatures two elaeomargaric acid tri-glyceride molecules unite through dissolution of one-half of their double bonds, as evidenced by their molecular weights and iodine number. Each elaeomargaric acid chain in the tri-glyceride loses one unsaturated linkage through the union with the other elaeomargaric acid chain. This union is shown by the molecular weight, and iodine number, and by the entire loss of the elaeomargaric acid. This intermediate product formed by polymerization of the elaeomargaric acid tri-glyceride is formed in every case of heat treatment of Chinese wood oil whether the wood oil is heated alone or in the presence of a solvent, and does not vary with the temperature. The amount formed is dependent upon several factors to be mentioned later. This soluble intermediate product has the power of forming, under favorable conditions, molecular complexes that constitute the colloidal gel. The intermediate product and colloidal mass are not identical, as thought by Fahrion. The colloidal state of the latter complexes is apparently the main cause of the insolubility of this product, as shown by the extraction experiments.

The formation of these complexes is largely dependent upon the concentration, and is influenced by the presence of certain substances acting as accelerating or retarding catalyzers, the presence of a solvent acting as a diluent as well as upon the inertness of the separate mass particles, as pointed out by the German Patent No. 211,405.

The rate of formation of this intermediate product is also dependent upon the temperature, and is influenced by the presence of certain substances acting as catalyzers, and the freedom of the separate mass particles. This product is the same, however, in every case.

The solid gel may be dissolved by simply heating with rosin, oleic acid or other solvents of the same type for a time at 300° C. By this treatment the di-molecular tri-glyceride is again formed. Since the initial polymerization occurs through the unsaturated linkages, the writer sees no reason why Fahrion should expect a complete depolymerization.

Fahrion<sup>1</sup> stated that gel formation takes place when a certain concentration of the polymerized glyceride in the unchanged oil is reached. In other words, he assumes that the percentage of polymerized glyceride is the same in every case when gel formation takes place. He then concludes that since changes for the constants differ on heating to different temperatures, the polymerization of Chinese wood oil and styrolene are not analogous.

The reasons given by Fahrion are untenable and not

in keeping with actual facts. Not only is an intermediate product actually formed, but it can be isolated. Further, this intermediate product is soluble in all the ordinary, organic solvents with the exception of extra light petroleum ether, as well as in unchanged wood oil, rosin, and like solvents. Its solubility in benzol is not dependent upon the presence of a certain minimum amount of unchanged wood oil as claimed by Fahrion.

Schapring, in order to explain this difference in constants, presumes, as mentioned before, that at different temperatures different intermediate products are formed, also assuming, as did Fahrion, that for gels of the same consistency, the proportion of polymerized oil present is the same. He concluded that the course of polymerization cannot be followed by the iodine number alone, but requires a correlation with the refractive index and specific gravity, since the iodine number varies with the different gels, being greater with the gels formed at the higher temperatures than those formed at lower temperatures.

These assumptions of Fahrion and Schapring as to the lack of variation of the different gels in the percentage of polymerized glyceride, caused them to draw wrong conclusions. The writer has given the various conditions under which gels are subject to variation, stating that the concentration of the intermediate product alone is not the factor determining gel formation, as assumed by Fahrion and Schapring. Wolff<sup>1</sup> stated that the gel formation was dependent upon the concentration and temperature, and drew the conclusion that the theory, assuming the solidification of wood oil to be due to the formation of a homogeneous polymerization product, as well as the theory that it is due to a chemical reaction, must be abandoned.

The course of polymerization in Chinese wood oil, inasmuch as it takes place only through the union of double linkages in the elaeomargaric acid tri-glyceride, may be followed by the iodine number alone, and does not require correlating with the specific gravity and refractive index as stated by Schapring. This would apply only to mixtures heated out of air, for upon heating in air, the oxyacids must be determined and the drop in iodine number allowed for, due to oxidation.

We may have complete polymerization of the tri-glyceride of the elaeomargaric acid to the di-molecular intermediate product without gel formation taking place. This is possible when a small quantity of decomposition products are present, or in the presence of a diluting solvent.

#### V—POLYMERIZATION IN VARNISH MANUFACTURE

ACTION OF ROSIN—It was originally supposed that addition of rosin to Chinese wood oil acted to prevent polymerization in a heat-treated mixture. This was found not to be the case, the rosin acting rather in preventing gel formation, while the polymerization of the elaeomargaric acid tri-glyceride took place even more rapidly than when raw wood oil was heated alone.

<sup>1</sup> *Farben-Ztg.*, **18** (1913), 1171 to 1173.



Upon using the potassium soap method<sup>1</sup> for the detection of Chinese wood oil in rosin-chinawood oil varnish, it was found that only a very small percentage of the tung oil could be precipitated out. The reason for this was first thought to be due the solvent action of the rosin present, preventing quantitative precipitation. This was not the case, however, for, with mixtures of rosin and wood oil that had not been treated, the potassium soap of elaeomargaric acid could be quite completely separated out. The heat treatment interfered with the separation to an extent that was dependent upon the temperature and time of heating. On prolonged heat treatment it was impossible to separate out any potassium elaeomargarate.

Since the heat treatment gave such varying results it was thought advisable to make a thorough study of the rate of polymerization with mixtures of rosin and Chinese wood oil at the temperatures 150, 175, 200, 225, 250 and 275° C.

As stated in the preliminary paper,<sup>1</sup> the ordinary procedure for the making of a rosin-chinawood oil varnish is to heat alone until the oil will gel slightly on cooling. It is then mixed with rosin and heated at higher temperatures for a short time.

In order to obtain more uniform and comparable results it was thought advisable to permit the rosin to exert its influence during the whole heat treatment, even at the expense of color, which was considered an unimportant factor.

The rosin used throughout the following experiments graded water-white and gave the following constants:

Saponification value	Acid number	Unsaponifiable
180.8	156.1	5.9 per cent

It was found that 25 per cent rosin was not sufficient to prevent gel formation, and in Series A mixtures of 50 per cent Chinese wood oil and 50 per cent rosin were heated together. In Series B, 50 per cent limed rosin (limed with 4 per cent hydrated lime) was heated with 50 per cent Chinese wood oil. In Series C, 49 per cent rosin and 50 per cent Chinese wood oil, to which 2 per cent litharge had been added, were heated at only 200° C., a temperature found to show a typical rate of reaction for the various mixtures.

Heat treatments were carried out in air and with exclusion of air. The container used for heat treatment out of air consisted of a 250 cc. distilling flask sealed at the mouth with the side arm bent downward at an angle of 90° dipping into mercury, acting as a trap to allow volatile products to escape while preventing the entrance of air. The mixtures to be heated in the air were treated in uncovered porcelain beakers of 400 cc. capacity. The heating was carried out in an electric furnace especially constructed for this purpose, in which constant temperatures could be readily maintained.

**ROSIN SEPARATION**—The method found to work satisfactorily for separating the rosin from the chinawood oil is based upon the fact that all drying oils as well as most semi-drying oils give a comparatively insoluble sodium soap in cold absolute alcohol, while the sodium soap of rosin is comparatively soluble in that menstruum. When the proper conditions are observed as to temperature and concentration of the absolute alcoholic saponifying solution, the soaps

resulting from the saponification of the rosin-chinawood mixture will precipitate in a sufficiently granular form to permit of ready filtration.

**PROCEDURE**—Ten grams of the rosin-chinawood oil mixture are saponified in 200 cc. of *N*/2 absolute alcoholic sodium hydroxide solution in the cold, the operation requiring from 12 hours, for mixtures containing but little polymerized elaeomargaric acid tri-glyceride, to several days, for those containing a large percentage of the polymerized product. This solution is then warmed and allowed to cool slowly to 0° C. It is then filtered upon the ice-cooled copper Buchner funnel, and the sodium soaps are washed with cold absolute alcohol. They are then removed, dissolved in warm water and the acids liberated in a separatory funnel by the addition of hydrochloric acid. The fatty acids on standing will separate out on top, and the watery solution may be drawn off; the fatty acids are then taken up in ether and transferred to a weighed flask; the weight is then determined by evaporation of the solvent and drying by the addition of absolute alcohol and redistillation of the alcohol.

In every case except at the temperatures above 250° C. the fatty acids amounted to approximately the same weight, 4.760 g. This is what we should expect, assuming that the rosin does not combine with the Chinese wood oil but exhibits the same behavior toward the oil as did naphthalene in the experiments in which that material was used as the diluting solvent.

**FATTY ACIDS**—As mentioned above, the mixtures heated at the higher temperatures did not give the same weight of fatty acids, but less in every case, the loss in fatty acids being a function of the temperature and length of heating. Further investigation revealed that this loss was due to decomposition. The unsaponifiable matter thus formed passed into the filtrate, and the acid formed as one of the products of decomposition gave a soluble sodium soap in absolute alcohol. This loss in fatty acids gave a fair approximation of the percentage decomposition, assuming that the samples of oil should ordinarily give 4.760 g., if no decomposition had taken place.

When rosin is heated alone out of air at the higher temperatures, the acid number drops, the decrease depending upon the temperature used for heat treatment and the time of heating at those temperatures. The saponification number, however, remains the same. Apparently ordinary anhydrides are formed.

When Chinese wood oil is heated below decomposition temperatures the acid number drops, and at the point of gelatination the acid number has practically disappeared. When heated to higher temperatures the acid number increases and unsaponifiable matter is formed, but not in proportion to the actual amount of decomposition. This is due to the fact that an acid volatile at these temperatures is formed which is not indicated in the acid number. Gelatinized wood oil heated at 250° C. for several days, out of air, again becomes liquid, as mentioned by Schapinger<sup>1</sup> and was found to have an acid number of 76.5. A very large per cent of decomposed products had been formed, which in turn had caused a de-gelatination of the remaining complexes of the di-molecular tri-glyceride.

Since the acid number of the rosin falls and that of

<sup>1</sup> Loc. cit.

<sup>1</sup> Dissertation.

the Chinese wood oil rises it is impossible to follow the rate of decomposition of the oil from the acid number of the mixture.

**COLOR**—When rosin is heated, out of air, at temperatures as high as 275° C. for as long as 24 hours it remains as clear as the original rosin, in striking contrast to heating in air at the same temperature, or even at considerably lower temperatures. When heated for 24 hours in air at the above temperature it is so badly decomposed and dark colored as to be valueless as a varnish material.

Like results occur in the heat treatment of Chinese wood oil, especially when heated in metal vessels. Chinese wood oil driers may be made with but little change in color if heat-treated out of air.

This was found to be due to the fact that the oxidation products are quite susceptible to decomposition by heat, and the resulting decomposition products darken the mass.

When chinawood oil or rosin-chinawood oil mixtures were heated at high temperatures around 275° C. out of air they remained as clear as the original mass, and upon being blown at 150° C. for hours they darkened only to a very slight degree, although there were considerable oxidation products formed. It is apparent that the oxidation products are not much darker than the original oil. The manufacture of varnishes out of air is to be recommended since the matter of color is important. This is especially true in the manufacture of driers that tend to be highly colored by the ordinary procedure.

The results obtained upon the rosin-chinawood oil mixtures are given in Table I, from which the curves in Figs. I and II have been plotted.

TABLE I—POLYMERIZATION AND OXIDATION OF MIXTURES OF CHINESE WOOD OIL AND ROSIN

CONDITIONS OF EXPERIMENTS Temp. °C.	Time Hrs.	SERIES A Chinese wood oil 50% Rosin 50%				SERIES B Chinese wood oil 50% Limed rosin (4%) 50%			
		% POLYMER		OXYACIDS		% POLYMER		OXYACIDS	
		Out of air	In air	Out of air	In air	Out of air	In air	Out of air	In air
150	5 1/4	23.2	41.5	5.2		26.1	43.0	6.1	
	16 2/3	35.0	48.1	15.0		43.4	53.1	23.6	
	24	42.7	52.1	21.8		46.3	55.1	8.6	
	5 1/4	44.3	53.6	7.9		67.9	72.4	21.5	
175	16 2/3	64.4	71.2	20.0		80.7	83.3	29.4	
	24	77.7	82.8	27.7		52.1	53.4	12.8	
	1	37.9	35.8	11.9		82.4	77.6	16.7	
	4	67.1	73.6	15.6		100.0	100.0	20.6	
200	8	79.2	93.1	19.4		...	...	26.8	
	24	100.0	100.0	25.7		87.6	83.2	8.8	
	1	85.6	80.4	9.1		100.0	100.0	11.0	
	4	100.0	98.7	11.3		100.0	100.0	3.4	
225	8	...	100.0	10.8		100.0	100.0	9.6	
	1	100.0	97.8	3.0		100.0	100.0	6.3	
	3	100.0	100.0	9.6		...	...	...	
	24	100.0	100.0	30.3		...	...	...	
250	1	53.4	55.1	14.6		SERIES C Chinese wood oil..... 50% Rosin..... 49% Litharge..... 1%			
	4	84.7	79.6	18.2					
	8	100.0	100.0	22.6					
	24	...	...	30.3					

**FILM**—The pure polymerized tri-glyceride dries exceedingly slowly, which is to be expected from its small iodine number. It gives, however, an excellent film, very resistant to saponifying action as compared with the elaeomargaric acid tri-glyceride, and does not turn white as is the case with the latter glyceride, but remains clear and glossy. This change in color and sudden setting of the film in the case of the raw chinawood oil, is as suggested by Meister,<sup>1</sup> beyond doubt due to the transformation of elaeomargarine

into its stereoisomeride,  $\beta$ -elaeostearine, as shown by the following experiments:

A small quantity of Chinese wood oil was spread over the interior of a thin-walled, round-bottomed flask, making as thin a film as possible. The flask was then evacuated and filled with hydrogen; this was done several times and then placed in direct sunlight. At the end of two days the oil had turned white, and had been transformed into a soft, greasy film, somewhat softer than a like film formed in the air, which may be due to the lack of an exterior tungoxyn film. It was found to be largely insoluble in light petroleum ether, as is the case with the light break, but soluble in the other organic solvents, showing that oxidation had not occurred in sufficient quantity to affect the solubility of the film.

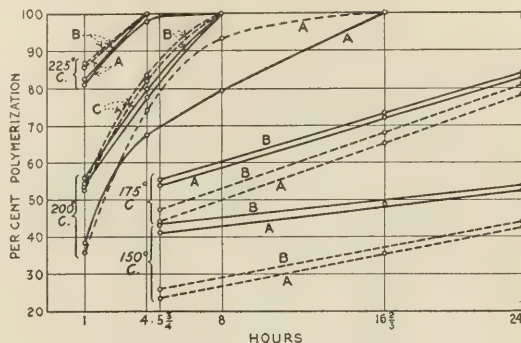


FIG. I—POLYMERIZATION CURVES  
Solid Lines Refer to "Out of Air" Treatments  
Broken Lines Refer to "In Air" Treatments

These results indicate that considerable elaeomargaric acid tri-glyceride is transformed into its stereoisomeride,  $\beta$ -elaeostearic acid tri-glyceride during the drying process, and is responsible for the change in color of the film, as suggested by Meister. This is further shown by the drying of the heat-treated wood oil to a clear film, for the polymerized tri-glyceride exists in a sufficient quantity to mask the partial change of the remaining elaeomargaric acid tri-glyceride into its stereoisomeride, if not to prevent it

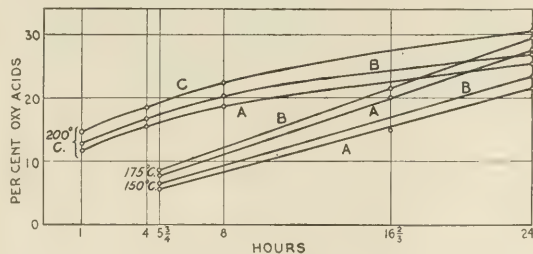


FIG. II—OXIDATION CURVES—ALL TREATMENTS "In Air"

entirely. The initial setting must also be due to this change, and does not take place with the heat-treated wood oil containing considerable polymerized tri-glyceride.

**RATE OF OXIDATION**—The rate of formation of oxidation products is slow when blowing the polymerized material. Superheated oils, subjected to blowing at 150 to 160° C., exhibit the same tendency as does

<sup>1</sup> J. Soc. Chem. Ind., 30 (1911), 95.



the pure dimolecular triglyceride. It is possible that the unsaturated linkages which have been neutralized through polymerization were originally more susceptible to oxidation than the remaining double bonds, though the slow oxidation of the polymerized tri-glyceride may be due to a certain rate of formation of oxy-products dependent upon the extent of unsaturation. This slow rate of drying characterizes rosin-chinawood oil varnishes that contain considerable polymerized oil.

**RATE OF POLYMERIZATION:** Upon examination of the curves representing the rate of polymerization at 150 and 175° C. (Fig. I), the polymerization is found to be decidedly less than for 200° C.; further, the rate is about the same for heat treatment in air and out of air, the oxidation products having but a small influence. The rate of polymerization for the mixture containing the limed rosin is slightly higher than for the rosin-chinawood mixture alone.

At 200° C. the rate of polymerization for the rosin-chinawood oil mixture containing litharge and the mixture containing limed rosin have the same approximate rate in and out of air. The rosin-chinawood oil mixture without the addition of any material exhibits considerable difference from the rate of the mixtures above. Here the oxidation products have considerable catalyzing influence, and the rate for the mass heated in the air is decidedly greater than for the mixture heated out of air. The former has a rate approaching that of the other two series.

At 225° C. the rate for the limed rosin-chinawood oil mixture and for the 50 : 50 mixture is very nearly the same, in or out of air. A reverse occurs, however, in the rate in and out of air, the latter having a higher rate of polymerization than the former, which the writer believes is due to the cooling effect of the air in contact with the former mass predominating at this temperature over the catalyzing influence (see Fig. I).

At the temperatures of 250 and 275° C., although we should have more rapid oxidation at these temperatures than at the lower ones, we have pronounced decomposition, and the oxy-products appear to be decomposed as fast as they are formed. Complete polymerization takes place at the end of 1 hour, in and out of air, in both series. At the end of 4 hours the decomposition at the former temperature, and at the end of 1 hour the decomposition at the latter temperature was about the same, amounting to nearly 27 per cent.

The effect of the lime and litharge appear to be the same as the effect of oxidation products. They are decided catalysts at 200° C., somewhat less at the lower temperatures, but at the higher temperatures the rate of polymerization is so rapid that they have no pronounced influence (see Fig. I).

It is not surprising that the varnish maker finds great variations in the rosin-chinawood oil varnishes since a slight variation in the temperature changes the rate of polymerization considerably; also the rate is subject to catalyzing action by the presence of certain materials.

The ordinary procedure for making rosin-chinawood oil varnishes has no apparent advantage over heating the two materials together throughout the heat treatment, except to permit a shorter period for heating the rosin which, as mentioned before, is subject to darkening when heated for a time in the air. The method of heating together has decided advantages in giving uniform results, by permitting the control of the amount of polymerization by a judicious selection of temperature and length of heating, as well as permitting the heating out of air, in which case the mass remains perfectly clear at normal polymerizing temperatures. With a range of rate of polymerization of 25.7 per cent for 5 hours and 72.4 per cent for 66 hours at 150° C. to complete polymerization in 1 hour at 250° C., chinawood oil shows decidedly greater tendency for polymerization than linseed oil, which requires considerably higher temperatures. This fact must be taken into account in the use of chinawood oil at temperatures at which linseed oil works the most satisfactorily.

#### SUMMARY

I—The polymerization of Chinese wood oil takes place by the union of double bonds of the (wood oil) fatty acids, analogous to the polymerization occurring on heating linseed oil. This polymerization takes place through the dissolution of one unsaturated linkage in each elaeomargaric chain in the tri-glyceride, forming a tri-glyceride composed of di-molecular fatty acids. This intermediate product, or polymerized tri-glyceride, has the power of uniting, forming molecular complexes under favorable conditions, giving an insoluble colloidal mass, not, however, accompanied by a further loss of double linkages, as evidenced by the iodine number.

II—The polymerization is "mesomorphic" and the intermediate product can be isolated. It has been found to be the same in all cases whether the wood oil is heated alone or in the presence of a solvent, and does not vary with the temperature. The intermediate polymerization product is soluble in all the ordinary organic solvents, with the exception of extra light petroleum ether, as well as in unchanged wood oil, rosin, and like solvents; its solubility is not dependent upon the presence of unchanged wood oil.

III—The percentage of polymerized tri-glyceride in gels of the same apparent consistency is not necessarily the same, and the gel is not entirely dependent upon the concentration of the polymer or upon heat for its formation.

IV—A satisfactory method for the examination of wood oil may be based upon the property of elaeomargaric acid to crystallize from a dilute solution of alcohol, while the fatty acids from the polymerized tri-glyceride of wood oil as well as those from the other drying and semi-drying oils do not have this property.

V—Wood oil can be completely polymerized upon heating at abnormally high temperatures for a short time, such as at 350° C. for 15 minutes, due to the presence of decomposition products formed during the superheating process; it will not gelatinize under this treatment.

VI—The rate of polymerization for wood oil is considerably faster than for linseed oil at corresponding temperatures, taking place completely in one hour at 250° C. At 150° C. only about 72.4 per cent polymerization takes place in 66 hours.

VII—Wood oil is subject to decided oxidation when heated in air. Progressively increasing amounts of oxidized materials are formed whenever wood oil or wood-oil mixtures are heated in the air.

VIII—Lime, litharge and oxidation products catalyze the polymerization of the elaeomargaric acid tri-glyceride into the intermediate product. Oxygen does not catalyze the rate of polymerization except indirectly through the oxidation products. A large number of metals also act as positive catalyzers at the higher temperatures.

IX—The course of polymerization can be followed by the iodine number alone and does not require correlating with the specific gravity and refractive index.

X—Dissolving the solid gel in rosin or continually heating it above 250° C. constitutes a reformation of the soluble intermediate products. In the latter case considerable decomposition occurs, the products of which are responsible for the breaking down of the molecular complexes of the polymerized tri-glyceride. This decomposition is considerable on heating wood oil or wood oil mixtures above 250° C. for any length of time, and is accelerated by the presence of certain metals.

XI—The darkening of rosin or rosin-chinawood oil mixtures on heating in air is primarily due to the decomposition products from the oxidized oil, which are very sensitive to temperatures above 175° C. This decomposition may be largely avoided by carrying out the heat treatment out of air. This is also applicable to the manufacture of chinawood oil driers.

XII—The pure polymerized product of chinawood oil dries very slowly, as might be expected from the small iodine number. This slow rate of drying characterizes such rosin-chinawood oil varnishes as contain large percentages of polymerized tri-glyceride.

It is with great pleasure that acknowledgment is made to Professor E. E. Ware for his interest in this work and for his valuable suggestions and criticisms.

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## PURIFICATION OF SEWAGE BY AERATION IN THE PRESENCE OF ACTIVATED SLUDGE—II

By EDWARD BARTOW AND F. W. MOHLMAN

Received December 13, 1915

Since reporting the results of our preliminary work, experiments<sup>1</sup> on purification of sewage by aeration in the presence of activated sludge have been conducted on a larger scale. Four reinforced concrete tanks have been completed and put in operation. These tanks, operating on the fill and draw system, are designed for studying in a comparative manner the amount of air required, the best method for distributing the air, the time required for purification, and the quantity and quality of activated sludge formed.

The tanks are located in the basement of the University power plant (see Fig. 1). The room is not affected by heat from the boilers and conditions are similar to those which would be obtained by housing a plant. It was very easy to tap the city of Champaign main sewer which passes underneath the coal hopper (Fig. II) of the power plant. The sewage is pumped to the tanks by a 2 H. P. centrifugal pump run by a direct connected motor.

Each tank is 3 ft. 2 in. square, having an area of 10 sq. ft. Each tank is 8 ft. 5 in. in depth above 1 1/2-in. Filtros plates which are used for diffusing the air. In 2 tanks there are 9 plates, each 12 in. square, covering the entire floor. In the third tank there are 3 plates, covering 1/3 the area of the floor, forming the



FIG. 1.—TANKS FOR PURIFICATION OF SEWAGE BY AERATION IN PRESENCE OF ACTIVATED SLUDGE

bottom of a central trough. The remainder of the bottom slopes to the plates at an angle of 45°. In the fourth tank is a single plate in the center covering one-ninth the area with the bottom sloping to it at an angle of 45° from all sides. Below the plate is an air space 4 in. deep. A pet cock is provided to relieve the air pressure when draining the tank and to prevent air bubbles from rising and stirring up the sludge. The air obtained from the University compressed air plant at a pressure of 80 lbs. is reduced by a pressure reducing valve to 8 lbs. and is further regulated by a hand-operated valve before passing through meters on each tank. The pressure under which it enters the tank is sufficient only to overcome the pressure

<sup>1</sup> THIS JOURNAL, 7 (1915), 318.



of the sewage, equivalent to about 8 in. of mercury, or, a little less than 4 lbs. per sq. in.

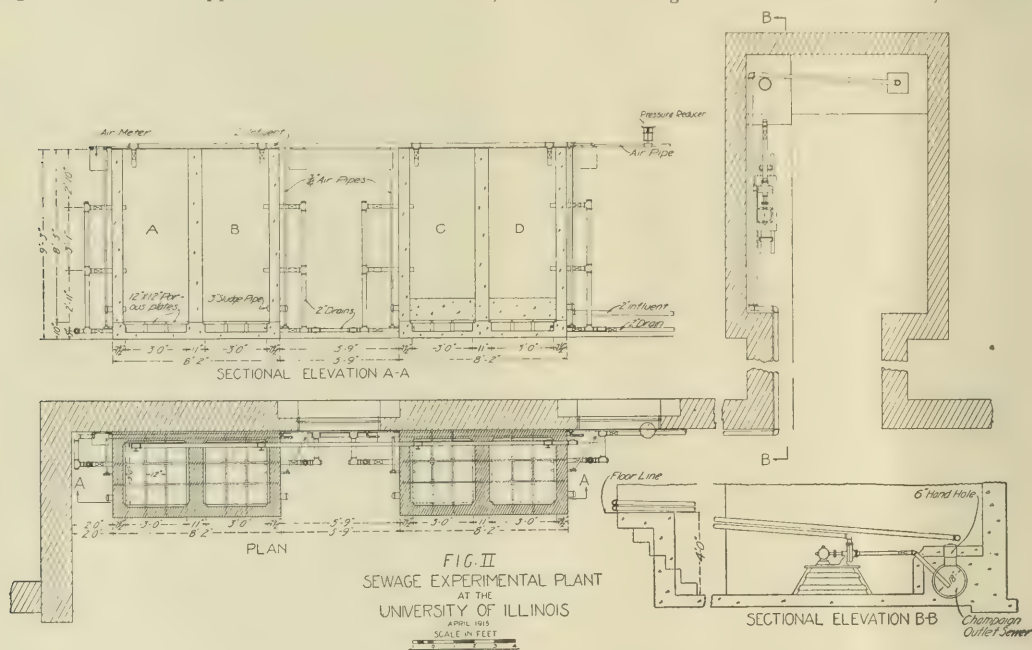
Two outlets for the effluent are, respectively, 2 ft. 6 in. and 5 ft. 7 in. above the porous plates. A tank can be filled in 6 minutes and drained to the lower outlet in 8 minutes.

Experience has shown that a lower outlet connected to a floating outlet would be preferable. A fixed outlet is objectionable because sludge is at times drawn out with the effluent. In fact, no accurate data have been obtained concerning the quantity of sludge formed, because we have been unable to determine how much has been lost with the effluent. In order to prevent this loss, a floating outlet made of 2-in. pipe connected together with loose joints, has been placed in tank C. The effluent flows to the outlet through a screen of copper wire of about 16 mesh,

aerated until it is aerobic and similar to activated sludge. Such a source of sludge would not be available in many places, especially at newly installed plants. We have attempted to shorten the period of sludge formation.

Tanks *A* and *B* were filled with the same kind of sewage on May 5, 1915. The sewage in tank *A* was aerated continuously; the sewage in tank *B* was aerated 23 hours, allowed to settle, the supernatant liquid withdrawn and refilled with fresh sewage in one hour. This cycle was repeated daily and determinations of the amount of sludge and of the degree of purification were made daily.

At the end of 10 days, after one hour's settling in Imhoff cones, 1.0 per cent of the volume in *A* consisted of sludge while about 10 per cent of the volume in *B* was sludge. The effluents from *A*, which had



which is fastened on both sides of an iron frame 1 ft. square. With this arrangement no sludge has been lost and we expect to obtain accurate data concerning the amount of sludge formed from the sewage.

The amount of sludge must be determined by weight on the dry basis for it has been noted that its volume and rate of settling vary with the amount of air applied. If an unusually large amount of air has been applied, the sludge will settle more slowly and will occupy a much greater volume even after prolonged settlement, than it does when less air has been applied.

**BUILDING UP OF SLUDGE**—If, in accordance with previous practice, activated sludge is built up by complete nitrification of each portion of sewage added, it would require several weeks to put a plant in operation.

In order to obtain sludge more quickly the English investigators have used sludge from sprinkling filters. At Milwaukee, Imhoff tank sludge has been

been aerated 10 days, and from *B*, which had been aerated one day, were equally stable while that from *B* was clearer.

Tank *B* was continued in operation, changing the sewage every 24 hours, until, after 15 days, nitrification was complete. Then the sewage was changed every 12 hours; nitrification was again complete after 8 days. Then the sewage was changed every 6 hours; many of the effluents with the 6-hour cycle were putrescible and it is necessary at intervals to aerate for longer periods. This comparison indicated, however, that sludge may be satisfactorily activated by changing the sewage before nitrification is completed, and that the sewage may be changed at frequent intervals.

Tank *A* was, therefore, cleaned and fresh sewage added every 12 hours. Stable effluents were obtained in 7 days; complete nitrification occurred in 18 days, after which the sewage was changed every 6 hours.

The effluents obtained from the tanks during this 6-hour cycle were not all stable, yet the average improvement was so great that the conclusion was reached that activated sludge may be built up by changing sewage at frequent intervals without complete nitrification of each dose of fresh sewage. A considerable degree of purification is also obtained from the beginning of the operation, and the time for building up adequate sludge for the process is cut down very decidedly. A later experiment with tank *C* showed that satisfactory activated sludge could be built upon a 6-hour cycle.

**DIFFUSION AREA REQUIRED**—The bottom of tank *C* contains 3 sq. ft. of Filtros plates as described above; the bottom of tank *D* contains 1 sq. ft. These tanks were put in operation July 6th and the sewage was changed every 6 hours. There was a noticeable difference in the working of these tanks. *C* gave some stable effluents after 5 days; *D* did not give stable effluents in 18 days. The sludge from *C* was of good appearance, while that from *D* was not as flocculent and at times had a septic odor. During the comparative experiment an average of 450 cu. ft. of air per 400 gallons of sewage was used with *C* and of 360 cu. ft. of air per 400 gallons of sewage with *D*. The amount of air given *D* was always sufficient to keep the sludge mixed with the sewage. In fact, the sewage in *D* was agitated much more violently than that in *C*. We have concluded that 1 sq. ft. of Filtros plate per 10 sq. ft. of floor area is hardly sufficient. Of the four tanks, *C*, with 3 sq. ft. of Filtros plate per 10 sq. ft. of floor area, has given the best results.

We have noted that it is quite essential that the plates be as nearly as possible at the same level. A variation of  $\frac{1}{4}$  in. in level will cause uneven air distribution. The distribution seems to become more uniform the longer the plates are used.

**QUALITY OF EFFLUENTS**—The quality of the effluents has usually depended more on the strength of the raw sewage than upon any other variable. The tanks, when operating on a 6-hour cycle, were filled at 9 A.M., 3 P.M., 9 P.M., and 3 A.M. The strength of the raw sewage, estimated by the free ammonia values, averaged for the 9 A.M. sewage between 20 and 25 parts per million, for the 3 A.M. sewage between 3 and 12 parts per million. Nearly all of the 3 A.M. sewages have given stable effluents, but the strong morning sewages have quite frequently given putrescible effluents. Unless the sludge is in good condition, and well nitrified, a strong sewage cannot always be purified in  $4\frac{1}{2}$  hours even by increasing the air to 800 cu. ft. per 400 gallons. In the normal working of the plant the sludge will usually regain its "activity" if 800 cu. ft. of air is applied for several periods after the strong sewage has been added.

At times, however, with a succession of strong sewages, it is necessary to increase the time of aeration in order to obtain good effluents. Ardern and Lockett<sup>1</sup> noted in their first paper that if the aeration was stopped before the sewage was well nitrified, the activity of the sludge would be inhibited. When strong sew-

ages are to be treated a definite cycle of operation cannot be established without provision for longer aeration of the sewage or separate aeration of the sludge. In order to keep the sludge in its most active state, complete nitrification of each sewage is necessary. Effluents are usually stable if 50 per cent of the free ammonia is removed, and 2 to 3 parts per million of nitrogen as nitrates are present. A completely nitrified effluent is neither necessary nor economical.

The greatest efficiency in air consumption will be obtained when enough air is used to make the sewage non-putrescible and to keep the sludge activated. The operation of the plant during six months has suggested the advisability of studying more carefully such other features of the process as the amount of sludge formed, the building up of nitrogen in the sludge and the composition of the effluent gases.

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### FERTILIZER VALUE OF ACTIVATED SLUDGE<sup>1</sup>

By EDWARD BARTOW AND W. D. HATFIELD

Activated sludge is an essential material and an important product in a new method of sewage disposal, which was first described by Ardern and Lockett,<sup>2</sup> of Manchester, England, in 1914.

At present, September, 1915, experimental plants are being operated at Baltimore, Md.; Chicago, Ill.; Cleveland, O.; Houston, Tex.; Milwaukee, Wis.; New York City; Regina, Saskatchewan; Urbana, Ill.; and Washington, D. C.<sup>3</sup> At Baltimore a modified Imhoff tank is to be operated with continuous flow. At Milwaukee both fill and draw and continuous flow processes are being operated on an experimental scale, and a 2,000,000 gallon plant is under construction. At Cleveland a 1,000,000 gallon plant is to be built. At Urbana an experimental plant of 6,000 gallons capacity is being operated on the fill and draw system.

As in other sewage disposal processes, the ultimate disposal of the sludge is of great importance. Near the seaboard it is possible to carry this sludge out to sea, but in the interior, the problem of sludge disposal is often very serious.

In the experimental plant at the University of Illinois, in Urbana, we have tried to study all phases of the process,<sup>4</sup> and have paid especial attention to the sludge.

The amounts of sludge formed and its chemical composition evidently vary with the concentration of the sewage, and with temperature conditions. The sewage treated in the experimental plant during rainy weather contains large amounts of diluting water, which reduces the amount of sludge per unit of water. The diluting water carries considerable dirt from the streets which reduces the nitrogen content of the sludge obtained. Also during warm weather, bacteriological action is more rapid, and,

<sup>1</sup> Presented at the 51st Meeting of the American Chemical Society, Seattle, August 31-September 3, 1915.

<sup>2</sup> *J. Soc. Chem. Ind.*, **33** (1914), 523, 1122.

<sup>3</sup> *Eng. News*, **74**, 164-70.

<sup>4</sup> *THIS JOURNAL*, **7** (1915), 318.



apparently, the amount of sludge is considerably reduced.

The sludge obtained in the process is flocculent, resembling a freshly formed precipitate of ferrous-ferrie hydroxide. It separates easily from the clarified water, and after one hour's settling contains from 96 to 98 per cent of moisture. On further standing, about one-half of this water can be removed. The remaining material can be dried by filter-pressing or by drying on beds of sand and evaporating over steam baths.

Experiments with the worms found in the wet sludge<sup>1</sup> have proved that they are not essential to the purification process. Nitrifying bacteria, and bacteria which have the power of destroying organic matter have been isolated from the sludge. The nitrifying bacteria alone will not purify sterile sewage. A combination of the nitrifying bacteria with the other varieties will purify sterile sewage very satisfactorily. This work carried on with R. Russell will be described in another article.

The disposal of the sludge can be most easily accomplished if it has manurial value. That activated sludge has manurial value is shown by its chemical composition, by its reaction with various soils, and by its effect on the growth of plants. Specimens of sludge obtained at the experimental plant have varied in nitrogen content from 3.5 to 6.4 per cent. The lower values were obtained during periods of high water. Street wash was getting into the sanitary sewers and since no grit chamber was provided to remove the grit, the nitrogen value of the sludge was greatly lowered. The tests of the fertilizer value have been made on the richer specimens which were first obtained.

Through the courtesy of Mr. Paul Rudnick, chief chemist, Armour & Company, Chicago, the availability, according to alkaline permanganate method as used by the New England states, was shown to be below 50 per cent (44.7 per cent), and the sludge would be classed as an inferior ammoniate, but the availability according to the neutral permanganate method which has been adopted by the southeastern states was shown to be above 85 per cent (89 per cent), and would therefore be classed as satisfactory.

Tests have been made by Professor C. B. Lipman, according to a method described by Lipman and Burgess,<sup>2</sup> in which a fertilizer and a soil are incubated for a month. The amount of nitrogen changed into nitrate is then determined. This amount is an index of the availability of the nitrogen with respect to the soil used. The results obtained were reported by Professor Lipman, as follows:

"The activated sludge used contained 6.2 per cent total nitrogen and no nitrate. The hundred grams of soil in every case contained nitrate as follows:

Anaheim soil, 1.0 mg. N. Davis soil, 0.3 mg. N. Oakley soil, 0.1 mg. N.

The amounts of nitrate produced in one month's incubation from the soil's own nitrogen and from the nitrogen of the sludge

mixed with the soil in the ratio of one part of sludge per hundred of soil is as follows:

Soil	Miligrams nitrate produced Without sludge	With sludge
Anaheim	6.0	10.0
Davis	4.2	14.0
Oakley	2.2	4.0

The Davis soil is the best nitrifying soil of the three, especially for high-grade organic material. Anaheim is next, and the Oakley by far the poorest. Indeed, the last named does not nitrify the nitrogen of dried blood at all in a period of a month in the incubator.

These figures indicate that the general tendency is to make available the nitrogen of sludge in type soils at about the same rate that nitrogen is transformed into nitrate in such organic nitrogenous fertilizers as fish guano. While it seems to hold a medium position, it nevertheless resembles very much more closely in its general characteristics, so far as available nitrogen is concerned, the so-called high-grade organic nitrogenous fertilizers, dried blood and high-grade tankage, etc., rather than the low-grade nitrogenous fertilizers, steamed bone meal, cotton-seed meal, garbage tankage, etc."

Although the chemical tests and the nitrification tests with soils indicate that the activated sludge has a high fertilizer value, the final test must be its effect on plant growth. Pot cultures, using wheat, were started in March, 1915,<sup>1</sup> under the general direction of Professor C. G. Hopkins and with the assistance of Mr. J. C. Anderson. The contents of the pots in which the wheat was planted were as follows, in grams:

Pot No.	White sand	Dolomite	Bone meal	Potassium sulfate	Activated sludge	Extracted sludge	Dried blood
1.....	19,820	60	6	3	0	0	0.0
2.....	19,820	60	6	3	0	0	8.61
3.....	19,820	60	6	3	20	0	0.0
4.....	19,820	60	6	3	0	20	0.0

Each pot contained an equivalent of 5 tons per acre of dolomite,  $1\frac{1}{2}$  ton per acre of bone meal, and 500 lbs. per acre of potassium sulfate.

Pot 1, the check pot, contained only the 60 mg. of nitrogen which were added in the bone meal: this small amount was without significance since the same amount was added to the other pots. Pot 2 contained an equivalent of 120 lbs. of nitrogen per acre added in the form of dried blood. Pots 3 and 4 contained an equivalent of 120 lbs. of nitrogen in the form of dried activated sludge (one ton of sludge) per acre. The sludge used analyzed as follows in percentages:

Total nitrogen	Phosphorus (P <sub>2</sub> O <sub>5</sub> )	ETHER SOLUBLE
6.3	2.69	3 hrs. extraction 4.00 16 hrs. extraction 11.8

Thirty wheat seeds were planted, 2 seeds in each of 15 holes, in each pot. In 4 days the plants were up in each pot and in 10 days were 5 in. high. At the end of 18 days the plants were thinned to 15 of the best in each pot, in most cases leaving one plant to each hole. In 20 days from date of planting there was a marked showing in favor of the plants in Pots 3 and 4. In 23 days the plants in Pots 3 and 4 (see Fig. 1) were growing far ahead of those in 1 and 2.

The plants in Pot 2 fertilized with the same amount of nitrogen grew much more slowly than those in 3 and 4. The reason for the poor showing of the plants in Pot 2 is not known.

In 30 days a slight brown mold appeared on the

<sup>1</sup> THIS JOURNAL, 7 (1915), 319.

<sup>2</sup> Univ. of Calif., Bull. 251 (1915).

<sup>1</sup> THIS JOURNAL, 7 (1915), 318-320.

larger plants, which may have been due to the dark, damp weather. Powdered sulfur was used to fight it.

During the fifth and sixth weeks the plants in the pots fertilized with the sludge, which had grown fully three times as large in height and in the amount of foliage as those in the pot fertilized with dried blood, began to yellow. About half of the foliage died,

The surprisingly rapid growth of the wheat fertilized by the sludge must be due for the most part to nitrogen present in a very available form. It may be due in part to the phosphorus (2.69 per cent) which is present in the sludge. At the time of making the pot cultures we did not consider the phosphorus since it was present in such a small quantity. The growth may be due in part to the organic matter

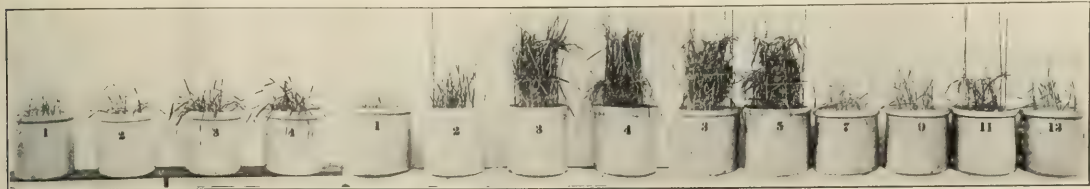


FIG. I—WHEAT SERIES I, 23 DAYS AFTER PLANTING      FIG. II—WHEAT SERIES I, 63 DAYS AFTER PLANTING      FIG. III—WHEAT SERIES II, 35 DAYS AFTER PLANTING

Each pot contained pure white sand to which the same amounts of plant food (except nitrogen) had been added below:

No. 1, the check, contained practically no nitrogen

To each of the other pots was added the nitrogen equivalent of 20 grams of dried activated sludge in the form indicated below:

Nos. 2 and 13	No. 3	No. 4	No. 5	No. 7	No. 9	No. 11
Dried Blood	20 g. Dried Activated Sludge	20 g. Dried Activated Sludge Extracted with Lignoïn	20 g. Dried Activated Sludge Extracted with Ether	Sodium Nitrate	Ammonium Sulfate	Gluten Meal

leaving two healthy stalks to each plant. The plants possibly grew so fast, at first, that all the foliage which had started could not develop. The remaining stalks immediately grew stronger and of a deeper blue-green color. After 9 weeks the plants were strong and healthy (see Fig. II).

In 14 weeks the plants in Pots 3 and 4 began to head and in 15 weeks there were about 20 good heads in each. The plants in Pot 1 were very weak, while those in 2 were just beginning to develop heads.

When it was first noticed that the plants fertilized with sludge were growing much better than those fertilized with dried blood, in order to confirm the results, a second series of pot cultures was started. In this series the sludge was compared with dried blood, nitrate of soda, ammonium sulfate and gluten meal. This series contained 14 pots: 2 check pots, 6 containing nitrogen equivalent equal to an application of 20 grams of sludge, and 6 nitrogen equivalent to 30 grams of sludge. The plants in this series grew faster than those in the first because of better weather. They showed exactly the same characteristics that the plants in the other series showed. The plants fertilized with sludge were the best. The results confirmed the results obtained in the first series. At the end of 5 weeks striking differences were noticeable (see Fig. III). The pots containing the equivalent of 30 grams of sludge gave no better results than those with an equivalent of 20 grams.

When the wheat matured it was carefully harvested and calculations made to determine the yield per acre. The results are shown in Table I.

TABLE I—AMOUNTS OF WHEAT AND STRAW OBTAINED IN THE FIRST SERIES

YIELD OF SEEDS			YIELD OF STRAW				
Pot No.	No. heads	No. seeds	Grams seeds (calculated)	Bu. per A.	Av. stalk Length (in)	Straw Grams (calculated)	Tons per A.
1...	14	85	2.38	6.2	19.4	2.25	0.18
2...	15	189	5.29	13.6	23.0	8.25	0.68
3...	22	491	13.748	35.9	35.4	26.75	2.23
4...	23	518	14.504	37.7	36.1	26.21	2.18

The control series gave results corresponding to those of the first series.

present in the sludge, since the sand used contains no organic matter. The cause of the molding of the leaves has not yet been determined. It was quite noticeable that the mold appeared chiefly on the leaves of rapidly growing plants. In the first series it attacked only plants fertilized with sludge. In the second series it also attacked the plants fertilized with gluten meal. The rapidly growing leaves are



FIG. IV—GARDENING EXPERIMENTS: TREATMENTS AS INDICATED RADISHES AND LETTUCE 38 DAYS AFTER PLANTING

naturally more tender than those which grow slowly and consequently are more easily attacked by mold spores. The mold evidently does not come from the sludge because the extracted sludge surely would be sterile, and plants fertilized with it showed the same mold. Plants fertilized with gluten meal also had the mold.

The sludge causes such a rapid growth of wheat that it should be valuable to truck gardeners for rush-



ing spring crops. To test its value to the market gardener, three plots each 2 ft.  $\times$  3 ft. were laid out in a field. One plot was not fertilized, one was fertilized with an equivalent of 126 lbs. of nitrogen, one ton of sludge per acre, and the third with an equivalent of extracted sludge. On April 24, 1915, two rows of radishes and lettuce were planted in each of the three plots. The plants in the plot where the extracted sludge was used came up first, a little ahead of those in the plot where the unextracted sludge was used. At the end of 2 weeks the lettuce and radishes of the treated plots appeared to be twice the size of those in the untreated plot. At the end of 4 weeks the plants were thinned. The roots of the radishes from the treated plots were already red and quite rounded near the tops while those from the untreated plots had not yet started to swell and had not become red. The lettuce plants from the treated plots were nearly twice as large as those from the untreated plots.

On June 1, 38 days after planting, the six best plants of lettuce and radishes were taken from each plot and are shown in Fig. IV. The differences in size are very marked.

COMPARISON OF THE LETTUCE AND RADISHES FROM UNFERTILIZED AND FERTILIZED PLOTS

Plot	Treatment	Wt. of lettuce	Wt. of radishes
1.....	None	4.5 g.	23.4 g.
2.....	Sludge	6.3 g.	63.0 g.
3.....	Extracted sludge	6.8 g.	68.0 g.

The increase in weight, due to the sludge, is 40 per cent in the lettuce, and 150 per cent in the radishes. The radishes from the sludge pots, when cut open and eaten, were found to be very crisp and solid, and to have a good flavor.

These pot cultures and gardening experiments show that the nitrogen in "activated sludge" is in a very available form and that activated sludge is valuable as a fertilizer.

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## EQUILIBRIUM RELATIONS AMONG AROMATIC HYDROCARBONS PRODUCED BY CRACKING PETROLEUM<sup>1</sup>

By W. F. RITTMAN AND T. J. TWOMEY

Received October 15, 1915

The results of several series of experiments on the cracking of petroleum in the vapor phase have served to furnish evidence as to the course and mechanism of the cracking reaction. It has been indicated that decompositions occur with two general effects: (1) decrease in size of molecule, and (2) decrease in saturation. A study of the relations among classes of hydrocarbons<sup>2</sup> has shown that certain conditions of temperature and pressure are favorable for the production of low-boiling aliphatic compounds, certain others for aromatics and still another set for the formation of carbon and gas: *viz.*, up to 500° C. for aliphatic formation, from 500° to 800° C. for aromatics, and above 800° C. for carbon and gas.

A special study<sup>3</sup> has dealt with the field of gas pro-

<sup>1</sup> Published with the permission of the Director of the Bureau of Mines.

<sup>2</sup> Rittman, *THIS JOURNAL*, **7** (1915), 945.

<sup>3</sup> Whitaker and Rittman, *Ibid.*, **6** (1914), 383, 472.

duction, and work has been done also to determine conditions obtaining in the temperature range favorable for aromatic formation. One section of this work<sup>1</sup> dealt with transformations in which pure aromatics were used as starting out material and cracked under carefully regulated conditions of temperature and pressure.

The results described in the present communication approach the same end in a different manner. Here petroleum has been subjected to cracking and, by the careful analysis of products, important relations have been discovered among the degrees of formation of certain aromatic compounds.

### THEORETICAL

In the other experiments of the present general series the effects of temperature and pressure have been studied with care. In the present study it has been necessary to minimize the importance of these factors on account of experimental conditions which will receive discussion later. It has been assumed that the extent to which cracking proceeds is in a general way proportional to the specific gravity of the recovered oil or tar. The absolute truth of this assumption may be open to some question but of its general correctness there is little doubt and it affords a convenient method of combining in one function the effects of the several variables in the cracking reaction—temperature, pressure, rate of feed and contact surface.

The scheme followed has been to note the variations, with specific gravity of cracked oil, of the percentages of five hydrocarbons: benzene, toluene, xylene, naphthalene and anthracene. These five have been selected, partly on account of their scientific and commercial importance and partly because convenient analytical methods are available for their estimation.

In connection with any series of experiments it is of importance to consider any indications which may appear on the basis of previous knowledge. For the cracking reaction in general it is possible to make clear-cut predictions as to the effects of temperature and pressure. By calculating approximate equilibrium constants according to the Nernst formula it is possible to discover how the course of reaction varies with temperature. For the effect of pressure it is to be noted that increase in this variable is favorable in accelerating the cracking reaction up to such a velocity that equilibrium may be attained in the time allotted. Beyond this point increase in pressure is favorable or unfavorable, according as the reaction proceeds with decrease or increase of total volume. For the work here described it may be noted that all indications point toward the fact that equilibrium was approached only remotely. The effect of pressure upon reaction velocity is therefore the one of importance.

In the present experiments primary consideration has not been given to the effects of temperature and pressure, but instead to the relative amounts of the various hydrocarbons produced under each set of cracking conditions. Temperature conditions were of course as significant as ever, but owing to mechanical

<sup>1</sup> Rittman, Byron and Egloff, *THIS JOURNAL*, **7** (1915), 1019.

difficulties no attempt was made to read and control them with a high degree of accuracy.

Previous experience has indicated that large paraffin molecules are less stable than small, that paraffins are less stable than olefines, and that stability increases with decrease in saturation. It appears, therefore, that benzene formation is favored by more strenuous cracking conditions than toluene formation, since the latter compound is in part aliphatic, due to the presence of the methyl group which makes up the side chain. Likewise, it appears that xylene, having two methyl groups, should show the same variation in stability as toluene but that it should always occur in about

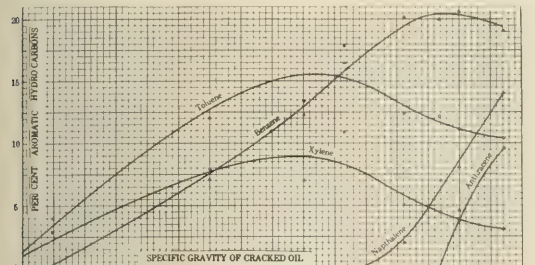


FIG. 1.—PERCENTAGES OF BENZENE, TOLUENE, XYLENES, NAPHTHALENE, AND ANTHRACENE IN CRACKED PETROLEUM OILS OF VARIOUS SPECIFIC GRAVITIES

half the quantity of the latter. The probability of its formation is half that of the formation of toluene and the probability of its decomposition twice as great.

The formation of naphthalene and anthracene seems to necessitate the decomposition of benzene nuclei. The formation of these polycyclic hydrocarbons should, therefore, be coincident with a decrease in the number of monocyclic molecules.

#### EXPERIMENTAL

The method of procedure adopted in the present experiments was the same in principle as that described in earlier connections but has varied considerably in detail. All earlier experiments made use of a small electrically heated furnace in which were maintained carefully regulated and measured conditions of temperature and pressure. In the present work it has been necessary to obtain larger quantities of cracked oil than could be produced conveniently under former conditions and, consequently, use has been made of one of the large experimental furnaces built in connection with the commercial development of the vapor phase cracking process.

The furnace proper was a tube 10 ft. long and 8 in. in diameter, heated by gas. Its use permitted a feed of from 15 to 20 gallons per hour of original oil and a correspondingly large recovery (20 to 50 per cent of the original).

To offset the advantage of yielding sufficiently large quantities of cracked oil to permit the making of satisfactory analyses there were the following difficulties which should receive mention, although in no way did they decrease the value of the results obtained. Pressures could be regulated as well in the large system as in the small, but the accurate control of temperature throughout the whole of a tube 10 ft. long and 8

in. in diameter was obviously a proposition involving difficulty. The runs of the present series were conducted with much care and with a knowledge of details of manipulation acquired in the course of several hundred previous experiments of the same sort. The temperatures recorded are, however, representative of only a moderately accurate average and no stress is laid upon them in the present connection. Conditions of the runs were so regulated as to produce cracked oils of specific gravities varying over a considerable range. One other source of error must be mentioned which helps explain the failure to obtain results which might be more regular, although not more conclusive than those at present recorded. The furnace was equipped with condensers which were insufficient to cool properly the cracked oil, and errors were introduced on this account.

GENERAL SCHEME OF PROCEDURE—The original material was a special fuel or gas oil, a distillate obtained from Pennsylvania crude. Its specific gravity was 0.83 and its boiling range between 300° and 400°.

Runs were made with the furnace described above, the condensed liquid (cracked oil) being the only product collected and examined. Percentage recoveries were determined and specific gravities measured. The method of analysis was that of distillation and specific gravity. A detailed description of this is to be found in another communication,<sup>1</sup> and is essentially as follows: The oil is distilled through an efficient fractionating column of the Hempel type and a cut made at 175°. This cut is then subjected to two successive refractionations and divided into: (1) Benzene fraction,

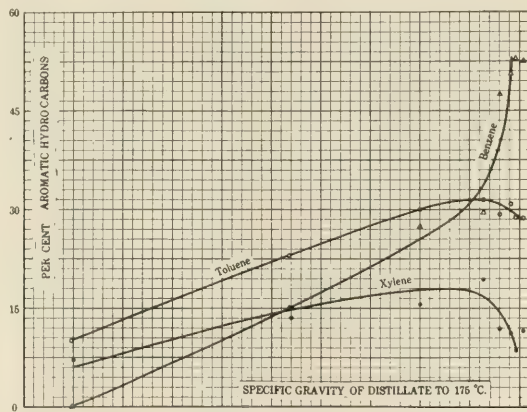


FIG. 2.—PERCENTAGES OF BENZENE, TOLUENE, AND XYLENES IN 175° PRIMARY DISTILLATION CUTS OF VARIOUS SPECIFIC GRAVITIES

0° to 95°; (2) Toluene fraction, 95° to 120°; (3) Xylene fraction, 120° to 175° C. A careful series of experiments has established the specific gravities of the non-aromatic constituents present in these cuts as: 0.720, 0.730 and 0.740. Knowing the gravities of the pure aromatics and measuring those of the distillates it is a simple matter to calculate percentages of the three hydrocarbons.

The methods used for naphthalene and anthracene were not of the same degree of accuracy as those for

<sup>1</sup> Rittman, Twomey and Egloff, *Met. and Chem. Eng.*, **13** (1915), 682



the monocyclic hydrocarbons, but the results have proven to be satisfactory in the present connection. These two hydrocarbons are contained in the cut above 175° left after the first distillation. This cut was subjected to further fractionation and two portions separated, one boiling from 175° to 270°, the other from 270° up to the point where actual tar begins to come over. The two hydrocarbons were estimated by the simple process of chilling, pressing out and weighing the separated solid.

#### DISCUSSION OF RESULTS

The results of the experiments, given in Table I, are not particularly easy to interpret. By plotting, however, the indications of importance are brought out in a striking manner. In Fig. I the abscissas are specific gravities of recovered oils, and the ordinates, percent-

aromatics, benzene, toluene and xylene. Curves similar to those in Fig. I are obtained except that since benzene is now an end product there is no falling off in its curve. By the use of a diagram similar to Fig. II it is possible to estimate the percentages of the three aromatics as functions of the specific gravity of the 175° cut. A quick and simple method of testing is thus furnished which is often of sufficient accuracy for practical purposes. These indications were checked up by analyses of recovered oils obtained by cracking Oklahoma crudes and a fair agreement obtained. Figures for the latter set of experiments are omitted as they add nothing to those already given; data regarding furnace conditions are lacking and irregularities are a little greater, due to less care in handling the cracked oil.

TABLE I—RESULTS OF "CRACKING" EXPERIMENTS (PERCENTAGES BY WEIGHT)

RUN No.	FURNACE CONDITIONS		Feed Gals. per hr.	Percent original	Sp. gr.	DATA ON RECOVERED ("CRACKED") OIL				DATA ON CUT TO 175° C.			
	Pressure Lbs. per sq. in.	Temp. ° C.				Per cent aromatics found	Per cent constituents	Per cent aromatics found	Per cent constituents	Per cent aromatics found	Per cent constituents	Per cent aromatics found	Per cent constituents
						Xy- lene	Tol- uene	Naph- thalene	Anthra- cene	Xy- lene	Tol- uene	Xy- lene	Tol- uene
1.....	200	(600)	14	30.0	1.018	19.1	10.4	3.1	14.1	9.6	36.2	0.874	52.9
2.....	200	700	14	20.0	1.000	20.7	11.2	4.6	8.1	3.8	39.3	0.876	52.6
3.....	250	650	15	23.5	0.992	20.0	12.2	4.4	7.0	0.0	39.5	0.873	50.6
4.....	250	700	15	22.5	0.978	20.2	12.4	5.0	2.0	0.0	42.4	0.870	47.6
5.....	250	650	15	23.5	0.954	16.5	17.8	10.8	0.0	0.0	55.8	0.866	29.6
6.....	200	625	14	30.0	0.938	12.3	13.4	7.0	0.0	0.0	44.8	0.850	27.4
7.....	250	600	15	31.2	0.900	7.9	12.0	7.1	0.0	0.0	52.2	0.817	15.1
8.....	200	550	14	55.0	0.837	0.0	4.0	2.8	0.0	0.0	39.0	0.762	0.0

ages by weight of the five hydrocarbons contained in the oil. Average curves are given, as the irregularities due to experimental error (probably imperfect condensation) would otherwise make less clear the indications obtained. It is to be noted that also no pretense is made of having analyzed the cracked oils for all constituents. The five hydrocarbons were chosen on account of their commercial importance and because they were typical.

It will be noted that toluene and xylene are found in a sample which yielded no benzene and that the curves for toluene and xylene bear a more or less constant relation to each other. Xylene percentages are about half those of toluene and the maximum for each of the two curves occurs at the same point on the horizontal axis, this representing most favorable conditions for the formation of these two aromatics. Benzene is a product of more strenuous conditions of cracking: it begins to form at a higher point on the scale adopted and has a higher maximum. Its content runs between those of toluene and xylene until the latter two pass their maximum. The benzene maximum is, however, greater than that of toluene.

Figures for naphthalene and anthracene are few but furnish important indications. Naphthalene formation begins at about the point where xylene and toluene commence to fall off. The naphthalene curve is ascending rapidly at the upper limit of the present range and there is no indication that it has begun to approach its maximum. Anthracene is formed under even more strenuous conditions than naphthalene.

One other point is of importance. Noting the relations shown on the basis of gravity of recovered oil led to a belief that a similar condition might obtain if the first (175°) distillation cut were considered. In Fig. II the specific gravity of each 175° cut is plotted against its percentage content of each of the three

#### SUMMARY

When petroleum is cracked there are definite relations among the percentages of the various aromatic compounds formed, said percentages being fixed by the degree of cracking. The factors which control the latter may be summed up and represented by the specific gravity of the cracked oil.

I—Toluene and xylene show the same variation in percentage formation, xylene being present in approximately one-half the quantity of toluene. Both are at a maximum in a recovered oil of about 0.95 specific gravity.

II—Benzene formation requires more strenuous cracking than is needed for the production of toluene and xylene. Benzene formation is at a maximum at a point where toluene and xylene have fallen off considerably in their content.

III—Naphthalene begins to form at about where the toluene-xylene content passes its maximum, indicating that naphthalene is a product of the decomposition of the monocyclic hydrocarbons. The maximum for naphthalene is necessarily much higher on the scale here chosen than that for any of the monocyclic compounds.

IV—Anthracene behaves similarly to naphthalene, requiring even more strenuous conditions for its formation.

V—The relations above indicated may, if desired, be so applied as to furnish a method for the approximate estimation of benzene, toluene and xylene from the primary 175° distillation cut obtained from the cracked oil.

CHEMICAL SECTION OF THE PETROLEUM DIVISION  
U. S. BUREAU OF MINES

#### OILS OF THE CONIFERAE: V—THE LEAF AND TWIG, AND BARK OILS OF INCENSE CEDAR

By A. W. SCHORGER

Received August 2, 1915

Incense cedar (*Libocedrus decurrens* Torrey) is largely restricted in its range to the state of California.

DISTILLATION EXPERIMENTS<sup>1</sup>

**EFFECT OF STORING NEEDLES**—A quantity of leaves and twigs weighing 1642 lbs. was collected from trees 6 to 14 in. in diameter. The material was thoroughly mixed with a fork, divided into three portions, and weighed. One portion was distilled while fresh, and the remaining portions after having been stored for two weeks and four weeks, respectively. The needles were kept on a platform in the open air and partially shaded from the sun by surrounding trees. During the first two weeks, six days were cool and cloudy and about three inches of rain fell on the material. Both heaps of leaves were slightly moulded in the center and those kept for four weeks began to turn yellow. The yields of oil obtained based on the weights before and after storing are given in Table I.

TABLE I—YIELD OF OIL FROM FRESH AND STORED NEEDLES

Sample number	Weight of material—Lbs.		Per cent yield of oil based on weight	
	Fresh	After storing	Before storing	After storing
2444	500	.....	0.206	.....
2467	565	511 (stored 2 weeks)	0.210	0.240
2479	577	480 (stored 4 weeks)	0.222	0.267

It is interesting to note that there is a slight increase in the yield of oil from the stored material even when based on the original weight before storing. The properties of the oils represented by Samples Nos. 2444, 2467, and 2479 will be found in Table II.

**YIELD AND COMPOSITION OF OIL THROUGHOUT THE SEASON**—The effect of the time of the year on the yield and composition of the oil is shown in Fig. 1. The

## LEAF AND TWIG OILS

The majority of the oils were pale, greenish yellow in color, though some samples were dark greenish

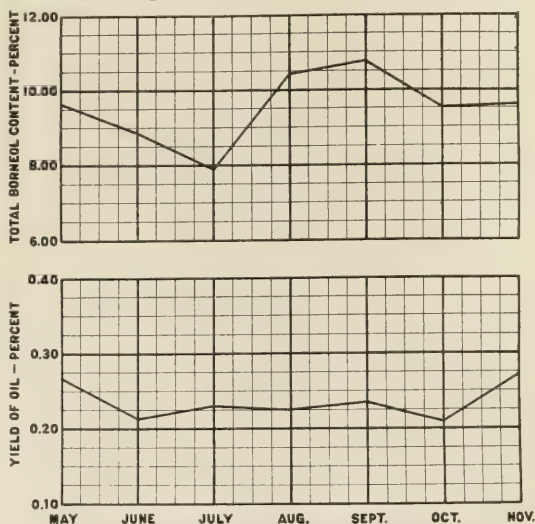


FIG. 1—YIELD AND COMPOSITION OF INCENSE CEDAR LEAF OIL THROUGHOUT THE PERIOD MAY TO NOVEMBER

brown. Their properties will be found in Table II. The oil distilled as follows: b. p. 159–165°, 10 per cent; 165–170°, 20 per cent; 170–180°, 46 per cent; 180–

TABLE II—PROPERTIES AND YIELDS OF LEAF AND TWIG OILS FROM INCENSE CEDAR

Sample number	Specific gravity 15° C.	Refractive index 15° C.	Optical rotation $\alpha_{D_{20}}$	Acid number	Ester number	Ester number after acetylation	Acetate Per cent	Free alcohol Per cent	Total alcohol Per cent	Yield of oil Per cent
2153	0.8655	1.4754	+38.68°	0.67	21.34	30.06	7.47	2.41	8.28	0.300
2154	0.8723	1.4763	+11.41	0.74	23.63	39.83	8.27	4.51	11.01	0.220
2205	0.8727	1.4766	+18.12	0.68	23.59	31.77	8.26	2.26	8.75	0.166
2206	0.8733	1.4765	+18.23	0.49	21.32	32.60	7.46	3.13	9.00	0.240
2418	0.8680	1.4766	+25.33	0.60	19.19	28.64	6.72	2.62	7.90	0.230
2444(a)	0.8731	1.4768	+2.71	0.48	24.27	37.81	8.49	3.76	10.44	0.206
2467(a)	0.8739	1.4770	+2.02	0.93	23.91	37.33	8.37	3.73	10.31	0.210
2479(a)	0.8729	1.4768	+2.65	1.00	23.67	34.91	8.28	3.12	9.63	0.222
2480	0.8721	1.4767	—3.20	0.48	21.82	34.48	7.64	3.51	9.51	0.255
2528	0.8724	1.4770	+1.60	0.74	20.45	36.67	7.16	4.51	10.14	0.210
2559	0.8677	1.4775	+28.12	0.48	20.26	34.73	7.09	4.02	9.59	0.270
2451(1)	0.8692	1.4762	+7.10	0.49	18.49	33.49	6.47	4.17	9.31	0.180
2451(2)	0.8712	1.4767	+6.13	1.30	23.03	37.61	8.06	4.05	10.39	
2451(3)	0.8697	1.4761	+5.36	0.60	24.59	38.33	8.54	3.87	10.58	
2451(4)	0.8766	1.4778	+4.80	0.96	27.82	46.24	9.74	5.14	12.79	

(a) See Table I.

Nos. 2451 (1 to 4)—See text.

results indicate a slightly greater yield of oil during May and November, while the total borneol content is greatest during August and September. Open-grown trees gave larger yields of oil than those surrounded by other timber.

**CHARACTER OF OIL FRACTIONS**—To determine the properties of the oil at different stages of the distillation, the distillate from one run was collected in four fractions as follows:

Fraction I—Oil obtained during first 1/4 hr.	133 cc.
Fraction II—Oil obtained during next 3/4 hr.	129 cc.
Fraction III—Oil obtained during next 3 hr.	184 cc.
Fraction IV—Oil obtained during next 6 hrs.	53 cc.

About 90 per cent of the oil passed over during the first 4 1/4 hrs. The properties of the oils from the four fractions are given in Table II under Sample No. 2451. The fourth fraction, No. 2451 (4), has abnormal properties, while the first three fractions would pass for normal oils.

<sup>1</sup> The distillation experiments were conducted by Mr. G. M. Hunt of the Forest Products Laboratory to whom acknowledgment is made.

200°, 6 per cent; 200–250°, 8 per cent; 250–280°, 6.5 per cent; 280–310°, 2 per cent.

**FURFURAL**—This aldehyde was qualitatively detected in an aqueous extract from the first fraction by means of the color reaction with aniline and hydrochloric acid.

**$\alpha$ -PINENE**—On repeated fractionation 58.3 g. (11.7 per cent) of oil were obtained between 155–160°. The portion boiling at 155–157° had the constants:  $d_{15}^0$ , 0.8635;  $\alpha_{D_{20}}$ ,  $-17.12^\circ$ . An  $\alpha$ -pinene fraction having  $d_{15}^0$ , 0.8627,  $\alpha_{D_{20}}$ ,  $-19.88^\circ$ , was obtained from Sample No. 2153, whose rotation was  $+38.68^\circ$ . The pinene nitropiperidine obtained melted at 117–118°.

A fraction amounting to 5 per cent distilled between 160–166° and had:  $d_{15}^0$ , 0.8603;  $\alpha_{D_{20}}$ ,  $+2.09^\circ$ . Examination for camphene and  $\beta$ -pinene gave negative results.

**SYLVESTRENE**—The fraction boiling at 170–171° was dissolved in ether, saturated with HCl gas and allowed to stand some time in the ice-box. On evapora-



tion of the solvent the residue was made to crystallize without difficulty. The crystals obtained softened at 60° and melted at 67–68°. By repeated crystallization from ethyl acetate the compound finally melted at 72–72.5°. The crystals obtained from the fraction boiling at 172–174° contained a greater amount of dipentene dihydrochloride than the fraction boiling at 170–171°. The sylvestrene regenerated from the purified dihydrochloride gave a beautiful, deep blue color with acetic anhydride and concentrated sulfuric acid. A 3.21 per cent ethereal solution of the sylvestrene dihydrochloride had the rotation  $\alpha_{D24} + 1.9^\circ$ .

**LIMONENE AND DIPENTENE**—Dipentene tetrabromide having the melting point 124–124.5° was obtained from a fraction boiling at 174–174.5°. Ten grams of a fraction having the boiling point 175–176°,  $\alpha_{D24} + 56.34^\circ$ , and  $d_{15} 0.8536$  after treatment with bromine and standing in the cold 24 hrs. gave 0.87 g. of crystalline tetrabromide. By fractional crystallization it was possible to obtain two tetrabromides melting at 123.5 and 113°. The original mother liquor, on standing, deposited an additional 2.4 g. of crystals that were richer in limonene tetrabromide since the first fraction on fractional crystallization melted at 115–116° after three additional crystallizations from ethyl acetate. The behavior of the tetrabromides shows the presence of both limonene and dipentene.

The total sylvestrene, limonene, and dipentene fractions amounted to 269.5 g. (53.9 per cent).

**BORNEOL**—The fraction boiling at 200–235° after saponification yielded an oil having  $\alpha_{D28} - 12.32^\circ$ . By means of the phthalic ester an oil was obtained having a strong odor of borneol. On oxidation camphor melting at 173–174° was obtained.

**ACETIC ACID**—The oil decomposed to some extent above 177° during distillation, a strong odor of acetic acid being produced. The presence of this acid was confirmed by analysis of the silver salt as follows:

0.2218 g. silver salt gave 0.1427 g. Ag = 64.34 per cent Ag.

Silver acetate,  $\text{CH}_3\text{COOAg}$ , requires 64.63 per cent Ag.

The acids obtained by saponification of the esters contained a second acid, two fractions of whose silver salt contained 39.32 per cent and 39.13 per cent Ag. The precipitates probably consist of silver caprinate with a small amount of silver acetate.

**SESQUITERPENE**—After removal of the esters 32.8 g. of oil distilled between 250–280° and 10 g. of a deep green oil between 280 and 310°. The fraction boiling at 250–280° contained a sesquiterpene having the properties: b. p., 260–280°;  $d_{20} 0.9292$ ;  $n_{D20} 1.4994$ ;  $\alpha_{D26} + 6.4^\circ$ . The fraction yielded a hydrochloride crystallizing from ethyl acetate in thin plates and melting at 132–133°. This sesquiterpene has not been identified with any of the sesquiterpenes recorded in the literature and has been tentatively called “libocedrene.” Lack of material prevented further study.

#### BARK OIL

The bark oil had the following properties: Color, faint greenish yellow;  $d_{15} 0.8621$ ;  $n_{D15} 1.4716$ ;  $\alpha_{D20} + 1.10^\circ$ ; acid No., 0.60; ester No., 3.22; ester No. after acetylation, 9.53; yield of oil, 0.14 per cent.

The sample consisting of 179 g. distilled as follows:

Temperature . . .	157–160	160–165	170–190	190–250	250–290
Per cent . . . . .	55.0	27.0	9.5	3.5	3.0

**FURFURAL**—This aldehyde was qualitatively detected in the fraction boiling at 157–158°.

**$\alpha$ -PINENE**—The total oil boiling below 168° amounted to 90 grams. This distilled almost entirely between 156° and 160°. A small portion distilling between 160–168° was examined for  $\beta$ -pinene with negative results. Ten grams of a fraction boiling at 156–157°,  $\alpha_{D18} + 1.46^\circ$ ,  $d_{15} 0.8630$ , gave 4 g. of pinene nitroschloride. The pinene nitrolpiperidine melted at 117–118°.

**DIPENTENE**—Nine grams (5 per cent) of oil distilled between 168–173° and had  $\alpha_{D20} - 1.46^\circ$ . Dissolved in dry ether and saturated with dry HCl gas a dihydrochloride melting at 48–49° was obtained.

**ALCOHOL FRACTION**—The ester fraction boiling at 190–235° amounted to 2.6 g. and was not further examined, owing to the small quantity. The free alcohol and ester content have been calculated as borneol and bornyl acetate.

**“GREEN OIL”**—A greenish yellow oil weighing 5.5 g. (3 per cent) was obtained between 250–290°. When a drop was dissolved in acetic anhydride and a drop of concentrated  $\text{H}_2\text{SO}_4$  added, a dark green color changing to greenish yellow was obtained. When the oil was dissolved in glacial acetic acid and bromine vapors added the pink color at first obtained changed to purple, finally becoming deep blue. An ethereal solution of oil when saturated with HCl gas became deep crimson and yielded no solid hydrochloride.

#### SUMMARY

The leaf and twig, and bark oils of incense cedar have approximately the following percentage composition:

CONSTITUENTS PRESENT	LEAF AND TWIG OIL	BARK OIL
Furfural . . . . .	Trace	Trace
l- $\alpha$ -Pinene . . . . .	12–16	75–85
d-Sylvestrene . . . . .	54–58	
d-Limonene . . . . .	8	5–6
Dipentene . . . . .	4	1
Bornyl acetate . . . . .	4	2
Free borneol . . . . .	6–7	3
“Libocedrene” . . . . .	2	3
“Green oil” . . . . .	6	6
Losses . . . . .		

FOREST PRODUCTS LABORATORY FOREST SERVICE  
U. S. DEPARTMENT OF AGRICULTURE  
(In cooperation with the University of Wisconsin)  
MADISON, WISCONSIN

#### REAGENTS FOR USE IN GAS ANALYSIS II. CHROMOUS CHLORIDE

By R. P. ANDERSON AND J. RIFFE

Received July 31, 1915

Chromous chloride seems to have been first prepared by Moberg<sup>1</sup> and by Peligot<sup>2</sup> working independently, the latter making special reference in his description of this substance to the avidity with which it unites with free oxygen. Otto von der Pfordten<sup>3</sup> proposed that the compound be used as an absorbent for oxygen, with particular reference to its removal from hydrogen sulfide. In his method of preparing the reagent, chromous acetate was first made by a method essen-

<sup>1</sup> Jour. prakt. Chem., **29** (1843), 175; **44** (1848), 322.

<sup>2</sup> Ibid., **35** (1845), 27; Ann. chim. phys., [3] **12** (1848), 528.

<sup>3</sup> Ann. der Chem., **228** (1885), 112.

tially that of Moissan<sup>1</sup> and then decomposed by hydrochloric acid with the formation of the chloride. Jannasch and Meyer<sup>2</sup> used chromous chloride with excellent results for the removal of oxygen from nitrogen in connection with the combustion of organic substances containing the latter element. They purchased chromous acetate in paste form and treated it with hydrochloric acid for the production of chromous chloride. They found that the reagent decomposes with the evolution of hydrogen if an excess of acid is employed, and therefore recommend that a small amount of undecomposed chromous acetate be allowed to remain in the solution. Berthelot<sup>3</sup> found that hydrogen is always obtained from a solution of chromous chloride in water unless the preparation is pure and free from any trace of acid. Peters<sup>4</sup> states that acid solutions of chromous chloride liberate hydrogen. Doring<sup>5</sup> substantiated the results obtained by Berthelot.

Chromous chloride has found but little application as a reagent in gas analysis. Some text books on the subject include it among the absorbents for oxygen and one communication<sup>6</sup> was found in which chromous chloride is suggested as a reagent for the determination of oxygen in flue gases in the presence of carbon dioxide and hydrogen sulfide; but nothing seems to have been accomplished in the way of the proper composition of the reagent or the proper method of its use. The following experiments were performed to obtain information on these points.

#### EXPERIMENTAL WORK

It seemed desirable to prepare the reagent first according to the method used by Otto von der Pfordten and by Jannasch and Meyer. Chromous acetate in paste form was not available on the market at the time that these experiments were performed and accordingly a considerable quantity of this material was prepared for conversion to chromous chloride as needed.

Three hundred grams of green chromic chloride were dissolved in a minimum amount of water and the solution transferred to a large Erlenmeyer flask fitted with a rubber stopper carrying an inlet tube, a separatory funnel, and an outlet tube long enough to reach to the bottom of the flask. The chromic chloride was reduced to chromous chloride by nascent hydrogen prepared from zinc and hydrochloric acid, about twice the theoretical amount of zinc being placed in the flask and the hydrochloric acid added from time to time in small amounts from the separatory funnel. During this operation the inlet tube was kept closed and the hydrogen which escaped oxidation in the flask was allowed to pass through the outlet tube, the lower end of which was raised above the level of the solution. After complete reduction of the chromic chloride had been obtained, as evidenced by the appearance of the characteristic blue color of chromous chloride in solution, the end of the outlet tube was lowered below the

surface of the solution, and carbon dioxide admitted to the flask through the inlet tube, thus forcing the solution through the outlet tube, and through a glass-wool filtering device, into a 5-liter bottle containing the theoretical amount of sodium acetate. These auxiliary portions of the apparatus had previously been freed from air by the waste hydrogen from the Erlenmeyer flask. A red precipitate of chromous acetate was formed, which was washed repeatedly by decantation, first with dilute acetic acid, saturated with carbon dioxide, to dissolve any basic zinc carbonate that may have been thrown down, and finally with distilled water saturated with the same gas. These operations were performed in an atmosphere of carbon dioxide and the resulting paste of chromous acetate was kept in the same bottle, tightly stoppered, with carbon dioxide above it.

To prepare the reagent, the desired amount of chromous acetate was transferred to a 300 cc. Erlenmeyer flask. A rubber stopper carrying an inlet tube, a separatory funnel, and an outlet tube was placed in the neck of the flask, the air was displaced from it by a current of carbon dioxide, and dilute hydrochloric acid was added through the separatory funnel to effect the decomposition of the acetate. The solution of chromous chloride thus obtained was then forced into a Hempel double pipette for liquid reagents<sup>1</sup> until it was filled to the proper point, and finally water was placed in the trap in the usual fashion.

Solutions were prepared using varying amounts of hydrochloric acid in proportion to the chromous acetate, but none of them was found to be stable. When sufficient acid was employed to decompose all of the chromous acetate, decomposition took place rapidly; when some undecomposed acetate was left in the solution, it was found, contrary to the statements of Jannasch and Meyer,<sup>2</sup> that minute bubbles of gas formed in the reagent and collected in the upper portion of the pipette, from 30 to 50 cc. being thus obtained during the first week. The gas was analyzed and found to consist largely of hydrogen, some carbon dioxide being present as a result of the saturation of the reagent with this gas during its preparation. Several attempts were made to prepare a stable solution of chromous chloride by decomposing chromous acetate with insufficient hydrochloric acid, using two different preparations of the paste of chromous acetate, but none of the attempts was successful. It thus appears that the statement of Berthelot<sup>2</sup> and others concerning the effect of acid upon chromous chloride is correct and that the acetic acid formed on the decomposition of chromous acetate by hydrochloric acid is responsible for the instability of chromous chloride thus prepared. Accordingly the attempt to prepare the reagent by this method was abandoned.

Chromous chloride was next prepared by the reduction of violet chromic chloride in a current of hydrogen. A piece of Jena glass tubing was filled with violet chromic chloride and heated to 400–500° C. in a combustion furnace. A current of hydrogen,

<sup>1</sup> *Compt. rend.*, **92** (1881), 792; *Ann. chim. phys.*, [5] **25** (1882), 401.

<sup>2</sup> *Ann. der Chem.*, **233** (1886), 375.

<sup>3</sup> *Compt. rend.*, **127** (1898), 24.

<sup>4</sup> *Z. physik. Chem.*, **26** (1898), 193.

<sup>5</sup> *Jour. prakt. Chem.*, [2] **66** (1902), 65.

<sup>6</sup> Anonymous, *Zeit. f. Chem. Apparatenkunde*, **3** (1908), 315.

<sup>1</sup> A modified form was employed. See *THIS JOURNAL*, **6** (1914), 237.

<sup>2</sup> *Loc. cit.*



freed from oxygen by alkaline pyrogallol and from water vapor by strong sulfuric acid, each in a Friedrichs washing bottle, was passed through the chromic chloride, the hydrogen chloride resulting from the reduction being absorbed in water in a third Friedrichs washing bottle. The reduction was carried on until the contents of the tube took on the yellowish white color of chromous chloride.

In the preparation of the reagent, the desired amount of the product of the reduction was rapidly transferred to a 300 cc. Erlenmeyer flask fitted with a rubber stopper carrying an inlet tube, a separatory funnel, and an outlet tube. Treatment of the material with water and the transfer of the resulting solution to a pipette was carried out in a fashion similar to the procedure described for the preparation of the reagent from chromous acetate, except that instead of carbon dioxide, hydrogen was employed throughout to avoid the difficulties due to the high solubility of the former gas.

The product of the reduction of chromium chloride with hydrogen is not entirely soluble<sup>1</sup> in water and it was found that if the solution was transferred to the pipette without filtering, hydrogen was gradually liberated in small amounts; on the other hand, if the solution was filtered through glass wool during the passage from the Erlenmeyer flask to the pipette, it was found to be stable.

On treating the filtered reagent with samples of air, the greater portion of the oxygen was absorbed during the first few seconds of shaking, but the absorption was not complete even after several minutes' shaking, the decrease amounting in most cases to 20.4 to 20.5 per cent. Four solutions prepared by the above method were examined with the same result in each case. That the absorption of oxygen was actually incomplete was demonstrated by treating the residual gas with alkaline pyrogallol, a procedure which resulted in a slight decrease in volume in every case and which gave the correct percentage of oxygen in air.<sup>2</sup>

#### SUMMARY

I—The preparation of chromous chloride according to the method followed by Otto von der Pfordten and by Jannasch and Meyer does not result in a stable solution and hence the reagent thus prepared is unsatisfactory for gas-analytical work.

II—The preparation of chromous chloride by the reduction of violet chromic chloride by means of hydrogen results in a solution which, when properly filtered, is stable, but the absorption of oxygen, although rapid, is not complete, and therefore the reagent thus prepared is unsatisfactory for gas-analytical work.

While the foregoing results are unfavorable as regards the possible wider application of chromous chloride as an absorbent for oxygen, nevertheless they should not be construed as necessarily indicating that a solution of this substance which shall be suitable for gas-analytical work can not be prepared. It is not likely, however, in view of the high cost of the ma-

terials and the probable inconvenience of preparation, that chromous chloride will ever be widely used except in cases, such as the absorption of oxygen in the presence of carbon dioxide and hydrogen sulfide, where other reagents can not be employed.

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#### A RAPID CONTROL METHOD FOR THE DETERMINATION OF SULFUR IN PYRITES CINDER

By H. C. MOORE

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Many methods for the determination of sulfur in pyrites, blendes and cinders have been proposed, but apparently no one of the methods thus far reported has been generally adopted. Some methods require costly apparatus, the expense of which is hardly justified in many laboratories; others require one or more standard solutions, which are hardly worth while for many analysts to prepare, owing to the few determinations to be made.

There have been proposed a few rapid methods requiring no expensive apparatus, and if standard solutions, only those found in every laboratory, but, for various reasons, no one of these methods has come into general use.

The so-called rapid control methods may be divided into five classes as follows:

1—Dry oxidation by fusion and subsequent precipitation as barium sulfate.

2—Dry reduction by heating with powdered metal, such as iron or aluminum or a mixture of the two, with the subsequent determination of sulfur by expelling as hydrogen sulfide and determining the latter volumetrically.

3—Direct combustion of cinder at high temperature, preferably in an electric tube furnace, collecting the sulfur as sulfur dioxide in standard alkali.<sup>1,2</sup>

4—Heating the cinder with sodium bicarbonate of known alkalimetric value, leaching, filtering and determining the excess of bicarbonate.<sup>3</sup>

5—Heating the cinder with a mixture of sodium carbonate and some oxide, such as zinc oxide, leaching and filtering, determining the sulfur gravimetrically as barium sulfate; or by precipitating in neutral solution with standard barium chloride, determining the excess of barium chloride by titration against standard sodium carbonate, using phenolphthalein as indicator.<sup>4</sup>

There are a few methods which will not fall in these classes, but in referring to some of them, Lunge says on page 74, "Sulfuric Acid and Alkali," Vol. I, Part I, "expeditious assays of pyrites have been proposed in many ways but none of them are sufficiently accurate to be employed for estimating the sulfur in fresh pyrites and some of them are not even accurate enough to test sulfur remaining in burnt ore."

The number of determinations to be made, and the time permitted for an analysis are the important factors in selecting the method to be used. If a result is desired in the shortest possible time, probably the method of Nitchie, and its modification by Conner stand preëminent. These methods, however, require an

<sup>1</sup> Nitchie, *THIS JOURNAL*, **4** (1912), 30.

<sup>2</sup> Conner, *Ibid.*, **5** (1913), 399.

<sup>3</sup> Lunge's "Technical Chemists' Handbook," p. 113.

<sup>4</sup> *Chem. Ztg.*, **37** (1913), 1107

<sup>1</sup> According to Moberg, some metallic chromium is formed.

<sup>2</sup> The departure of the junior author from the University prevented further investigation of this problem under the present joint authorship.

electric tube furnace, pyrometer, rheostat, etc., the expense of which is hardly justified where but a few samples are tested each week. To such laboratories the method to be described here may appeal as being rapid, requiring very little actual manipulation and no expensive apparatus.

We have taken the time to try but few of the proposed rapid methods since we have had but few determinations of sulfur in cinder to make. The reduction methods in Class 2 appear promising, but two standard solutions, iodine and thiosulfate, are required. Our few attempts to use the method of von Horhorst<sup>1</sup> have not been successful. The method which we have been using for a year follows:

Transfer 1.3738 grams of cinder (ground to pass 100 mesh) to a 50 cc. wrought iron crucible<sup>2</sup> containing 7 grams powdered sodium peroxide; mix carefully with glass rod, wipe off glass rod with small piece of filter paper and add to contents of crucible. Sprinkle a thin layer of peroxide over the surface, cover the crucible and place over a low flame until nearly melted, finally raising heat until contents are melted and in quiet fusion, and continue heat for one minute longer. A moderate flame is sufficient for this fusion and the lower the heat used the longer will be the life of the crucible. Let the crucible and contents cool, rinse the crucible cover into a 400 cc. beaker, and add water to make about 50 cc. Dip crucible into water, letting it rest on its side in the bottom of the beaker, covering quickly with a watch glass. When the action is over, remove and rinse the crucible, as well as the cover glass and side of the beaker. Add hydrochloric acid slowly, until iron residue is dissolved, avoiding any considerable excess of acid and transfer to a 500 cc. volumetric flask. Add aluminum powder in slight excess (about 0.4 to 0.5 g. in all), shake well until the iron is reduced, heat to boiling and continue heating until the aluminum is nearly all dissolved (which aids in subsequent filtration). Cool and make to mark, mix and pass through a dry filter; pipette 200 cc. into a 600 cc. beaker and dilute to 450 cc. with water, add 1 cc. concentrated hydrochloric acid, mix, and precipitate cold without stirring, by adding 25 cc. 5 per cent barium chloride solution slowly (about 5 cc. per minute), either from burette or by means of a special precipitating cup such as is described by Allen and Bishop.<sup>3</sup> After the barium chloride has run in, stir the solution and allow it to settle for one hour. Filter through a No. 4 Gooch crucible (E. H. Sargent & Co., No. 1488), packed with asbestos and wash thoroughly with cold water. When the amount of barium sulfate is small, the crucible and contents may be dried quickly by carefully "flipping" through the flame, though large amounts should be dried in an oven to avoid loss by spattering and also to avoid cracking of the crucible by too rapid heating while wet. The weight of barium sulfate divided by 4 and multiplied by 100 gives the percentage of sulfur.

The following tabulation shows results by this method as compared with results by the wet oxidation method, using the method of Allen and Bishop for pyrites, with slight modifications. In employing this latter method, we weighed three portions of 1.3738 grams, transferred to 400 cc. tall form beaker and added 10 cc. bromine-carbon-tetrachloride mixture followed, after fifteen minutes, with 15 cc. concentrated HNO<sub>3</sub>, evaporating, etc. Since this method did not seem to dissolve the sample appreciably, one portion of each sample (marked "x" on tabulation) was treated by making in all cases a second evaporation with 10 cc. of a mixture of 3 parts of concentrated nitric acid and 1 part of concentrated hydrochloric acid, finally making one evaporation with 10 cc. concentrated hydrochloric acid. The residue (after being dried in oven) was treated with 4 cc. hydrochloric acid and 100 cc. hot water and warmed until solution was complete. The iron was reduced by aluminum powder, the solution filtered and washed with hot water and diluted to 450 cc. with cold water, 1 cc. concentrated hydrochloric acid added and the precipitation made cold, without stirring, by adding 25 cc. 5 per cent barium chloride solution.

TABLE I.—PERCENTAGES SULFUR BY ALLEN AND BISHOP AND NEW FUSION METHODS

Sample No.	ALLEN AND BISHOP METHOD			NEW FUSION METHOD		
	Determinations	"x"	Av.	Determinations		Av.
11818	1.11	1.12	1.15	1.13	1.26	1.31
11819	2.04	2.06	2.05	2.05	2.17	2.18
12250	2.74	2.74	2.73	2.74	2.74	2.77
12251	3.33	3.33	3.38	3.36	3.30	3.30
12424	3.44	3.44	3.48	3.46	3.64	3.65
12518	2.96	2.97	2.92	2.95	3.09	3.06
9000-B	1.41	1.41	1.42	1.41	1.53	1.54
17345	9.60	9.60	9.62	9.63	9.44	9.48
20704	2.37	2.38	2.38	2.38	2.38	2.38

In this method as described we have combined the features of several methods. The use of sodium peroxide was proposed by Glasser<sup>1</sup> and List<sup>2</sup> and the reduction of iron to ferrous condition by aluminum powder by Allen and Bishop.<sup>3</sup> Our results, however, are very satisfactory as noted from the tabulation above. Samples 11818 and 11819, for which the wide differences are noted, were drawn from a cinder dump, several years old, though this would appear to offer no reason for the greater differences in the case of these two samples. The same is true of 9000-B although this cinder was from another grade of ore. On the whole, however, the agreement is about as good as is usual in the case of rapid compensating methods and is much better for fresh than for weathered cinder. The actual time required for a test is from 2 to 2½ hours and the actual working time from 20 to 25 minutes.

Since fusion with sodium peroxide would decompose barium sulfate and make silica soluble, tests were made to determine the error, if any, resulting from the application of this method to samples containing a large percentage of either of these ingredients. Two samples of pyrites, which had been carefully analyzed by the Allen and Bishop Method, were used for this purpose. The results appear in Table II.

<sup>1</sup> *Chimiste*, **2**, 97-99.

<sup>2</sup> A nickel crucible may be used instead of iron but the iron crucible is cheaper.

<sup>3</sup> 8th Intern. Congr. Appl. Chem., **1**, 33-51.

<sup>1</sup> *Chem. Ztg.*, **18** (1894), 1884.

<sup>2</sup> *Z. anorg. Chem.*, **16** (1903), 414.

<sup>3</sup> *Loc. cit.*



TABLE II—EFFECT OF BARIUM SULFATE AND SILICA  
Results in Percentages of Sulfur on the Dry Basis

Sample	No. 5—Armenian ore					No. 6—Rio Tinto ore				
Method	Determinations					Determinations				
Allen and Bishop										
New Boston Method										
Unmodified	39.86	39.41	39.20			47.12	46.95	47.34		
	39.82	39.72	39.27		39.55	47.32	47.08	47.15		47.36
	39.70	39.85				47.86	47.17	47.19		
Added 0.2 g. BaSO <sub>4</sub>	39.76	39.55			39.65					
Added 0.2 g. SiO <sub>2</sub>	39.64	39.23			39.43					
Added 0.2 g. BaSO <sub>4</sub> and 0.2 g. SiO <sub>2</sub>						47.34	47.40			47.37

From Table II it would appear that any barium sulfate present in the ore and decomposed by the sodium peroxide would be precipitated by the addition of hydrochloric acid. It is generally claimed that the precipitation of barium sulfate under such conditions is incomplete but the results in Table II show that the addition of as much as 2.75 per cent sulfur, as barium sulfate, and silica amounting to about 13 per cent, has no appreciable influence on the results.

The results in Table II further show that this method would serve as a rapid approximate method for determining sulfur in pyrites and with some care and study would doubtless furnish quite accurate results. The effect of barium sulfate and silica was studied on samples of pyrites instead of cinder since these two samples had been very carefully standardized in other work.

Doubtless such a method as this would meet admirably the needs of those who have to make but an occasional determination of sulfur in cinder. It has been in use in our laboratory for about a year and has been found to be entirely satisfactory. Prior to the adoption of the method as described above, we used a similar one for about two years. By the old method, solution of the sample was effected in the same manner but the iron was precipitated with ammonia and the precipitation of barium sulfate made in a hot solution.

ARMOUR FERTILIZER WORKS, ATLANTA, GEORGIA

## THE DETERMINATION OF SUCROSE IN CONDENSED MILK<sup>1</sup>

By G. W. KNIGHT AND G. FORMANEK

Received July 1, 1915

Agricultural and dairy chemists<sup>2</sup> usually estimate sucrose in condensed milk by deducting the milk solids from the total solids. This is unquestionably the simplest, and probably the most satisfactory way of estimating the quantity of cane sugar present. When sucrose is the only constituent that one needs to determine, however, it is necessary to have resource to some other method.

### WORK OF PREVIOUS INVESTIGATORS

As early as 1893 Bigelow and McElroy<sup>3</sup> published a biological method in which the sucrose is inverted by fermentation with compressed yeast at 55° C. for five hours and the percentage calculated by Clerget's formula from the polariscopic readings before and after inversion. The milk proteins are precipitated by an acetic acid solution of mercuric potassium iodide.

<sup>1</sup> Contributed with the permission of the Secretary of the Treasury and the U. S. Appraiser, Port of New York.

<sup>2</sup> Bureau of Chemistry, Bull. 107 (Rev.), 123.

<sup>3</sup> J. Am. Chem. Soc., 15, 668.

If invert sugar is present in appreciable amount the procedure is modified by conducting the fermentation for ten days at a temperature of 25° to 30° C. in the presence of potassium fluoride.

Wiley claims that it is fair to assume that no invert sugar is present in condensed milk. In the samples we have analyzed to determine this point we have been unable to detect enough invert sugar to materially affect the result.

Baker and Hulton,<sup>4</sup> working with dilute sugar solutions of from 0.3 to 3.0 per cent strength, have tested this method of fermentation with lactose alone and with lactose mixed with other fermentable sugars, allowing the fermentation to proceed for 60 to 70 hours at a temperature of 27° C. The unfermented sugar, lactose, was determined volumetrically with Fehling's solution. They obtained low results in most cases, the difference between the amount of lactose known to be present and that found varying up to 10 per cent of the lactose present. Other investigators have noticed similar losses of the lactose in attempting to determine sugars by this fermentation method.

Inasmuch as there is always danger of fermentation of the lactose due to the possible presence of bacteria and symbiosis between the yeast and bacteria, one is never certain of obtaining reliable and accurate results by any fermentation method.

Nowak<sup>5</sup> has recently worked up an interesting method proposed by Jolles<sup>6</sup> which depends on the fact that all mono- and disaccharides, with the exception of sucrose, are rendered optically inactive when heated under pressure in a steam bath for 45 minutes with 16 per cent sodium hydroxide solution. After destroying the lactose in this way, the amount of sucrose present is determined by the polariscope. The solution polarized is so dilute that the error of reading the instrument makes the final result uncertain to  $\pm 1$  or 2 per cent, and as Jolles particularly states that the amount of sugars other than sucrose present in the solution treated with the sodium hydroxide must not exceed 2 per cent, it would appear that this method could not be made to give the desired degree of accuracy.

The A. O. A. C.<sup>4</sup> did some coöperative work a few years ago on two gravimetric methods in which the milk was prepared and clarified and the reducing sugars before inversion determined in the same manner as described in their provisional method<sup>5</sup> for lactose in milk. In one method the sucrose was inverted by heating the solution on a water bath for 40 minutes with 4 g. of citric acid in the manner proposed by Stokes and Bodmer,<sup>6</sup> in the other method the sucrose was inverted in the cold with concentrated HCl as described in the official method<sup>7</sup> of the A. O. A. C. for the determination of sucrose in foods. After inversion the invert sugar was determined gravimetrically with

<sup>1</sup> Analyst, 35, 512.

<sup>2</sup> Z. anal. Chem., 51 (1912), 610.

<sup>3</sup> Z. Nahr. Genussm., 20 (1910), 631.

<sup>4</sup> Proc. of A. O. A. C., 1909, Bur. of Chem., Bull. 132, 171.

<sup>5</sup> Bur. of Chem., Bull. 107 (Rev.), 123.

<sup>6</sup> Analyst, 10, 10.

<sup>7</sup> Bur. of Chem., Bull. 107 (Rev.), 41.

Fehling's solution. The average percentage obtained from nine chemists by the first method was 42.27 per cent, by the second method 42.95 per cent. The percentage of sucrose obtained by subtracting the average per cent milk solids from the average per cent total solids was 42.98. The agreement between the last two results is remarkable. The highest result obtained by the first method was 44.36 and the lowest 39.90 per cent. The highest obtained by the second method was 44.30 and the lowest 41.23 per cent. Although this is a rather wide variation, the other determinations show a corresponding proportional variation. These discrepancies are undoubtedly due to lack of homogeneity in the condensed milk analyzed—a matter which will be discussed later. From the results obtained in this cooperative work, it would appear that the second method is a reliable one; but a polariscopic method is preferable where a large number of samples have to be analyzed, owing to the greater rapidity and ease of manipulation of polariscopic methods.

Of the polariscopic methods published, Cochran<sup>1</sup> has described one in which he utilizes Wiley's acid mercuric nitrate solution both as clarifying and inverting agent. This method is based on his discovery that this acid mercuric nitrate solution completely inverts sucrose when heated with it on a water bath for eight minutes, while at temperatures below 15° C. it inverts very slowly.

Quite recently Revis and Payne<sup>2</sup> have published a polariscopic method for the determination of lactose and sucrose in condensed milk, in which they use acid mercuric nitrate solution similarly for clarifying and inverting the sucrose. Their formulas for calculating the percentages of the sugars include correction factors for the change in concentration caused by the volume of fat and protein present which involve a determination of the percentages of these substances.

To show the inadequacy of acid mercuric nitrate solution as a clarifying agent to remove the proteins occurring in condensed milk, Richmond<sup>3</sup> has published some interesting data. He found that on adding phosphotungstic acid to a solution of milk, clarified by acid mercuric nitrate, a voluminous precipitate was formed. Further, on analyzing whey powders containing about 70 per cent of lactose, an error amounting to 4 per cent occurred, owing to the presence of protein unremoved by the acid mercuric nitrate solution. He recommends using phosphotungstic acid after the milk has been partially clarified with the acid mercuric nitrate solution.

We have used phosphotungstic acid in conjunction with lead acetate for a number of years, to remove troublesome proteins in making polariscopic determinations of sugars in meat extracts, milk preparations and galenicals, with very satisfactory results; the polariscopic determinations check very well with gravimetric determinations.

Chemists familiar with commercial condensed milk know that there is a tendency for lactose crystals to

collect and pack on the bottom of the can, and it is difficult to obtain a representative sample of the milk for analysis. The official organ<sup>1</sup> of the A. O. A. C. recommends that the sample be mixed thoroughly by transferring the contents of the can to a large evaporating dish and stirring it with a pestle until homogeneous. Bache<sup>2</sup> has lately published analyses showing the inaccuracies that may be caused by failure to obtain a sample representative of the contents of the can, through lack of homogeneity of the different kinds of milk. The greatest difficulty was encountered in the cases of milk having a thick consistency and thin milk that had stood for a long time. He showed that the only way to obtain an absolutely reliable sample was to dilute the milk with water before analyzing. Bache states that possibly a separation of the constituents of the condensed milk also takes place in the process of manufacture, and that may explain the fact that tins from the same manufacturer do not always analyze the same. The writers have sometimes obtained a higher percentage of sucrose than that put in by the manufacturer; but generally they obtained slightly less. These results could be explained only by Bache's theory. In the manufacture of condensed milk, as in the manufacture of certain kinds of confectionery, there undoubtedly occurs a slight destruction of sucrose due to contact with the steam-heated surfaces used in evaporation, and this would account for slightly lower results.

#### DISCUSSION OF GENERAL CONSIDERATIONS

The lactose crystallized out in the cans of condensed milk evidently has assumed the  $\beta$  form. The official method of the A. O. A. C.<sup>3</sup> specifically mentions the fact that it is not necessary to heat the solution before polarizing in the determination of lactose in milk. The writers have never noticed any evidence of mutarotation in any of the samples they have analyzed to determine this point.

Invertase is unquestionably the most ideal inverting agent to use in general work as it possesses a more or less selective inverting action, and inverts very few substances other than sucrose. Hudson<sup>4</sup> has worked out a method for determining cane sugar, using invertase.

For practical analytical work, however, the use of invertase has many drawbacks. Among these are the time required and the inconvenience of preparing and preserving the solution; and the uncertainty as to the strength of the solution, which necessitates the occasional running of blanks of known sugar content to determine the inverting power of the solution, unless a new supply is made every few months.

The use of organic acids also has serious drawbacks. Tolman<sup>5</sup> has shown that in the presence of soluble acetates, as when lead acetate is used to clarify, the inverting action of citric acid is greatly retarded. The results obtained in the cooperative work of the A. O. A. C. mentioned above tend to show incomplete in-

<sup>1</sup> *Bur. of Chem., Bull.* **107** (Rev.), 122.

<sup>2</sup> *Analyst*, **36**, 138.

<sup>3</sup> *Bur. of Chem., Bull.* **107** (Rev.), 119.

<sup>4</sup> *THIS JOURNAL*, **2**, 143.

<sup>5</sup> *Bur. of Chem., Bull.* **73**, 69.

<sup>1</sup> *J. Am. Chem. Soc.*, **29** (1907), 555.

<sup>2</sup> *Analyst*, **39**, 476.

<sup>3</sup> *Ibid.*, **35**, 516.



version of the sucrose by the use of oxalic acid in the analysis of condensed milk, although pure sucrose treated similarly is completely inverted. Many reasons have been given for this lowering of inverting action. Perhaps the best explanation is that offered by the dissociation theory.

Concentrated hydrochloric acid, acting in the cold as described in the official methods of the A. O. A. C., inverts sucrose completely except where an unusual amount of lead acetate has been used to clarify the solution. The writers have made a number of analyses of lactose under similar conditions and have been unable to discover enough inversion of the lactose to affect the polariscopic reading for any concentration.

The invert reading should be made in neutral solution to eliminate inaccuracies caused by the effect of free acid on the polarization of levulose for different concentrations. The Clerget factor for neutral solutions for a concentration of 13 grams of sucrose in 100 cc. is 141.7, the same as that determined by Hudson for invertase inversion. For lower concentrations the factor is slightly different, owing to change in the specific rotation of invert sugar for different concentrations as shown by Gubbe,<sup>1</sup> but the polarization is less so that the difference obtained by using the more correct factor is less than the error of reading the instrument.

Unless the per cent of fat and protein in the sample of condensed milk has been determined, the double dilution method of Scheibler<sup>2</sup> should be used to correct for the error due to the volume occupied by these substances and any precipitate caused by clarification, since the percentages of these substances vary over wide enough ranges to seriously affect the accuracy of the determination of sucrose.

#### EXPERIMENTAL WORK

A solution of condensed milk that has been completely clarified by the use of phosphotungstic acid and lead acetate does not show any trace of protein with picric acid or any of the other more delicate protein precipitants.

Test analyses made with pure sucrose using the same quantities of phosphotungstic acid, lead acetate and potassium oxalate as that found necessary to thoroughly clarify the condensed milk showed that the free acetic acid, acetates, and oxalates left in the solution do not reduce the concentration of the hydrogen ions sufficiently to prevent thorough inversion of the sucrose with the amount of hydrochloric acid used.

It was found that 0.5 gram of potassium oxalate was generally sufficient completely to de-lead the solutions when the specified quantity of lead acetate solution was used, and that a large excess should not be used, since it seems to redissolve the lead precipitate and cause a milky filtrate, in addition to causing errors by diluting the solution.

In order to determine any error due to change in volume caused by the addition of the potassium oxalate used in de-leading, 0.5 gram of potassium oxalate was dissolved in 100 cc. of water and the increase in volume measured. The solution of 0.5 gram of potassium

oxalate caused an increase in volume of 0.2 cc. A filtrate from condensed milk that had been clarified with the required amounts of phosphotungstic acid and lead acetate was de-leaded with 0.5 gram of potassium oxalate, the precipitate filtered off, washed with water, alcohol, and ether, dried and then added to 100 cc. of water. The addition of the dried precipitate caused an increase in volume of 0.2 cc. Since the increase in volume caused by the solution of the potassium oxalate needed to de-lead the filtrate is compensated for by the decrease in volume caused by the space occupied by the precipitate, no correction is needed for either source of error.

To study the combined effect of the various constituents occurring naturally in the milk and those added incidental to the clarification, de-leading, inverting and neutralizing on the specific rotation of the sugars and consequently on the Clerget factor, some chemically pure sucrose was added to commercial samples of evaporated unsweetened whole milk, in the proportions that it occurs in commercial condensed milk, and the Clerget factor calculated after the solutions had been treated exactly as in the method given below. The factor obtained in each case was 141.7.

The chemically pure sugar used was carefully prepared, contained no moisture, no ash, and had an average direct polarization of 99.87, and analyzed 99.85 per cent sucrose by Clerget, reading the invert solution neutralized. The readings were made at 20° C. in standardized tubes of the Bates type, on a Bates type polariscope, using a bichromate cell and setting the instrument for maximum sensitiveness. All the apparatus used was carefully standardized. Since Bates and Jackson<sup>1</sup> have recently shown that the 100° S. point is approximately 0.1° S. too high on the present types of saccharimeter, this sucrose may be considered pure enough for our purpose.

The method given below was tested in the following manner. Four cans of unsweetened evaporated whole milk, dried in a desiccator and weighed full and empty to obtain the weight of milk in each can, were transferred to volumetric flasks. The four cans were from the same manufacturer and were of the same grade milk. The flasks were filled with water and shaken to dissolve any crystallized lactose and make the solution homogeneous. An aliquot was evaporated to dryness to obtain the percentage of total solids. Then, using this percentage of solids as a basis for calculation, such quantities of the C. P. sucrose mentioned above were added to three other aliquot portions that the respective solutions contained 33.40, 40.00 and 43.60 per cent sucrose of the evaporated milk and sucrose contained therein. After the sucrose had been thoroughly dissolved, the resulting solutions were analyzed for sucrose by the polariscopic method given below and also gravimetrically by Munson and Walker's Method,<sup>2</sup> using the corrected tables for lactose.<sup>3</sup> The solutions clarified in the same way as in the polarimetric determination were used for the latter determination.

<sup>1</sup> Bur. of Standards, *Bull.* 10, 538.

<sup>2</sup> Bur. of Chem., *Bull.* 107 (Rev.), 241.

<sup>3</sup> Bur. of Chem., *Circ.* 82.

<sup>1</sup> *Ber.*, 18, 2207.

<sup>2</sup> *Z. Ver. Deut. Zuck.*, 25, 1054.

The following results were obtained:

PER CENT SUCROSE ACTUALLY PRESENT	PER CENT SUCROSE FOUND	
	Polariscopic method	Gravimetric method
33.40	33.20	33.25
40.00	39.99	40.24
43.60	43.56	43.51

#### METHOD

After removing the label, the can of condensed milk is heated for a short time in a 100° oven, cooled in a desiccator, weighed, the contents, weighing from 12 to 15 ounces, transferred by means of hot water and a suitable funnel to a 500 cc. volumetric flask. This may be accomplished most readily by punching two holes in opposite positions near the circumference of the top of the can, inverting the can over a funnel in a fixed position and allowing the can to drain till practically empty, then removing the top and washing out the remainder. The empty can is then dried and weighed in the same manner as before and the weight of milk in the can ( $W$ ) thus determined. The contents of the flask are shaken until all crystals of lactose and cane sugar are dissolved and the milk solution homogeneous; then the flask is filled to the mark with water, cooled to room temperature and shaken. Two aliquot portions of 50 and 100 cc. measured in volumetric flasks, are transferred with rinsings to 200 cc. volumetric flasks and clarified by the addition first of 1.7 cc. of 5 per cent phosphotungstic acid solution for each 10 grams of condensed milk contained in the aliquot, and then after shaking, by the addition of 2.1 cc. of a 25 per cent neutral lead acetate solution for each 10 grams of condensed milk contained in the aliquot portion. The flasks are well shaken and then made up to the mark, well shaken again, and filtered. To the filtrates measuring about 100 cc. are now added potassium oxalate crystals in portions of 0.1 gram at a time, with constant shaking, until a curdy precipitate forms which quickly settles leaving a clear liquor. Usually 0.5 gram of the potassium oxalate is sufficient, and a large excess should be avoided. The solutions are again filtered, using a hardened filter containing 3 to 5 grams Fuller's earth placed in the apex and testing the first 10 cc. or so with more potassium oxalate crystals for complete removal of lead, and a portion of the filtrates polarized at 20° C., preferably on a Bates instrument set for maximum sensitiveness and using a bichromate cell.

Multiplying the reading of the dilute solution by 4 and subtracting the reading of the stronger solution from the product gives the direct polarization ( $P$ ) of the solution corrected for the volume of precipitate.

Two aliquot portions of 50 cc. of the filtrates are measured into 100 cc. flasks by means of pipettes; 5 cc. of concentrated HCl (38.8 per cent) added to each, and the resulting solutions allowed to stand over night at room temperature. The room temperature should not be below 20° C., but preferably around 25° C. In the morning a few drops of phenolphthalein are added to the solutions and they are then neutralized with strong NaOH solution. A few drops of  $N/10$  HCl are added to dispel the pink color, the solutions are made up to the mark, cooled to room temperature

if necessary, and then polarized in the same manner as before inversion, preferably using 400 mm. polariscope tubes on other instruments than those of the Bates type. The corrected invert polarization is obtained by subtracting the polarization of the strong solution from 4 times the polarization of the weaker solution, in the same manner as before inversion. Multiplying this corrected invert polarization by 2, except where 400 mm. tubes have been used, gives ( $P^1$ ) the invert polarization corresponding to ( $P$ ) the polarization before inversion.

Substituting these values in the following equation gives the per cent of sucrose in the condensed milk.

$$\text{Per cent sucrose} = \frac{26000 (P - P^1)}{W (141.7 - T/2)}$$

Where  $W$  = weight of condensed milk contained in can and  $T$  = temperature in degrees centigrade at which invert reading is made. All flasks and pipettes used should be carefully standardized for true cubic centimeters at 20° C.

U. S. CUSTOMS SERVICE  
PORT OF NEW YORK

### THE DETERMINATION OF MOISTURE IN SYRUPS BY THE CALCIUM CARBIDE METHOD

By R. M. WEST  
Received June 4, 1915

#### INTRODUCTION

The determination of moisture in organic, as well as in inorganic, substances is a source of much difficulty. This is due largely to the fact that in many instances chemical changes, either increasing or decreasing the weight of the material, take place at the temperature necessary for the evaporation of the moisture and, in others, compounds are present which volatilize with the water during the determination.

Attempts have been made to correct for the errors inherent in the ordinary drying process by drying (1) *in vacuo*, (2) in an atmosphere of neutral gas, (3) at low temperatures over dehydrating agents, and (4) by distilling the moisture from large samples, together with oil, and measuring the water obtained. None of these modifications, however, are entirely satisfactory.

Syrups, fruit juices, substances with a high fat content, and those containing other volatile compounds are particularly troublesome. The syrups, after concentration to a point at which only five or ten percent of the water remains, become so viscid as practically to prevent further drying. The addition of sand or pumice, as prescribed by the A. O. A. C. official method,<sup>1</sup> results more or less satisfactorily, depending upon the proportion used and the original moisture content of the syrup.

Tables I and II show quite clearly the variation to which results by this method are subject. Furthermore, the long continued heating to which it is necessary to subject a syrup in order to arrive at nearly constant weight, results in some inversion of the sucrose, thus decreasing the apparent moisture content. This is especially marked when considerable amounts of acid

<sup>1</sup> U. S. Department of Agriculture, Bureau of Chemistry, *Bull.* 107, (revised) 64-65.



are present, the inversion varying with the acidity of the syrup and with the length of time required for drying. It is clear, too, that attempts to dry a syrup to absolute constant weight must be unsuccessful, as the syrup will continue to lose weight as long as the patience of the analyst will permit the experiment to continue.

A number of methods have been proposed as substitutes for the official method and its modifications. One of these<sup>1</sup> is to treat the material to be analyzed with an alkyl magnesium halogen compound and measure the methane evolved. Another, first suggested in 1900 by Danne,<sup>2</sup> is to treat similarly with calcium carbide and measure the acetylene either by loss in weight or gasometrically. Danne originally proposed the method for the determination of moisture in substances containing other volatile constituents; Dupré<sup>3</sup> reports success with the method when used for moisture in ammonium oxalate, cordite and similar substances containing volatile matters other than water; Cripps and Brown<sup>4</sup> proposed using Danne's method for moisture in spices and aromatic drugs; and from time to time analysts<sup>5</sup> have reported the satisfactory extension of the method to other substances.

#### EXPERIMENTAL

Incidental to a project on sorghum syrup, it soon appeared that some method for moisture, more satisfactory and reliable than the A. O. A. C. official method, would have to be adopted. This necessity was due, *first*, to the fact that the experiment included a moisture determination on so large a number of samples that the time required for the repeated weighing and drying by the official method was an objectionable feature; and, *second*, because the plan of the work involved a comparison of the finished syrups with the respective raw and defecated juices from which they were made. This comparison could be made properly only on an absolute dry matter basis, and previous experience with the official method had shown it to be of doubtful value for such a purpose.

Attempts were made, therefore, to utilize the calcium carbide method. The experiment as conducted by Danne, Dupré and others, consisted in separating the carbide from the sample to be analyzed with a layer of dry sand or wool and then, through heating the container, the moisture was driven off and in contact with the layer of carbide. Many of the objections to the official method, however, would be equally

<sup>1</sup> Th. Zerewitinoff, "The Quantitative Determination of Water in Substances by Means of Alkyl Magnesium Halogen Compounds," *Z. anal. Chem.*, **50** (1911), 680-91; abstr. C. A., **6**, 203.

<sup>2</sup> Paper read before Society of Chemical Industry of Victoria, 1900; cf. also, *Chem. Eng.*, **6** (1912), 163-164.

<sup>3</sup> *Analyst*, **30** (1905), 266-273; **31** (1906), 213-218.

<sup>4</sup> *Ibid.*, **34** (1909), 519-523.

<sup>5</sup> R. W. Roberts and A. Fraser, "Easy Process for Estimating Water in Petroleum," *J. Soc. Chem. Ind.*, **29** (1910), 197; Irvine Masson, "The Use of Calcium Carbide for Determining Moisture," *Chem. News*, **103** (1910), 37-38; Irvine Masson, "The Action of Water of Crystallization on Calcium Carbide," *J. Chem. Soc.*, **97** (1910), 851-867; A. C. D. Rivett, "The Determination of Water in Butter," *Chem. News*, **104** (1911), 261; Irving C. Allen and Walter A. Jacobs, "Method for the Determination of Water in Petroleum and Its Products," *Orig. Com. 8th Inter. Congr. Appl. Chem.*, **10** (1912), 17-23; Korff-Petersen, "The Use of Calcium Carbide in Estimating the Moisture in Mortar," *Z. Hyg.*, **75**, 236-44; abstr. C. A., **7** (1913), 4056; F. H. Campbell, "The Determination of Moisture in Organic Substances," *J. Soc. Chem. Ind.*, **32** (1913), 67-70.

valid as applied to this, since the same factors which interfere with complete evaporation of the water would prevent the formation of acetylene equivalent to the total amount of moisture originally present in the syrup. Roberts and Fraser,<sup>1</sup> Masson, Rivett and others had modified the original method to the extent of mixing the carbide directly with the material under examination. An apparatus similar to that described by McNeil<sup>2</sup> was tried and the details of the method as described by him were followed. The addition of the carbide directly to the syrup, however, refused to give concordant results, due largely, as experience showed, to the incomplete mixing of the two.

Admixture of barium sulfate and silica, as proposed for liquids, was abandoned as failing to give satisfactory results. This failure was judged to be due to loss of moisture by evaporation while incorporating the inert materials, and to the fact that the local increase in temperature caused by the first addition of the carbide was sufficient to fuse the particles of syrup-coated silica together, thus preventing a thorough mixing with the carbide.

An attempt was made to utilize some solvent which, containing little or no water itself, would leave the syrup in a liquid condition after the moisture had been removed as acetylene. The only solvents lending themselves to such a use are alcohol, glycerine, and acetone. The alcohol was discarded, since in concentration sufficient to eliminate excessive error due to added water, it was impossible to obtain a homogeneous mixture with the syrup. With acetone, the solubility of acetylene is so high and so variable, with the changes in temperature to which the apparatus is subjected, that the errors introduced made the method not feasible. Glycerine, the most promising of the three solvents, apparently reacts with the carbide or the lime produced in the reaction, since a constant gas volume could not be obtained. As a result of these experiments it was concluded that no satisfactory method could be devised unless a thorough mixture could be obtained between the syrup and the carbide. Attempts to determine the moisture by loss in weight of acetylene, when the syrup and carbide were well stirred in an open container, were equally unsuccessful, due to loss in moisture driven off by the heat of the reaction before it was acted upon by the carbide.

It became clear, then, that some means of thoroughly mixing the carbide and the syrup within a closed container would have to be devised, and since the measurement of loss in weight due to the evolution of acetylene introduces a larger experimental error than the measurement of the volume of the gas, it seemed preferable to measure the gas volumetrically.

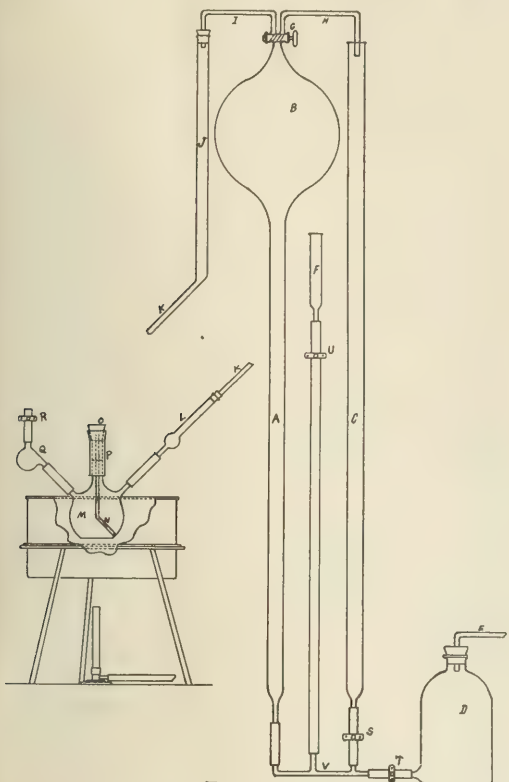
#### DESCRIPTION OF APPARATUS

The diagram shows the apparatus that was finally adopted for the determination. This is practically a modified alkalimeter and differs in principle from that proposed by McNeil (1) in the form of generating flask, to which a stirring device has been added and

<sup>1</sup> See foot-note 5 in preceding column.

<sup>2</sup> "The Calcium Carbide Method for Determining Moisture," U. S. Dept. Agr., Bur. of Chem., 1912, *Circ.* **97**, 1-8.

(2) in the introduction of a drying tube, containing calcium chloride, between the gas burette and the generating flask as protection against too high yields of acetylene, due to the action of the water vapor from the burette. *A* is a burette graduated to contain 1250 cc., enlarged at the upper end to a bulb, *B*, of approximately one liter capacity. The cylindrical



APPARATUS FOR MOISTURE DETERMINATION BY CALCIUM CARBIDE METHOD

portion of the burette is graduated in 0.2 cc. and the scale reads from 1000 to 1250 cc. *C* is a tube of about the same bore as the burette by means of which a fairly constant pressure may be maintained in the burette throughout the determination. The smaller tube *F*, attached to the burette by means of flexible tubing, can be raised or lowered at the conclusion of the determination, in order to read the gas within the burette at atmospheric pressure. *D* is a reservoir connected through the outlet *E*, to a water pressure pump and through the tube *V* to the burette *A* and the tubes *C* and *F*. At the top of the burette is a three-way stopcock, *G*, leading through *H* to the tube *C* and through *I* to the drying tube *J* which is filled with calcium chloride. *M* is a flask in which the acetylene is generated; it is connected to the calcium chloride tube through the drying tube *L* containing calcium carbide, which serves to convert to acetylene the moisture driven off by the heat of the reaction. The stirring rod *N* is inserted part way into

the rubber stopper *O* and is bent so as to enable it to reach all points of the generator. The stopper is connected to the neck of the flask by means of a heavy-wall rubber tube, *P*. The distance between the cork and the flask is 3 or 4 cm., and the flexible tubing permits the stirring rod to be turned in all directions and thorough stirring and mixing of the contents of the flask, with neither the loss of acetylene nor increase in volume, due to the admixture of air. *Q* serves as a container for the carbide previous to mixing with the contents of the generating flask, and is fitted with a stopcock, *R*, which may be opened and closed immediately preceding the determination in order to equalize the pressure within the generator. The tube *K* should be long enough to permit sufficient distance between the burette and the water bath so that the temperature of the gas will not be affected. The apparatus is not complicated and, with the exception of the burette *A* and the generating flask *M* with the bulb *Q*, can be assembled from such supplies as are usually to be found in any laboratory storeroom.

#### DETAILS OF THE METHOD

The determination of moisture is carried out as follows: The generating flask *M* is weighed, from 5 to 10 grams of the sample introduced (if a syrup or other liquid, by means of a pipette), and the flask and contents reweighed. The bulb *Q* is filled with finely powdered calcium carbide, about 25 grams being used for each determination. This amount is a large excess over that actually required to complete the reaction, but it was found that the time required to reach the end point of the reaction could be materially shortened by using larger quantities. The stirring rod and calcium carbide bulb are attached to the generator and the generator, in turn, to the burette. These rubber connections are wired with copper wire for each determination, as the agitation to which the flask is subjected together with the pressure occasionally caused by the rapid generation of the acetylene, render the use of ground glass connections impracticable. The stop-cock at the top of the burette is opened into the tube *C* and the burette and tubes *C* and *F* are filled from the reservoir with water previously saturated with acetylene. This is done by opening the stopcocks *S*, *T* and *U* and forcing the water up the tubes by pressure from a water blast. The stopcocks, except at *G*, are then closed. Pressure in the flask *M* is equalized by opening and closing pinch-cock *R*. The stop-cock *G* is turned so as to open into the tube *I*. Communication between *A* and *C* is established by opening *S*, and the stop-cock *T* leading to the reservoir of water is then opened so as to allow the liquid in *C* to recede about 20 or 25 cm.

The apparatus is now ready for the moisture determination. The calcium carbide is gradually transferred from the bulb *Q* to the generating flask and with each addition the mixture is thoroughly stirred. The water in *C* is kept slightly below the level in the burette so as to maintain the pressure as nearly constant as possible. It was found that this precaution, while not absolutely necessary, is desirable in that leaks through the rubber connections are less likely to occur,



than when such connections are subjected to the pressure of the full column of water. During the addition of the calcium carbide, the flask should be immersed in cold water. This will prevent both the too rapid action of the carbide and temperatures so high as to cause decomposition. Thorough and continuous stirring is necessary, not only for the proper mixing of the syrup, but to prevent foaming into the outlet tube *L*. The mixture should become apparently dry and fairly well broken up by the time half or two-thirds of the carbide has been added. The balance is then transferred rapidly to the generating flask, stirred up with the mixture contained there, and the flask with its contents is thoroughly shaken so as to bring the fresh carbide in touch with all parts of the generator, flask, stirring rod and connecting tubes. The carbide is thus given an opportunity to act upon any moisture which may have been driven off by the heat of the earlier reaction and condensed upon the upper portions of the generating flask. The flask is then immersed in a water bath filled with a saturated solution of sodium sulfate and the solution brought to a boil. The mixture will boil at a few degrees above the boiling point of water. This temperature is maintained until the gas volume in the burette is constant for fifteen minutes. Experience has shown that a volume constant for that length of time does not further increase, except as it may vary due to the variations in the temperature of the laboratory. As soon as the volume is constant, the generating flask is removed from the boiling water bath, immersed in cold water, and, after a few minutes, removed and exposed to the air until a constant volume of gas indicates that the room temperature has been reached. The gas is then brought to atmospheric pressure by means of the tube *F* and the volume recorded and reduced to the corresponding volume for normal temperature and pressure.

Several blank determinations, using weighed amounts of recently boiled distilled water, gave results corresponding to Dupré's value for the water equivalent of the acetylene formed by the reaction. This equivalent is 0.001725 g. of water for each cc. of acetylene and differs from the theoretical value of 0.00162 g. due, according to Dupré, to the retention of small amounts of moisture by the hydrated lime formed during the reaction. McNeil suggests, on the other hand, that this discrepancy may be due to the presence of calcium oxide in the carbide. This latter explanation, however, does not appear tenable in view of the uniformity found in different lots of carbide. Until the cause for the variation is known, it is suggested that a blank determination be made on each lot of carbide used.

When the factor has been determined, multiply by the corrected volume of gas to obtain the equivalent weight of water, and the per cent of water in the original sample may then be calculated.

#### COMPARISON OF THE RESULTS OF THE CALCIUM CARBIDE AND A. O. A. C. METHODS

Table I shows a comparison of the results obtained by the calcium carbide method and the official method of the A. O. A. C. as applied to sorghum syrups. Six

samples were selected for this comparison and determinations were made in duplicate by each method.

TABLE I—A COMPARISON OF RESULTS OF THE DETERMINATION OF MOISTURE IN SORGHUM SYRUP BY THE CALCIUM CARBIDE AND A. O. A. C. OFFICIAL METHODS

Laboratory No.	Calcium Carbide			A. O. A. C. Official		
	I	II	Av.	I	II	Av.
3317	34.7	34.4	34.6	35.4	35.0	35.2
3352	33.6	33.5	33.6	30.5	30.8	30.7
3328	29.7	30.1	29.9	26.9	26.4	26.7
3324	25.2	25.4	25.3	25.3	25.5	25.4
3329	20.0	20.2	20.1	20.1	20.3	20.2
3322	16.3	16.1	16.2	15.6	15.4	15.5

These samples were selected in order to compare the methods as affected by high and low moisture content and include two with the minimum amount of moisture, two with the maximum amount and two with an average moisture content. The A. O. A. C. method was followed exactly as prescribed, considering the end point to be that at which not more than three milligrams loss was noted during an hour's drying. Examination of the table shows that both methods are subject to about the same variation between duplicate determinations, the average variation being slightly in favor of the carbide method. The average of the determinations by the calcium carbide method as compared with the corresponding averages by the official method, show, with the exception of two of the samples, fairly concordant results. The variations of approximately three per cent in Samples 3352 and 3328 are evidence, however, that the drying was incomplete although continued drying of these samples finally yielded results fairly comparable with those obtained by the carbide method (*cf.* Table II). The drying of the samples was continued and in all cases with continued loss in weight indicating that, while the end point adopted by the A. O. A. C. is usually that at which the loss in weight is equivalent to the moisture content of the syrup, there is no surety that such will be the case. Furthermore, since it is not practical to dry to constant weight, agreement between duplicate analyses may be deceiving as evidenced by the results obtained with Samples 3352 and 3328.

TABLE II—RESULTS OBTAINED BY CONTINUED DRYING OF PORTIONS WEIGHED OUT FOR THE DETERMINATION OF MOISTURE IN SYRUPS BY THE A. O. A. C. OFFICIAL METHOD

Lab. No.	Wt. sample taken for 9.0 g. sand	Per cent moisture when loss in 1 hr. was not more than 3 mg.	Time required Hrs.	Per cent moisture after additional drying of			
				20 hrs.	40 hrs.	60 hrs.	80 hrs.
3317-I	5.0610	35.4	26	36.1	36.4	36.8	37.1
3317-II	5.1071	35.0	27	35.8	36.3	36.7	37.1
3352-I	5.2061	30.5	28	32.7	33.4	34.0	34.4
3352-II	5.2671	30.8	28	32.8	33.5	34.2	34.9
3328-I	5.0093	26.9	28	27.6	28.1	28.6	29.0
3328-II	5.1354	26.4	28	27.6	28.0	28.4	28.8
3324-I	5.1104	25.3	26	26.1	26.5	27.0	27.3
3324-II	5.2420	25.5	26	26.6	27.0	27.7	28.2
3329-I	5.7053	20.1	29	21.5	22.1	22.8	23.6
3329-II	5.1753	20.3	27	21.5	22.3	22.9	23.5
3322-I	5.3344	15.6	26	16.3	16.6	17.2	17.6
3322-II	5.6095	15.4	26	16.3	16.8	17.4	17.8

#### APPLICATION OF THE METHOD TO OTHER SUBSTANCES

In addition to the work with sorghum the method was tried with butter and with fruit juices. In the case of the butter, results were obtained in close agreement with those reported by Rivett<sup>1</sup> and it is apparent

<sup>1</sup> A. C. D. Rivett, "The Determination of Water in Butter," *Chem. News*, **104** (1911), 261.

that in the case of such substances, high in fat, the use of the stirring rod is of no additional value although equally well suited to the determination.

The principal advantage to be gained by the carbide method is that of a definite end point. In drying fats, the increase in weight due to oxidation may introduce serious error. With the calcium carbide method, the end point is very clearly defined, and it is reasonable to suppose that oxidation is prevented by the atmosphere of acetylene with which the fat is in contact. On the other hand, it should be borne in mind that in the case of a fat containing free glycerine some error may be introduced by the interaction between the carbide and the glycerine. This same fact should be taken into consideration in applying the method to soaps, containing glycerine. The official method is, of course, equally faulty in such cases, due to the difficulty of drying glycerine and to the fact that glycerine slowly volatilizes at the temperatures employed.

The method as applied to fruit juices requires further investigation. A few facts regarding the determination are worth noting, however, at the present time. The presence of acid in the fruit juice causes some hydrolysis on continued heating, thus decreasing the apparent moisture content if the latter is determined by the official method. Furthermore the presence of volatile compounds, such as acetic acid and alcohol, is a factor tending to increase the apparent moisture content.

In the carbide method the acids are also a source of error in that they react with calcium carbide to produce a calcium salt and acetylene. Attempt to neutralize the acid would be valueless as the reaction would result in the formation of water which would similarly increase the apparent moisture present.

The carbide method has an advantage over any method depending upon the evaporation of the moisture, however, in that the error may be definitely determined in each case and corrected for. Since the increase in apparent moisture due to the action of the acid on the carbide is proportional to the hydrogen ion concentration, it is necessary to determine only the total acidity of the juice and correct the volume of acetylene accordingly.

The presence of alcohol does not influence the results by the carbide method unless present in sufficient concentration to materially affect the vapor pressure within the burette or to dissolve appreciable quantities of acetylene.

#### CONCLUSIONS

I—The calcium carbide method for moisture is accurate within three- or four-tenths of a per cent and equal in this respect to the present official method of the A. O. A. C.

II—The proposed method is more satisfactory than the official method inasmuch as the end point is clearly defined, and the determination may be completed within a much shorter period of time.

III—The official method is open to criticism because of the uncertainty of results where there has been variation in stirring or variation in the relative amounts

of solids in the syrup sample and sand on which the syrup is dried.

IV—The carbide which is used should be subjected to a blank determination to determine the water equivalent.

V—The method is especially adapted to substances easily denatured at high temperatures and to those which lose other volatile substances (not permanent gases) during the usual process of drying.

VI—The method can be used when acids are present by correcting the volume of acetylene for the total acidity.

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#### ACID SOILS AND THE EFFECT OF ACID PHOSPHATE AND OTHER FERTILIZERS UPON THEM

By S. D. CONNER

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#### INTRODUCTION

Soil acidity is of such complex and variable character that soil investigators have not been able to agree as to its exact nature. For a long time it was supposed to be due entirely to the presence of organic acids. Humic acid was the name given to the first of these. Afterwards ulmic acid, crenic acid and apocrenic acid were discovered. It is now generally held that the above-named acids are not definite chemical compounds, but probably represent groups of organic compounds of a more or less acid character. They are generally spoken of by recent writers as "humic or humus acids."

In recent years inorganic compounds of an acid reaction have been recognized as important factors in soil acidity. In regard to mineral soil acidity there is great difference of opinion as to whether it is of a chemical or a physical nature. Among the numerous contributors to the literature on the subject may be mentioned: Cameron,<sup>1</sup> Kohler,<sup>2</sup> Parker,<sup>3</sup> Harris,<sup>4</sup> Wiegner,<sup>5</sup> Gans,<sup>6</sup> Van Bemmelen,<sup>7</sup> Sullivan,<sup>8</sup> Veitch,<sup>9</sup> Loew,<sup>10</sup> and Daikuhara.<sup>11</sup>

#### THE EFFECT OF SOLUBLE SALTS ON ACID SOILS

Practically all methods for quantitatively estimating soil acidity depend upon the reactivity which the soil may have with bases, either free or combined. The reason different soil acidity methods do not give accordant results is due to the variable composition of soils and to the fact that the various acid constituents of soils show different degrees of reactivity with

<sup>1</sup> F. K. Cameron, "The Soil Solution," 1911, p. 66.

<sup>2</sup> E. Kohler, *Ztschr. Prakt. Geol. Jahrg.*, **11** (1903), 49.

<sup>3</sup> E. G. Parker, U. S. Dept. of Agr., *Jour. Agr. Res.*, **1**, No. 3 (1913).

<sup>4</sup> J. E. Harris, *J. Phys. Chem.*, **18**, No. 4 (1914), 355.

<sup>5</sup> G. Wiegner, *Jour. Landw.*, **60**, No. 2, p. 111; **3** (1912), 197.

<sup>6</sup> R. Gans, *Internat. Mitt. Bodenk.*, **3**, No. 6 (1913), 529-571; *Centbl. Min. Geol. U. Pol.*, No. 22, p. 699; **23** (1913), 728, and No. 9, p. 273; **10** (1914), 299.

<sup>7</sup> J. M. Van Bemmelen, *Deut. Chem. Ges. Ber.*, **11** (1879), 2223; *Landw. Versuchs. State*, **35** (1888), 69.

<sup>8</sup> E. C. Sullivan, U. S. Geol. Sur., *Bull.*, **312** (1907).

<sup>9</sup> F. P. Veitch, *J. Am. Chem. Soc.*, **26** (1904), 637; see also Hopkins, Pettit and Knox, U. S. Dept. Agr., *Bur. Chem.*, *Bull.*, **73** (1903).

<sup>10</sup> O. Loew, *Porto Rico Expt. Sta.*, U. S. Dept. Agr., *Bull.*, **13** (1913); *Landw. Jahrb.*, **46** (1914), 161.

<sup>11</sup> G. Daikuhara, *Bull. Imp. Cen. Expt. Sta. Japan*, No. 1 (1914), 1-4.



different bases as well as with the same base when free, or when combined with different acids.

The experiment reported in Table I was planned to investigate this point. Neutral normal solutions of the various salts indicated were prepared with  $\text{CO}_2$ -free water. The materials were as described in Table I.

Ten grams of the silicate, or soil, were put with 100 cc. of the salt solution, shaken at intervals and allowed to stand over night. Then it was again thoroughly shaken and immediately filtered, and refiltered through the same filter until the filtrate was clear.

Twenty-five cc. aliquots of the filtrates were titrated with  $N/20$  NaOH solution, using phenolphthalein. New 25 cc. aliquots were analyzed for  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . (There was no iron in the solution from aluminum silicate and a negligible trace only in the soil solutions.) The determinations were all made at the same time under uniform conditions of time and temperature, and with the same manipulation and reagents. Figs. I and II graphically present the data in Table I and show that the basic as well as the acid radicle of the salt varies the amount of acidity developed and that this variation is not uniform with different soils.

It will be seen from Table I that while much higher acidities are obtained with acetates than with strong acid salts, the amounts of  $\text{Al}_2\text{O}_3$  found in solution are very much less with the acetates than with salts of strong acids. This is in accordance with the results obtained by Parker.<sup>1</sup> The acidities obtained with salts of strong acids can be accounted for to a large extent by the presence of salts of aluminum. The acidity obtained when acetates are used cannot

TABLE I TREATMENT OF SILICATE AND SOILS WITH VARIOUS NORMAL SALT SOLUTIONS

No.	MATERIAL TREATED	Constituents in percentages	
		Volatile matter	Humus
A	Artificial aluminum silicate (Merek's)	25.34	None
B	$\text{Al}_2\text{O}_3$ 750 g., 100 cc. (12 analysis)	4.09	0.58
C	Acid silty clay soil, from Lawrence Co., Indiana	8.16	4.86
D	Acid peaty sand soil, from La Porte Co., Indiana	83.53	44.45

DETERMINATION:  Salt used	RELATIVE ACIDITY C <sub>6</sub> H <sub>5</sub> NaOH to neutralize 25 cc.				Al <sub>2</sub> O <sub>3</sub> DISSOLVED  Mgs. Al <sub>2</sub> O <sub>3</sub> in 25 cc.			
	A	B	C	D	A	B	C	D
K <sub>2</sub> SO <sub>4</sub>	7.5	1.3	1.7	5.6	0.90	0.23	0.25	0.32
KCl	26.0	4.1	6.8	39.4	0.07	0.05	0.04	0.03
KNO <sub>3</sub>	7.3	2.5	2.1	3.2	0.95	0.32	0.20	0.32
Na <sub>2</sub> SO <sub>4</sub>	6.1	2.6	2.0	2.6	0.71	0.37	0.12	0.37
Na <sub>2</sub> CO <sub>3</sub>	4.0	1.9	1.9	5.2	0.55	0.20	0.12	0.21
Na <sub>2</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ·3H <sub>2</sub> O	18.9	3.5	6.2	37.7	0.05	0.02	0.02	0.00
NaCl	2.3	2.0	1.4	2.3	0.40	0.19	0.12	0.17
NaNO <sub>3</sub>	2.0	1.9	1.9	2.2	0.37	0.14	0.08	0.13
Ca <sub>2</sub> (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·H <sub>2</sub> O	17.4	3.5	7.7	43.7	0.09	0.05	0.03	0.02
CaCl <sub>2</sub>	2.0	1.8	1.4	3.2	0.54	0.30	0.30	0.53
Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	1.6	1.9	2.4	4.9	0.51	0.25	0.22	0.46
MgSO <sub>4</sub> ·7H <sub>2</sub> O	2.8	1.8	2.1	5.2	0.58	0.37	0.33	0.60
Mg(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	17.7	3.6	6.6	41.0	0.06	0.06	0.06	0.07
MgCl <sub>2</sub> ·6H <sub>2</sub> O	2.4	2.3	2.0	3.4	0.47	0.32	0.26	0.42
Mg(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	2.4	3.3	2.9	4.5	0.63	0.49	0.40	0.60
Ba(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·H <sub>2</sub> O	22.2	3.9	8.1	44.0	0.15	0.12	0.14	0.12
BaCl <sub>2</sub> ·2H <sub>2</sub> O	3.9	2.3	3.2	6.2	0.71	0.30	0.39	0.51

aluminum forming potassium aluminum silicate, the replaced aluminum combining with the acetic radicle to form aluminum acetate. Aluminum acetate is soluble but very highly hydrolyzed. On hydrolysis the insoluble aluminum hydroxide would go out of solution, leaving free acetic acid in solution. Such double decomposition would go on until equilibrium was reached and in this way the presence of free acetic acid could be explained on a purely chemical basis.

Parker<sup>1</sup> explains selective adsorption of KCl by a soil as being due first to hydrolysis of the KCl, then a subsequent adsorption of KOH by the soil, leaving HCl free to react in turn with the soil bases. If this hypothesis were correct then it would seem true

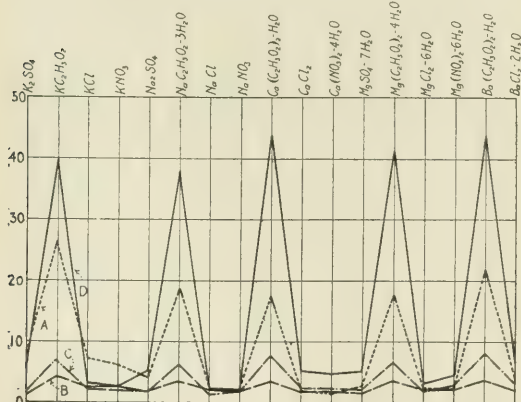


FIG. I—RELATIVE ACIDITY OF SOILS WITH VARIOUS NORMAL SALT SOLUTIONS

be accounted for in this way. As there is so little aluminum in solution and so much acid titrated, it is very evident that the acidity with the acetate is due to a free acid, and, in the case particularly of aluminum silicate, the acidity must be due to free acetic acid. While these results are in accordance with adsorption theories, they can also be explained on the basis of chemical double decomposition as follows: When potassium acetate, for instance, reacts with aluminum silicate, part of the potassium replaces part of the

<sup>1</sup> E. G. Parker, U. S. Dept. Agr., Jour. Agr. Res., 1, No. 3 (1913)

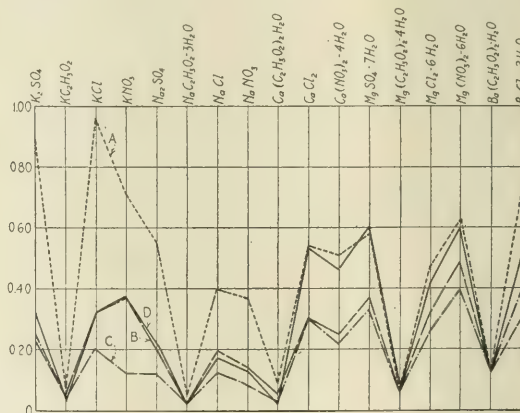


FIG. II—RELATIVE WEIGHTS OF  $\text{Al}_2\text{O}_3$  DISSOLVED FROM SOILS BY VARIOUS NORMAL SALT SOLUTIONS

that any reaction which might take place between a KOH solution and an acid silicate would throw some light upon the subject. With this in view the following experiment was planned to determine the heat of reaction between KOH and various silicates:

Ten grams of silicate were placed in a pint vacuum bottle, and 50 cc. of recently boiled distilled water of room temperature added and thoroughly stirred. A Beckmann thermometer was placed in

<sup>1</sup> E. G. Parker, U. S. Dept. Agr., Jour. Agr. Res., 1, No. 3 (1913)

the vacuum bottle and the temperature of the mixture read: 50 cc. of normal potassium hydroxide of the same temperature as the mixture in the bottle were then added and thoroughly mixed with the water solution of the silicate. The temperature was read again at the end of five minutes.

TABLE II.—HEATS OF NEUTRALIZATION(a) AND RELATIVE ACIDITIES(b) OF VARIOUS SILICATES WITH NORMAL KOH

SILICATES	FORMULAE(c)	Rise in temp. ° C.	Acidity (Lbs. CaCO <sub>3</sub> )
Artificial aluminum silicate	Al <sub>2</sub> O <sub>3</sub> .7SiO <sub>2</sub> .10H <sub>2</sub> O...	1.91	7120
Montmorillonite	Al <sub>2</sub> O <sub>3</sub> .4SiO <sub>2</sub> .7H <sub>2</sub> O...	0.27	2840
Pyrophyllite	Al <sub>2</sub> O <sub>3</sub> .4SiO <sub>2</sub> .H <sub>2</sub> O...	None	None
Halloysite	Al <sub>2</sub> O <sub>3</sub> .2SiO <sub>2</sub> .3H <sub>2</sub> O...	0.19	1600
Cyanite	Al <sub>2</sub> O <sub>3</sub> .SiO <sub>2</sub> ...	None	None
Kaolinite	Al <sub>2</sub> O <sub>3</sub> .2SiO <sub>2</sub> .2H <sub>2</sub> O...	None	None
Kaolinite (acid-washed).....		0.07	840

(a) Heat evolved on adding 50 cc. normal KOH to 10 g. silicate in 50 cc. water.

(b) Acidity determined by potassium nitrate method as given in *Bull.* 107 (revised), Div. of Chem., U. S. Dept. of Agr. Amounts given represent pounds CaCO<sub>3</sub> needed to neutralize one million pounds silicate.

(c) Formulae were confirmed by analyses.

Table II shows the relative increase in temperature on the addition of KOH solution to various aluminum silicates and also the relative acidity of the silicates as shown by the potassium nitrate method. It is seen that the more acid a silicate is, the greater is the heat evolved, and where no acidity is shown there is no heat given off. From the amount of heat evolved these results indicate very strongly that the reaction between potassium hydroxide and aluminum silicate is of a chemical rather than of a physical nature.

Table II is also interesting in that it shows two exceptions to Gans<sup>1</sup> hypothesis that silicates showing 3 molecules of SiO<sub>2</sub> to 1 of Al<sub>2</sub>O<sub>3</sub> are acid, while those with less than 3SiO<sub>2</sub> to 1Al<sub>2</sub>O<sub>3</sub> are not acid. Pyrophyllite (4SiO<sub>2</sub> to 1Al<sub>2</sub>O<sub>3</sub> to 1H<sub>2</sub>O) is not acid while halloysite (2SiO<sub>2</sub> to 1Al<sub>2</sub>O<sub>3</sub> to 3H<sub>2</sub>O) is acid. Kaolinite with the same relative silica and alumina as halloysite but with one less molecule of water is not acid. Thus it would seem that the acid or alkaline state of aluminum silicates depends upon the amount of water of constitution as well as upon the ratio of SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub>.

The acidity of the sample of acid-washed kaolinite may be accounted for because of the fact that it contains approximately 3 per cent less Al<sub>2</sub>O<sub>3</sub> and approximately 3 per cent more SiO<sub>2</sub> and about 0.5 per cent more water than the untreated kaolinite. Much more aluminum than silica was dissolved from the kaolinite by the dilute hydrochloric acid. The original sample of kaolinite did not contain any appreciable amount of base other than aluminum. In this connection it may be well to note that Daikuhara<sup>2</sup> has reported work on a number of samples of kaolin, some of which are acid, some neutral and others alkaline.

No soil samples were used in the heat of neutralization experiment, because it was found that potassium hydroxide reacts with soil organic matter to such an extent that more or less heat is evolved even with soils containing calcium carbonate. Many soils which are entirely satisfied so far as calcium is concerned are still unsatisfied so far as potassium is concerned. From work in this laboratory it has been found that

soils high in organic matter and containing an excess of calcium in the form of carbonate will set carbon dioxide free from a solution of potassium bicarbonate.

#### EFFECT OF HEAT ON ACIDITY

As further evidence that the degree of acidity of a silicate is affected by the amount of water of constitution the different samples were subjected to heat. In every case the acidity was lowered as the water was driven off. The artificial aluminum silicate (Sample A) had no acidity by the potassium nitrate method after being subjected to ignition at bright red heat.

Clay soils were very much reduced in acidity on ignition. Acid peat and acid peaty sand soils were rendered alkaline on burning. Soils and silicates also lost their affinity for lime, as determined by the lime-water method. This fact has already been noted by Veitch.<sup>1</sup> This characteristic of acid soils may be a partial explanation of the beneficial effect of the old European practice of "paring and burning" the soil, as by such practice a large part of the harmful acidity would be destroyed.

The foregoing results show that by the addition of various kinds of salt solutions to acid soils, soluble acids or acid-acting salts are set free. Without doubt a soil containing no soluble salts would be sterile and for this reason manures and fertilizers containing soluble salts are used. When nitrates, chlorides and sulfates are used as fertilizers on acid soils, the immediate tendency is for the base to combine with the organic matter and the silicate in the soil and for the acid radicle to combine with aluminum and to a less extent with iron. Of course, some of the acid would combine with the stronger bases, such as calcium and magnesium, but the acid condition of any soil is due to the fact that it does not have a sufficient supply of the strong bases, hence aluminum and iron are forced to supply the basic radicle for many of the soil reactions. The immediate effect, then, of the addition of soluble salts of nitric, hydrochloric and sulfuric acids would be the setting free of soluble aluminum and iron salts of these acids, and hence the presence in the soil of toxic acid solutions. Soluble salts of aluminum and iron have been found in unfertile acid soils and the toxic character of aluminum nitrate studied in this laboratory.<sup>2</sup> Soluble toxic iron and aluminum salts have also been found in acid soil at the Massachusetts Station<sup>3</sup> on plots receiving ammonium sulfate fertilization. Daikuhara<sup>4</sup> reports mineral soils which upon the addition of salts of strong acids set free soluble acid salts of aluminum and iron, thereby reducing their productivity. Veitch<sup>1</sup> says: "Further than this, the reaction which takes place between certain of these soil constituents and added chlorides, sulfates, etc., produces positively acid salts, as we have seen from the reactions of the sodium chloride method. There can be but little doubt

<sup>1</sup> F. P. Veitch, *J. Am. Chem. Soc.*, **26** (1904), 637.

<sup>2</sup> Abbott, Conner and Smalley, *Ind. Agr. Expt. Sta., Bull.* **170** (1913).

<sup>3</sup> Morse and Ruprecht, *Mass. Agr. Expt. Sta., Bull.* **161** (1915).

<sup>4</sup> G. Daikuhara, *Bull. Imp. Cen. Expt. Sta. Japan*, No. 1 (1914).

<sup>1</sup> R. Gans, *Internat. Mitt. Bodenkn.*, **3**, No. 6 (1913), 529-571.

<sup>2</sup> G. Daikuhara, *Bull. Imp. Cen. Expt. Sta. Japan*, No. 1 (1914).



that it is due partly, at least, to the acidity thus produced that the injury arising from the use of chlorides and ammonium sulfate on acid or neutral soils is to be ascribed.<sup>1</sup>

#### EFFECT OF PHOSPHATES ON SOIL ACIDITY

While the immediate effect of salts of the stronger acids on acid soils is to increase the soluble acidity, this is not ordinarily true in the case of salts of phosphoric acid. When phosphates are added as fertilizers to soils, even in the form of acid phosphate, the soluble phosphate is soon fixed and no increase of acidity follows.

For the purpose of studying the effect of acid phosphate on acid soils an investigation was started by the writer in August, 1912, on field and laboratory-treated soils.

**FIELD-TREATED SOILS**—The samples of the field-treated soils were taken from Set IV East, Purdue Experiment Station. This set of plots has been under fertilizer treatment since 1890. Corn, oats, wheat,

#### ETHYL ACETATE METHOD FOR ESTIMATING SOLUBLE ACIDITY IN SOILS

Weigh 10 grams of soil into a glass stoppered bottle. Add 100 cc. of a 5 per cent ethyl acetate solution, using freshly boiled and cooled distilled water. Shake at intervals through the day and let settle over night. At the end of a definite period pipette out 10 cc. of the clear supernatant solution and titrate with  $N/20$  alkali, using phenolphthalein as an indicator. By repeating the shaking and titration at definite periods, the value of the velocity constant can be calculated, if desired, by using the formula for a monomolecular reaction represented by the equation  $1/t \log_e a/a-x = K$ . A blank 5 per cent ethyl acetate solution without soil should be carried as a check. A  $N/1000$  acid or salt solution can also be carried for comparison. The determination should be carried at a constant temperature, preferably in a thermostat.

While this method is not advanced for the purpose of replacing any of the older soil acidity methods, it is believed that it is valuable for use in a study of the nature of soil acidity.

The results of the acidity determinations of Set

TABLE III—EFFECT OF ACID PHOSPHATE ON ACIDITIES OF FIELD-TREATED SOILS (SET IV EAST, PURDUE EXPERIMENT STATION)

PLOT	FERTILIZATION: 1890-1912 (inclusive) Total lbs. per acre				ANALYSES OF SOILS (Set IV East, Purdue Expt. Sta.)										ACIDITIES OF SOILS (Alkali for Neutralization)		
					PER CENT volatile matter	PER CENT TOTAL HUMUS	ACID Per cent	HUMUS % of total	Per cent total nitrogen	Nitrate nitrogen Pts. per million	Potassium nitrate method	Lime- water method	Ethyl acetate method	Lbs. CaCO <sub>3</sub> per million	Cc. $N/20$ NaOH(c)		
No. (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	NaNO <sub>3</sub>	Acid phosphate	KCl														
1 None	None	None	None	7.32	3.26	1.74	53.1	0.23	24	152	1607	10.5					
2 (a)	None	None	None	7.99	3.60	2.00	55.6	0.26	80	112	1607	11.0					
3 (b)	None	None	None	8.21	3.77	1.94	51.5	0.26	87	60	1071	13.0					
4 1407	3382	2633	1258	7.59	3.42	2.00	58.5	0.24	50	236	1428	10.5					
5 None	None	None	None	7.32	3.26	1.74	53.1	0.23	24	152	1607	10.5					
6 1407	3382	2633	None	7.46	3.22	1.88	58.4	0.225	44	352	1964	9.5					
7 None	None	2633	1258	7.69	3.38	1.82	53.9	0.235	40	176	1607	9.5					
8 1407	2382	None	1258	7.56	3.28	2.08	63.1	0.24	34	266	1607	9.0					
9 None	None	None	None	7.25	3.18	1.80	56.6	0.23	28	159	1607	10.0					
10 None	None	2633	None	7.40	3.14	1.68	53.5	0.23	40	143	1428	10.5					
11 1407	3382	None	None	7.21	3.05	1.84	60.3	0.225	32	364	1428	9.8					
12 None	None	None	1258	7.26	3.03	1.74	57.4	0.22	32	216	1428	9.5					
13 None	None	None	None	7.25	3.18	1.80	56.6	0.23	28	159	1607	10.0					

(a) Horse manure 70 tons.

(b) Cow manure 105 tons.

(c) Cc.  $N/20$  NaOH is the alkali required to neutralize acidity developed by 10 g. soil acting on ethyl acetate for 115 hrs. at 21° C.

clover and orchard grass have been grown in a five-year rotation. The fertilizers and manure have been applied only to the corn, oats and wheat crops. The different plots have been treated with various manures as indicated in Table III. On the plots receiving nitrogenous fertilizers, ammonium sulfate was used for the first five applications, then the treatment was changed and nine applications of sodium nitrate were made. For this reason the effect of the nitrogenous fertilization on soil acidity is not particularly significant as one type of fertilizer has tended to neutralize the effect of the other.

The analyses given show that the soil of Set IV E., is very uniform in character; hence it is believed that chemical differences in soil samples from the different plots can be largely attributed to the manurial treatment.

Determinations of soil acidity were also made, the methods used being: The potassium nitrate method,<sup>1</sup> the lime-water method of Veitch,<sup>2</sup> and the ethyl acetate method. The procedure in the latter method is original in this work and so far as the author knows is used for the first time in estimating acidity in soils.

IV E., are shown in Table III. In all four instances the effect of the acid phosphate has been to lower the acidity according to the potassium nitrate method. In the case of the lime-water method we find that Plot 10, which has received 2633 lbs. of acid phosphate per acre, is less acid than the check plot receiving nothing. In comparing Plots 7 and 12, and also 6 and 11, the phosphate appears to have increased the acidity. While comparing the complete fertilizer, Plot 4, with the nitrogen and potash, Plot 8, we find that acid phosphate has decreased the acidity.

Considering the results obtained with the ethyl acetate method we find that in two cases there is more soluble acidity where the phosphate is used, in one case just the same acidity and in one case less acidity with acid phosphate than without.

The ammonia test for acidity is sometimes used on soils high in organic matter. In this test the soil containing the greater per cent of humus soluble in ammonia water without previous treatment with acid, is considered the more acid. In Table III it will be seen that in all four instances the soil having had acid phosphate applied contains less acid humus than the correspondingly treated soil without acid phosphate. In view of the fact that in every case the soil receiving acid phosphate contains more total humus and more volatile matter than the soil not receiving phosphate,

<sup>1</sup> Hopkins, Petit and Knox, U. S. Dept. of Agr., Bur. Chem., Bull.

73 (1903).

<sup>2</sup> Loc. cit.

it would seem that the tendency of acid phosphate has been to render the organic matter less soluble in ammonia and hence the soil less acid.

LABORATORY-TREATED SOILS—In view of the results obtained on the soils from the field plots, experiments were undertaken on soils treated with acid phosphate in the laboratory.

The soils, as indicated in Table IV, were subjected to the potassium nitrate and to the ethyl acetate acidity methods.

To determine the effect on soil acidity, as shown by the potassium nitrate method, different phosphatic substances were applied to soils K and D in equivalent amounts carrying the same content of phosphoric acid. This amount was based upon an application of 8000 lbs. acid phosphate per acre, 2,000,000 lbs. of soil.

The resulting acidity as shown by titration is less where the phosphoric acid is used than it is with the untreated soil. All the phosphates, including acid phosphate, have given similar results.

a great capacity for fixing phosphoric acid, it is doubtful if acid phosphate would ever be applied in amounts large enough to increase acidity. Very sandy or peaty soils low in aluminum and iron silicate might, in some cases, be an exception to this. Other acid soils were treated with acid phosphate in the laboratory, and in every test the potassium nitrate method indicated a decreased acidity in the treated soil. As acid phosphate shows a distinct acidity toward phenolphthalein, which can be titrated, this decrease in acidity cannot be attributed to an apparent error of titration or to an effect of the phosphoric acid on the indicator. In fact, as a rule, the less phosphoric acid there is in solution (as determined gravimetrically), the less there is of acidity indicated by the potassium nitrate method.

When the effect of an application of acid phosphate at the rate of two tons per acre, 2,000,000 lbs. of soil, was tested by the ethyl acetate method, in the case of the artificial silicate and the mineral Montmorillonite no acidity was indicated either with or without acid

TABLE IV -EFFECT OF ACID PHOSPHATE ON LABORATORY-TREATED SOILS

No.		MATERIAL TREATED		Constituents in percentages							
				Volatile matter				Humus			
A		Artificial aluminum silicate, Al <sub>2</sub> O <sub>3</sub> .7SiO <sub>2</sub> .10H <sub>2</sub> O (by analysis) . . . . .		25.34				None			
C		Acid peaty sand soil from La Porte Co., Indiana. . . . .		8.16				4.86			
D		Acid peat soil from Kosciusko Co., Indiana . . . . .		83.53				44.45			
E		Montmorillonite (a natural silicate), Al <sub>2</sub> O <sub>3</sub> .4SiO <sub>2</sub> .7H <sub>2</sub> O . . . . .		21.02				None			
K		Acid clay soil from Ripley Co., Indiana. . . . .		3.86				0.64			
L		Acid silt soil from Jennings Co., Indiana. . . . .		3.02				0.86			
M		Unfertilized acid loam from Set IV E., Purdue Expt. Sta., Plots 9 and 13 . . . . .		7.25				3.18			

RELATIVE ACIDITIES BY POTASSIUM NITRATE METHOD												
Results on 25 g. Soil Digested with 250 cc. N KNO <sub>3</sub>						Results on 100 g. Soil Digested with 250 cc. N KNO <sub>3</sub>						
TREATMENT OF SAMPLE		ACIDITY		TREATMENT		ACIDITY		TREATMENT		ACIDITY		
		Lbs. CaCO <sub>3</sub> per million		G. acid phosphate		Lbs. CaCO <sub>3</sub> per million		G. acid phosphate		G. soluble P <sub>2</sub> O <sub>5</sub> per 250 cc. filtrate		
		D	K	C		D	L	M	C	D	L	M
None	.....	4000	4040	None	1835	2800	430	170	0.0025	0.0092	None	0.0010
0.0125 g. Phosphoric acid	.....	3840	3960	0.05	..	..	..	140	..	..	..	0.0010
0.024 g. Monocalcium phosphate	.....	3760	3720	0.1	..	..	..	140	..	..	..	0.0010
0.034 g. Dicalcium phosphate	.....	3600	3120	0.2	1790(a)	2640	370	200	0.0015(a)	0.0204	0.0045	0.0010
0.03 g. Tricalcium phosphate	.....	3520	3240	0.4	1725	2640	345	220	0.0020	0.0326	0.0038	0.0010
0.10 g. Acid phosphate	.....	3840	3840	0.8	1690	3260	415	300	0.0018	0.0520	0.0118	0.0048
0.5 g. Raw rock phosphate	.....	3760	3800	1.2	1720	3200	610	400	0.0033	0.0918	0.0245	0.0140
				1.6	1735	3200	935	580	0.0038	0.0918	0.0450	0.0250

(a) 0.2 g. acid phosphate alone titrates an acidity equal to 937 lbs. CaCO<sub>3</sub> per million and contains 0.023 g. soluble P<sub>2</sub>O<sub>5</sub>.

RELATIVE ACIDITIES BY ETHYL ACETATE METHOD												
Ce. N/20 NaOH per 10 g. Sample treated 100 hrs. at 21.5° C.						Acidity 100 cc. solution of various reagents						
TREATMENT	A	C	D	E	K	L	M	Ce. N/20 NaOH				
None	.....	0.0	39.0	36.5	0.0	10.4	11.0	10.0	0.02 g. acid phosphate..... 1.5			
0.02 g. acid phosphate	.....	0.0	37.5	37.0	0.0	8.4	8.0	8.0	N/1000 nitric acid..... 33.0			
									N/1000 aluminum nitrate..... 3.5			

Table IV also gives the results obtained with the potassium nitrate method on four typical acid soils when varying amounts of acid phosphate were added. One-tenth gram of acid phosphate per 100 grams soil represents an application of one ton per acre, 2,000,000 lbs. of soil. The acid phosphate used was ground to pass a sieve 100 meshes to the linear inch. It contained 11.5 per cent soluble P<sub>2</sub>O<sub>5</sub> when 0.2 gram was digested with 250 cc. normal KNO<sub>3</sub>. As the applications of acid phosphate were increased minimum acidities were reached; beyond this point further additions of acid phosphate caused the soluble acidity to increase. The peat soil (D), which has only 1.5 per cent of mineral bases soluble in strong hydrochloric acid, shows the least power of fixing phosphoric acid. Apparently the power of fixation of P<sub>2</sub>O<sub>5</sub> by acid soils is due to the inorganic more than the organic compounds. If acid phosphate is applied in greater amounts than the soil has the capacity to fix, then the acidity is increased in proportion to the acid phosphate applied. As ordinary soils have

phosphate. In every case except one, the addition of acid phosphate decreased the acidity of the soil. The peat soil proved an exception by this test, showing slightly more acidity after an application of acid phosphate. The 0.02 gram acid phosphate alone produced an increase of acidity, yet when added to ordinary soils it decreased the acidity even more than it increased it when alone. The action of the solutions of N/1000 nitric acid and of N/1000 aluminum nitrate are presented to give an idea of the strength of the soluble soil acids.

The results of the tests of the laboratory-treated soils (Table IV) confirm the results obtained with the field-treated soils (Table III) and together they are believed to be good proof that the effect of acid phosphate when added to acid soils in ordinary amounts is to decrease soluble acidity and in fact any insoluble acidity which might become soluble and toxic by the application of fertilizer or other salts. In this connection it is interesting to note that Meggitt<sup>1</sup> reports

<sup>1</sup> A. A. Meggitt, *Mem. Dep. Agr. India*, Chem. Ser., **3**, 235 A. I., 1212 (1912).



an experiment on a very acid soil in which the only plots which would grow grain were those which received alkaline manures and some which had superphosphate. The action of the latter manure in saving the crop notwithstanding the increased acidity(?) is attributed to its stimulating action on root growth, which would result in increased oxidation and in the destruction of the toxic substance. Is it not more probable that the superphosphate acted in a direct chemical way and thus precipitated the soluble acid toxic substance, and rendered it less harmful?

The acid reaction of acid phosphate will no doubt exist in ordinary soils until fixation is complete. The rapidity with which such fixation may take place depends largely upon the physical condition and especially the water content of a soil. In soils containing enough water for proper plant growth such fixation will occur in a very short time.

Without doubt both organic and inorganic acids occur in acid soils and either class of acids may exist in a soluble or an insoluble form. It is doubtful if soluble inorganic acids ever occur in appreciable quantities in ordinary acid soils other than as hydrolyzed salts of weak bases, such as aluminum and iron. Likewise it is still more improbable that free phosphoric acid or acid salts of phosphoric acid ever exist in ordinary soils. When calcium, magnesium or other strong bases are present the acid phosphate would be fixed by these bases in a non-soluble form. In acid soils deficient in strong bases aluminum and iron would largely furnish the base for fixation of phosphoric acid. Organic compounds are said by some to aid in the fixation of phosphoric acid in acid soils;<sup>1</sup> on the other hand, a case is reported by Petit,<sup>2</sup> where a forest soil rich in humus had no power of fixing phosphoric acid.

The reason acid phosphate and even free phosphoric acid tend to reduce soluble and active soil acidity probably lies in the fact that phosphoric acid tends to form insoluble compounds, both organic and inorganic. Acid phosphate would tend to hold iron and aluminum out of solution and hence in a non-acid form. The aluminum silicates containing the most water of constitution are the most acid; also they are the most active chemically. For this reason the phosphate would tend to combine with these active aluminum silicates and render them less acid. Such reaction could possibly go on until all the active aluminum was combined with phosphorus, leaving only calcium aluminum silicates or even free silicic acid.

Probably three-fourths of the soils of Indiana are more or less acid. These acid soils, almost without exception, respond favorably to fertilization with acid phosphate. Soils L and M which were used in part of the experiments reported in this paper have in field fertilizer tests shown large crop increases after treatment with acid phosphate. Soil C does not respond favorably or unfavorably to acid phosphate alone, but upon a partial neutralization by limestone it does respond favorably to such treatment.

<sup>1</sup> Rousseaux and Brioux. *Bull. Mem. Off. Renseign. Agr. Paris*, 8, No. 1 (1909).

<sup>2</sup> A. Petit, *Compt. rend.*, 152 (1911); 155 (1912).

The results of this paper are not advanced as an argument in favor of acid phosphate as a remedial treatment for soil acidity. The author does believe, however, that they show that acid phosphate can be used without danger on phosphorus-deficient acid soils, either with or without the additional use of lime.

#### SUMMARY

1—Various acid constituents of soils show different degrees of reactivity with different bases, also with the same base when free or when combined with different acids.

2—The acidity developed when acid soils or silicates are treated with neutral salt solutions is more probably due to chemical exchange of bases than to physical selective adsorption.

3—When aluminum silicates are treated with a solution of potassium hydroxide, heat is developed with the acid silicates, but not with neutral silicates. The heat developed is proportional to the acidity, indicating a chemical rather than a physical reaction.

4—The acidity of aluminum silicates is not only in proportion to the ratio of  $Al_2O_3$  to  $SiO_2$  but also in proportion to the water of constitution. The greater the proportion of water in the silicate the more acid is the reaction.

5—Heating and the consequent driving off of water of constitution in acid aluminum silicates lower the acidity until all the water is removed when neutrality is reached. Ignition of acid soils also destroys the acidity.

6—Much of the harmful acidity of acid soils is due to the presence of toxic acid salts of aluminum and iron.

7—The immediate effect of the addition of soluble fertilizer salts of the strong acids (nitric, hydrochloric and sulfuric) to acid soils, is to increase the soluble acid salts of aluminum and iron.

8—On experimental plots at Purdue Experiment Station, soils treated for twenty years with acid phosphate show less acidity than soils that have never had acid phosphate.

9—Acid soils and silicates treated in the laboratory with acid phosphate show less soluble acidity than untreated soils and silicates.

10—The reduction of soil acidity by acid phosphate is probably due principally to a combination of the soluble phosphoric acid with the acid salts of aluminum and the consequent formation of insoluble non-acid compounds.

11—A new soil acidity method in which the catalysis of ethyl acetate is taken as the measure of the soluble soil acidity, is used along with the potassium nitrate method, and the lime-water method of Veitch.

The author wishes to express his appreciation to Mr. Geo. I. Spitzer and Mr. H. A. Noyes for many valuable suggestions.

NOTE—Since the completion of this article, the writer has received *Bull. 162* of the Massachusetts Agricultural Experiment Station and it is gratifying to know that Dr. Brooks, the author, has concluded from a long-continued series of soil test experiments that "acid phosphate (dissolved bone-black) at least has not increased the necessity for lime. On the contrary, it seems clear that the bone-black has reduced this necessity."

## A RAPID METHOD FOR THE DETERMINATION OF CARBON DIOXIDE<sup>1</sup>

By W. H. WAGGAMAN

Received July 2, 1915

All the present methods for the determination of carbon dioxide require either considerable time or else the close attention of the analyst throughout the operation. The following method should prove useful for commercial and certain other purposes, as the apparatus runs automatically and the analytical results can be obtained quite rapidly.

The apparatus is very similar to that usually employed in such determinations. The train of absorption bulbs differs little from that described by Cameron and Breazeale;<sup>2</sup> the final member, however, consists of a tube containing barium hydroxide to indicate any loss of carbon dioxide due to too rapid passage of the gas through the apparatus. This bulb also proves of value in showing at once the exhausted condition of the potash absorption bulb.

In the usual method for the determination of carbon dioxide most of the time is consumed in heating the acid solution in order to drive off the last portion of the carbon dioxide, and care must be taken during the operation lest too rapid heating should cause the liquid to rise in the tube through which the current of air should enter, and to pass over into the auxiliary flask containing potash. Should this happen the whole determination is lost.

The use of a small flask (100 or 150 cc.) for the decomposition of the carbonate or organic compound has been recommended, since this does away with the large air space above the liquid. During preliminary experiments, however, it was found that the sudden expansion of gas confined in a small flask causes more trouble than in a larger flask where the

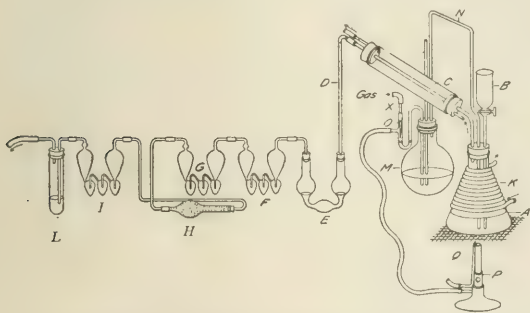


FIG. 1—APPARATUS FOR RAPID DETERMINATION OF CARBON DIOXIDE

mean temperature of the gaseous mixture is lower. A 300 cc. Erlenmeyer flask was finally employed, and it was kept cool by a coil of lead tubing through which cold water flowed. The cooling shortened the time required for the operation but did not do away with the necessity of watching the apparatus continually.

By means of an Ostwald regulator the flame under the flask was regulated automatically, so that the heating would decrease as the pressure in the flask increased and *vice versa*.

In the accompanying figure, A represents the flask in which the decomposition takes place, and is surrounded by the coil K of lead tubing. The gas evolved passes through the condenser C, inclined upwardly, through the capillary tube leading to the train of absorption bulbs. This train consists of the following: E, containing a solution of silver sulfate to remove any chlorine or hydrochloric acid; F, containing concentrated sulfuric acid to absorb water vapor; G (weighed before and after the operation), containing a strong solution of potash and attached to a tube, H, containing calcium chloride; I, containing concentrated sulfuric acid to prevent water vapor from passing back into G; and L, containing a saturated solution of barium hydroxide. Air is drawn through the solution of potash in the flask M and through the tube N passes below the surface of the liquid in A. Part of the U-tube of the regulator O is filled with mercury, the tube X being raised or lowered for regulation. A pilot flame, Q, lights the burner P, whenever the gas comes on.

In Table I are given the results obtained with two samples of calcium carbonate in which the quantity of carbon dioxide was determined by blasting a sample to constant weight.

TABLE I—ANALYSES OF TWO SAMPLES OF  $\text{CaCO}_3$   
Weight of  $\text{CaCO}_3$  employed for analysis = 0.5 gram

RESULTS BY BLASTING			Sample I			Sample II		
Weight of CO <sub>2</sub> in 0.5 g. CaCO <sub>3</sub>			0.2190 g.			0.2195 g.		
Per cent CO <sub>2</sub> in sample			43.80			43.90		
ANALYSES BY AUTHOR'S METHOD								
RESULTS ON SAMPLE I			RESULTS ON SAMPLE II					
Time	CO <sub>2</sub> FOUND		Time	CO <sub>2</sub> FOUND				
Min.	Gram	Per cent	Min.	Gram	Per cent			
Over 60	0.2178	43.6	60	0.2180	43.6			
Over 60	0.2195	43.9						
Over 60	0.2175	43.5	60	0.2195	43.9			
Over 60	0.2185	43.7	60	0.2175	43.5			
Over 60	0.2170	43.4						
50	0.2188	43.76	60	0.2170	43.4			
45	0.2175	43.5	30	0.2175	43.5			
45	0.2175	43.5						
45	0.2190	43.8	30	0.2170	43.4			
45	0.2190	43.8	30	0.2185	43.7			
40	0.2175	43.5						
40	0.2185	43.7	30	0.2178	43.6			

This method may also be employed for the rapid estimation of carbon dioxide in the organic matter of soils and in other organic compounds. Table II

TABLE II

SUBSTANCE	FORMULA	Weight taken		$\text{CO}_2$ found		Per cent recovered
		Gram		Gram		
Sugar	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	0.5		0.7625		98.83
		0.5		0.7650		99.16
		0.5		0.7680		99.55
Urea	$\text{CH}_4\text{N}_2\text{O}$	0.5		0.3655		99.87
		0.5		0.3630		99.18
		0.25		0.2955		100.85
Asparagine	$\text{C}_4\text{H}_8\text{N}_2\text{O}_3 \cdot \text{H}_2\text{O}$	0.25		0.2895		98.81
		0.20		0.5990		97.31(a)
		0.20		0.6090		99.02
Sulphanilic acid	$\text{C}_6\text{H}_7\text{NSO}_3$	0.5		0.7555		99.11(b)
		0.5		0.7590		99.57

(a) Some volatilized. (b) Potash bulb became exhausted

gives the results obtained on some known organic compounds. Since several of the substances decompose with great rapidity, some care was taken during the addition of acid, after which the action subsided somewhat and the regulator rendered further attention unnecessary. Forty minutes was found to be sufficient time for the determinations, although many were run for a full hour.

<sup>1</sup> Published by permission of the Secretary of Agriculture.

<sup>2</sup> J. Am. Chem. Soc., 26 (1904), 29.



# A PROPOSED RAPID METHOD FOR THE ANALYSIS OF LIMESTONE FOR AGRICULTURAL PROCESSES<sup>1</sup>

By A. S. BEHRMAN

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The object of this work was to devise a method for the analysis of limestone, which would be shorter than other procedures now in general use, and which would be sufficiently accurate for agricultural requirements. By "sufficiently accurate" we may more or less arbitrarily designate a limit of error of one per cent from the true value of the three agriculturally important factors—(1) insoluble residue and ammonia precipitate, (2) calcium carbonate, (3) magnesium carbonate.

A perusal of standard references and current literature revealed no information pertinent to the present subject. The most helpful suggestion was derived from an unpublished method developed by Mr. S. D. Averitt, of the Kentucky Agricultural Experiment Station. This differential method assumes that the sum of the percentages of the insoluble residue (from digestion in dilute hydrochloric acid), the ammonia precipitate weighed as aluminum and ferric oxides and the calcium and magnesium carbonates is 100. If a qualitative test shows considerable magnesia present, the calcium carbonate is determined by the usual oxalate method. This percentage subtracted from the total carbonates yields the percentage of magnesium carbonate. If, however, the qualitative test shows no more than about 5 per cent of magnesium carbonate, the calcium is not determined. The figure of the combined carbonates is then reported as calcium carbonate, with a qualitative statement as to the estimated amount of magnesium carbonate present.

Although the above procedure reports as calcium or magnesium carbonate any inclosed or combined water, this error has been shown to be insignificant by comparative analyses made at the Experiment Station.

The methods of analysis as ordinarily used have been employed for comparative purposes in this work. These will be found in any of the standard references, such as Fresenius, Treadwell, Talbot and Sutton.

## EXPERIMENTAL

The experimental portion of this work may be divided into two parts, each representing a distinctly different attempt to arrive at the solution of the problem under consideration.

### SERIES I

The first method sought to make use of the fact that pure calcium carbonate is very rapidly soluble in dilute hydrochloric acid and magnesium carbonate slowly soluble, while dolomites and magnesium limestones have a time solubility that varies with the proportion of magnesium carbonate present.

The object here was to see if such a variation was a quantitative one and if so, whether the time taken for solution of a definite weight of the sample could not be used as an estimate of the amounts of calcium and magnesium carbonates present, when compared

<sup>1</sup> Owing to the departure of the author for the Philippines, it was impossible for him to give further time to the development of this method and this record is presented in the hope that it may give an impetus to similar experimentation looking towards an entirely volumetric method for the agricultural analysis of limestone.

with that required for the solution of the pure carbonates.

The experiments detailed in Table I were carried out using 80-100 mesh calcite (99.5 per cent calcium carbonate) and magnesite (97.6 per cent magnesium carbonate) weighed out on a rough reagent balance into Erlenmeyer flasks. The stated amounts of hydrochloric acid were put into each of two beakers, heated on the steam bath, and when the highest temperature of the bath was reached (86° C.), the acid was poured into the carbonates. The flasks were kept on the bath and the solution periods taken with an ordinary watch.

TABLE I

No.	Flask used Cc.	Acid used Cc.	Strength of acid	Charge of carbonate Grams	Minutes required for solution of Calcite	% increase of mag- nesite over calcite
1.....	300	50	N	1.0	0.75	3.0
2.....	300	100	N/2	1.0	5.5	9.0
3.....	300	200	N/4	1.0	8.0	12.0
4.....	1000	500	N/8	1.0	17.0	23.0
5.....	1000	500	N/16	0.5	16.0	20.0

The results in Table I brought out the interesting though disturbing fact, that, as the dilution of the acid increases, the lengths of time required for the solution of equal weights of calcite and magnesite approach coincidence. Since dilute acids must be employed, however, in order to secure a sufficiently long time for measurement, it is evident that the uncertainty of the time element precludes the use of the suggested method as a means of analysis.

### SERIES II

The impracticability of the method suggested in Series I having been demonstrated, a more purely chemical procedure was next sought for. Without entering into the numerous difficulties encountered, which frequently necessitated extensive modifications of the proposed method, the final procedure adopted will first be stated, followed by the theory and experimentation in support of it.

### METHOD

One gram of the rather finely crushed sample is weighed into a 200 cc. Phillips beaker. Into this is now carefully pipetted 50 cc. of standard N/2 hydrochloric acid, followed by a few drops of a 3 per cent hydrogen peroxide solution. A small porcelain crucible is now set loosely in the top of the beaker, and the whole placed on the water bath. After remaining at this bath temperature (86° C.) for 30 minutes, the beaker is removed from the bath and cooled. When almost or completely cooled, 5 grams of dry ammonium chloride are added and dissolved by agitation: some macerated filter paper is also introduced: 25 cc. of a standard N/2 ammonium hydroxide solution are then added slowly with shaking. The beaker is stopped with a rubber stopper, agitated well and let stand for 15 minutes. Filtration is now made as rapidly as possible through an ashless filter into a 350 cc. Erlenmeyer flask, and the precipitate washed thoroughly with a neutral 10 per cent solution of ammonium nitrate until all the ammonia is in the filtrate. The precipitate is ignited and weighed. The weight thus obtained represents the insoluble residue, plus the aluminum and ferric oxides.

The filtrate and washings from the insoluble residue and ammonia precipitate are titrated with standard

*N*/2 hydrochloric acid, using methyl orange as an indicator.

From the hydrochloric acid required to put the carbonates into solution, and from the total carbonates (found by subtracting the insoluble residue and ignited ammonia precipitate from 100), can be calculated the percentages of calcium and magnesium carbonates present.

THEORETICAL

The assumption employed in the "differential" method of the Kentucky Agricultural Experiment Station is also used here, that we may find the combined percentages of calcium and magnesium carbonates by subtracting the percentage of insoluble residue and ignited ammonia precipitate from 100.

If *X* = grams of calcium carbonate,  
*Y* = grams of magnesium carbonate,  
*A* = grams of calcium carbonate plus magnesium carbonate,  
and *B* = grams of CO<sub>2</sub> in both carbonates,

then: *X* + *Y* = *A*, and 0.59946*X* + 0.71157*Y* = *B*.

*A* is known, being found by subtraction of the insoluble residue and ignited ammonia precipitate from 1.0000, as above. *B* also is known: 1 cc. of *N*/2 acid is equivalent to 0.015 g. of CO<sub>2</sub>. This value, multiplied by the number of cc. of *N*/2 acid required to put the calcium and magnesium carbonates into solution, yields the value *B* in the second equation.

Suppose, to take a concrete example, a one gram sample was dissolved in 50 cc. of *N*/2 hydrochloric acid, the ammonia precipitation was made with 25 cc. of *N*/2 ammonium hydroxide, and to titrate the excess of ammonia in the filtrate from the ammonium hydroxide requires 15 cc. of *N*/2 hydrochloric acid. Evidently then, 40 cc. of *N*/2 acid were required to put the calcium and magnesium carbonates into solution, and this 40 cc., therefore, represented 0.600 g. CO<sub>2</sub>.

0.59946 is the factor for converting calcium carbonate to CO<sub>2</sub>.

0.71157 is the factor for converting magnesium carbonate to CO<sub>2</sub>.

When the two simultaneous equations are solved, we find that

$$X = \frac{0.71157 A - B}{0.11211} \text{ and } Y = \frac{B - 0.59946 A}{0.11211}$$

i. e., the grams of calcium carbonate may be found by subtracting the total weight of CO<sub>2</sub> from 0.71157, the weight of the combined carbonate, and dividing the result of this subtraction by 0.11211.

The magnesium carbonate may be found either in the manner of solving for *Y* shown above, or from the equation *X* + *Y* = *A*.

ADVANTAGES OF THE METHOD PROPOSED

The chief advantage of the proposed method, if proven practical, would be in the saving of time and the number of operations required in the determination of the three values ordinarily reported in agricultural analyses of limestone, viz.: (1) Insoluble residue and ferric and aluminum oxides, (2) calcium carbonate, (3) magnesium carbonate.

By the judicious distribution of time, and with proper equipment, it is easily possible to analyze 8 samples for the three above factors in 4 hours—something which, in the writer's opinion, can not be done by any of the methods now in general use.

The following, expressed in decimal parts of an hour,

is a rough, though conservative estimate of the distribution of time taken for analysis:

	Hrs.
Weighing of charges and addition of reagents.....	0.50
Solution of samples, during which time empty crucibles may be ignited and weighed.....	0 50
Cooling of solutions, and addition of ammonium chloride and macerated filter paper.....	0.25
Ammonia precipitate allowed to stand, during which time filters can be folded, etc.....	0 25
Filtration and washing (using 8-hole filter rack).....	0.75
Titration.....	0.50
Ignition and weighing of residues.....	1.25
TOTAL.....	4.00

NOTES ON DETAILS OF MANIPULATION, ETC.

1—In the proposed method, a dilute solution of hydrochloric acid is heated on the water bath for 30 minutes. To determine whether, under these conditions, there is any loss of HCl, ten 25 cc. portions of *N*/2 hydrochloric acid were pipetted into as many Phillips beakers and a crucible set loosely in the top of each. Five of these portions were diluted to about 50 cc. with cold distilled water, and titrated with *N*/2 potassium hydroxide solution, using phenolphthalein as an indicator.

The other five portions were placed on the water bath, allowed to remain at the bath temperature (86°) for 30 minutes, cooled, diluted to about 50 cc. with cold distilled water, and titrated with 0.5 *N* potassium hydroxide. The results were as follows:

FOR PORTIONS	Cc. <i>N</i> /2 KOH required				
Not heated.....	25.45	25.48	25.45	25.46	25.47
Heated.....	25.47	25.45	25.48	25.48	25.45

Evidently no hydrochloric acid was lost by volatilization. This was very welcome information in view of the fact that experiments had shown that the non-volatile sulfuric acid could not be used, due to the large amount of calcium sulfate which was formed, and which was not entirely soluble even in the presence of an excess of ammonium salts.

2—The function of the 5 grams of ammonium chloride is to inhibit the precipitation of any calcium—and less probably any magnesium carbonate—that might be re-formed by the carbon dioxide retained in solution when the same is made alkaline during the ammonia precipitation. To obtain definite information on this point, four 1.0000 gram charges of pure precipitated calcium carbonate, free from iron and aluminum, were dissolved in 50 cc. of *N*/2 hydrochloric acid in loosely covered Phillips beakers, and placed on the water bath. After remaining at bath temperature for 15 minutes two of the beakers were removed. To one of these ammonium hydroxide was added to alkalinity. A heavy precipitate of calcium carbonate resulted. To the other, before making alkaline, 5 grams of dry ammonium chloride were added; when this solution was made alkaline with ammonium hydroxide, only a very light precipitate occurred. The other two beakers were allowed to stand on the bath for 30 minutes. At the expiration of this time, the contents of one beaker were made alkaline with ammonium hydroxide; a marked precipitation of calcium carbonate resulted. To the other beaker was first added 5 grams of dry ammonium chloride, followed by ammonium hydroxide to alkalinity: no precipitation of calcium carbonate occurred, even upon standing. As this was the condition desired, and as time did not permit further investigation, no attempt was made to derive any quantitative data on this point.

To determine whether or not this inhibition would take place under conditions of actual analysis, as well as in the blanks, four 1.0000 gram charges of sample No. 8 were analyzed for the insoluble residue and ammonia precipitate. Nos. 1 and 2 were each digested with 25 cc. of hydrochloric acid (sp. gr. 1.12), a few drops of 3 per cent hydrogen peroxide solution, and boiled well to expel all carbon dioxide. After a slight cooling, some macerated filter paper was added, followed by ammonium hydroxide to alkalinity. After about 10 minutes digestion just below the boiling point, the precipitate was transferred to a



quantitative filter paper, washed well with hot neutral ammonium nitrate solution, ignited and weighed. Nos. 3 and 4 were digested on the water bath for 30 minutes with 50 cc.  $N/2$  hydrochloric acid, with a few drops of 3 per cent hydrogen peroxide solution. At the expiration of this time, 5 grams of ammonium chloride were added, followed by some macerated filter paper and then by ammonium hydroxide to alkalinity. After agitating well and allowing to stand a few minutes at room temperature, the precipitate was transferred to a filter, and treated from this point on, as before. The comparative results follow:

	1	2	3	4
Grams Insol. Res. + Amm. Ppt.	0.1014	0.1016	0.1015	0.1016

3—It will be noticed that the ammonia precipitation is made cold. This is due to the fact that, at the temperature of the water bath, some ammonia is lost from the  $N/2$  ammonium hydroxide solution, as was shown by the following experiment:

Six 10 cc. portions of  $N/2$  hydrochloric acid were pipetted into Phillips beakers, and diluted to about 50 cc. with distilled water. Three of the beakers, covered with crucibles, were placed on the water bath, and when at bath temperature 25 cc.  $N/2$  ammonium hydroxide were added. After rapid cooling, the excess of ammonia was titrated with  $N/2$  hydrochloric acid. To the other three beakers, which had not been heated, were also added 25 cc. of  $N/2$  ammonium hydroxide and, as before, the excess of ammonia titrated with  $N/2$  hydrochloric acid. The comparative results follow:

PORTIONS	Cc. of alkali required		
Not heated.....	14.36	14.32	14.34
Heated.....	14.10	14.12	14.15

Evidently, then, the ammonia precipitation must be made cold, if the proposed method is to be employed. To ascertain if the precipitate obtained under these conditions corresponds to that obtained under more favorable circumstances, three 1.0000 gram charges of the same sample used in (2) were digested on the water bath for 30 minutes with 50 cc.  $N/2$  hydrochloric acid, and a few drops of a 3 per cent solution of hydrogen peroxide added. At the end of 30 minutes the beaker was removed from the bath, and cooled rapidly by agitating in cold water. Five grams of dry ammonium chloride were then added to each beaker, followed by some macerated filter paper, and then by 25 cc. of  $N/2$  ammonium hydroxide. After agitating well, the precipitate was allowed to stand for 15 minutes, then filtered, washed, ignited and weighed as in (2). The weights follow:

As made above.....	0.1014	0.1012	0.1013
Average as derived in (2).....			0.1015

Evidently, then, under the conditions of the proposed method, the ammonia precipitation is practically complete.

4—The function of the hydrogen peroxide is, of course, to convert all iron present to the ferric condition, to insure its complete precipitation.

5—No error arises from the fact that the iron and aluminum compounds require some acid for their solution, for, since the iron and aluminum are precipitated before titration, only that acid that has been used up for solution of the calcium and magnesium carbonates will be determined.

#### ANALYSES

Practically all of the experimental work was done on 13 limestones, 8 of which approached dolomite in their high magnesium content. Duplicate analyses, reported in Table II, were made of all these samples by standard methods, including double precipitation of both the calcium oxalate and magnesium ammonium phosphate, and the titration of the acidified calcium oxalate with  $N/10$  potassium permanganate.

TABLE II—PERCENTAGE ANALYSES OF SAMPLES BY STANDARD METHODS AND BY PROPOSED METHOD

No.	Results by standard methods				Results by author's method(b)			
	Insol. res. + amm. ppt.	CaCO <sub>3</sub>	MgCO <sub>3</sub>	Total	Insol. res. + amm. ppt.	CaCO <sub>3</sub>	MgCO <sub>3</sub>	Total
1	10.50	51.60	43.70	99.8	10.50	50.24	44.26	105.0
2	10.54	54.55	41.77	99.82	10.48	50.47	43.15	104.1
3	8.92	53.18	48.07	100.17	8.90	50.61	40.44	100.0
4	8.95	53.31	38.00	100.19	8.86	50.75	40.29	100.0
5	3.75	63.00	33.90	100.15	3.95	58.73	38.05	100.7
6	3.22	63.04	33.84	100.10	3.24	58.61	38.15	100.0
7	3.94	66.82	29.39	100.15	3.95	64.69	31.36	100.0
8	3.97	66.90	29.25	100.12	3.97	64.66	31.37	100.0
9	3.24	59.19	37.63	100.06	3.21	56.28	40.48	100.0
10	3.30	59.19	37.66	100.09	3.20	56.34	40.36	100.0
11	11.40	49.02	39.60	100.02	11.36	49.06	39.58	100.0
12	11.36	49.05	39.63	100.04	11.30	49.12	39.58	100.0
13	11.32	50.85	37.65	99.80	11.30	54.06	35.64	101.0
14	11.33	50.82	37.71	99.86	11.33	53.88	34.79	100.0
15	10.20	49.70	39.76	99.66	10.15	53.28	36.57	100.0
16	10.16	49.74	39.72	99.62	10.18	53.09	36.73	100.0
17	4.20	68.85	26.95	99.86	4.18	70.04	25.78	100.0
18	4.25	68.79	26.96	99.90	4.15	69.95	25.90	100.0
19	2.04	92.28	5.62	100.07	2.12	94.71	3.17	100.0
20	2.04	92.36	5.60	100.02	2.08	94.75	3.12	100.0
21	22.65	77.25	(a)	99.90	22.70	77.22	0.08	100.0
22	22.71	77.22	(a)	99.93	22.64	77.35	0.01	100.0
23	6.33	92.85	0.89	100.07	6.31	90.89	2.80	100.0
24	6.36	92.79	0.86	100.01	6.41	90.85	2.74	100.0
25	8.62	91.32	(a)	99.94	8.74	90.25	1.01	100.0
26	8.66	91.26	(a)	99.92	8.72	90.28	1.00	100.0

(a) Not determined.

(b) It is obvious that in this method the total is always 100 per cent.

TABLE III—AVERAGES OF DUPLICATES IN TABLE II

No.	Insol. res. + amm. ppt.		Calcium Carbonate		Magnesium Carbonate		Carbonate
	Standard	Author's	Standard	Author's	Standard	Author's	
1	10.52	10.49	54.57	56.31	34.74	33.21	
2	8.93	8.88	53.21	50.68	38.04	40.37	
3	3.23	3.23	63.02	58.67	33.87	38.10	
4	3.95	3.96	66.86	64.68	29.32	31.37	
5	3.27	3.22	59.19	56.31	37.65	40.42	
6	11.38	11.32	49.03	49.09	39.62	39.59	
7	11.33	11.32	50.83	53.97	37.68	35.22	
8	10.18	10.16	49.72	53.19	39.72	36.65	
9	4.23	4.16	68.82	70.04	26.96	25.84	
10	3.27	3.10	92.32	94.73	5.61	5.15	
11	22.68	22.67	77.23	77.29	(Not det.)	0.04	
12	6.35	6.36	92.82	90.87	0.88	2.76	
13	8.64	8.73	91.29	90.27	(Not det.)	1.01	

From the averages in Table III it will be seen that the combined weights of the insoluble residue and ammonia precipitate agree well within the limits of experimental error in both methods; that in two cases (Nos. 6 and 11), the values for calcium carbonate are well within one per cent of each other; and that in the remaining instances the deviation is about 2 or 3 per cent, varying from 1.02 per cent in No. 13, to 4.35 per cent in No. 3. As these variations represent both abnormally large and abnormally small differences, no constant could be used.

#### SUMMARY AND CONCLUSIONS FROM SERIES II

I—If the limit of inaccuracy for agricultural analysis is set at one per cent, the proposed method, in its present state at least, is hardly to be recommended, but where only an approximation is desired, it might be employed.

II—However, in the opinion of the writer, since the theory of the method does not appear to be incorrect, there is required only a little further study of the experimental conditions involved to make the method entirely applicable for agricultural purposes.

III—Three minor points of interest were developed during the investigation: (1) Ammonia precipitations may be made quantitatively in the cold, in the presence of ammonium salts, and with the aid of some macerated filter paper to facilitate coagulation; (2) a half-normal hydrochloric acid solution may be heated, under the proper conditions, for 30 minutes or more on the water bath (86°), without loss of HCl; (3) ammonium chloride exerts an inhibitory action upon the precipitation of calcium carbonate to a much greater extent than is generally ascribed to it.

In conclusion, the writer desires to express his indebtedness to Dr. F. E. Tuttle, head of the School of Chemistry, State University of Kentucky, not only for his general advice and suggestions during this investigation, but for his assistance in surmounting experimental difficulties that at the time seemed insurmountable.

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### THE PHENOL COEFFICIENT OF GERMICIDES<sup>1</sup>

By FRED B. KILMER, A. WAYNE CLARK AND POWELL HAMPTON

The desire for a method of comparing the disinfecting or germ-killing power of disinfectants with some standard and of expressing the results in definite figures is one of long standing. The "Rideal-Walker" and the "Lancet" methods have been a prolific source of discussion in England and in our country as well. The problem herein discussed is an attempt to show some of the experiences involved in an attempt to follow the so-called hygienic laboratory method and arrive at results concurrent with that of another laboratory. The problem is at once trite and practical for the reason that disinfecting preparations are apt to be examined in several laboratories under somewhat varying conditions with the consequent liability of discordant figures.

### THE HYGIENIC LABORATORY METHOD

Under date of April, 1912, there was published by the U. S. Public Health and Marine Hospital Service a pamphlet known as Hygienic Laboratory Bulletin No. 82. This contained a "Method of Standardizing Disinfectants," by John F. Anderson and Thomas B. McClintic. The method has since become known as the "Hygienic Laboratory Method" according to the suggestion of the writers. It has, we believe, been generally recognized that this method has become the official U. S. procedure for determining the value of disinfectants. A casual examination of this publication is sufficient to indicate that the subject has been thoroughly gone over and that the older methods have received attention and criticism. The authors have attempted to retain the good points of each of these older methods and at the same time to improve and revise in those points which seemed to them to be open to objection. On the whole, the points brought forward seem to be well taken and the improvements to be along the line of making the method more practical, more easily carried out by the average operator, less liable to variations due to the personal equation, and capable of being carried out without the use of unusual or special apparatus.

The testing laboratory of Johnson and Johnson has tried out the method thoroughly and applied it to those substances manufactured by Johnson and Johnson which lay claim to germicidal properties.

This being a new and not yet well-tried method, it was determined beforehand to have the results carefully checked by an outside independent laboratory

so that notes and results could be compared in order to arrive at a thoroughly satisfactory and safe conclusion. This work was done by the Lederle Laboratories of New York City, and will be referred to later.

### CULTURE MEDIUM

A critical examination of the document containing the official method, with the object of proceeding with the work, immediately brought out the fact that there was therein no positive statement as to the formula of the culture medium used. This statement is made on that subject:

"Standard extract broth is used. . . . The broth is made from Liebig's extract of beef and is in exact accordance with the standard methods adopted by the American Public Health Association for water analysis. It is important that the reaction of the media is just +1.5."

Careful reading of the above mentioned A. P. H. A. publication for 1912 shows it to contain these statements:

"Infusion of fresh lean meat, and not meat extract, shall be used as the basis of various media" and "the standard reaction of culture media shall be +1.0 per cent."

It is evident, therefore, that there is no standard method for water analysis in which there is used broth made of beef extract or having a reaction of +1.5 per cent. The reaction is, of course, easily adjusted but we call attention to the exceedingly loose statements made in this Bulletin, No. 82, and the consequent impossibility of complying accurately with its requirements on the information furnished.

The formula for nutrient broth for water analysis given in the A. P. H. A. publication for 1912 is:

Meat.....	500	Water.....	1000
Peptone.....	10		

As ordinary broth is seldom used in water analysis we examined the formulas for gelatin and agar media, these being the commonly used media. We find that of gelatin to be:

Meat.....	500	Water.....	1000
Peptone.....	10	Gelatin.....	100

and for agar:

Meat.....	500	Water.....	1000
Peptone.....	20	Agar.....	10 to 15

It is plainly evident, therefore, that it is impossible to choose the formula intended, but as the agar formula is the one used where the culture is incubated at 37° C., it was decided that that one should be used for this work on disinfectants because the incubation temperature is stated to be at that figure. Also it was thought that the exactness of the formula of the broth was probably not a very important factor. How far wrong was this belief will be seen later. Note that SALT is not mentioned in any of these formulas, and also that in the 1905 edition of the A. P. H. A. "Methods of Water Analysis" it says:

"Sodium chloride shall not be added to any culture medium herein specified."

The amount of beef extract to be used was presumed to be 3 grams and our formula was:

Liebig's beef extract....	3 grams	Water.....	1000 grams
Peptone (Witte).....	20 grams	Reaction . . .	+1.5 per cent

<sup>1</sup> Presented at the 50th Meeting of the American Chemical Society, New Orleans, March 31 to April 3, 1915.



## MANIPULATION

To a novice in the manipulation of this method it seemed to be very difficult to keep a correct record of the position and contents of each of the many tubes, for the work must be done rapidly and practically automatically. As referred to later, we decided to make tests only at the 2<sup>1</sup>/<sub>2</sub> and 15-minute intervals and we constructed a time table for working by the clock from any even hour so that the attention need not be taken from the actual manipulation. This time table is printed herewith.

TIME TABLE FOR WORKING BY THE CLOCK  
PHENOL-COEFFICIENT BY HYGIENIC LABORATORY METHOD  
2<sup>1</sup>/<sub>2</sub> and 15-minute tests

O'CLOCK	PHENOL	DISINFECTANT
0.00	SEED S	SEED A
0.01	SEED T	SEED B
0.02	SEED U	SEED C
0.02 <sup>1</sup> / <sub>2</sub>	Inoculate S 2 <sup>1</sup> / <sub>2</sub>	Inoculate A 2 <sup>1</sup> / <sub>2</sub>
0.03	SEED V	SEED D
0.03 <sup>1</sup> / <sub>2</sub>	Inoculate T 2 <sup>1</sup> / <sub>2</sub>	Inoculate B 2 <sup>1</sup> / <sub>2</sub>
0.04	SEED W	SEED E
0.04 <sup>1</sup> / <sub>2</sub>	Inoculate U 2 <sup>1</sup> / <sub>2</sub>	Inoculate C 2 <sup>1</sup> / <sub>2</sub>
0.05	SEED X	SEED F
0.05 <sup>1</sup> / <sub>2</sub>	Inoculate V 2 <sup>1</sup> / <sub>2</sub>	Inoculate D 2 <sup>1</sup> / <sub>2</sub>
0.06	SEED Y	SEED G
0.06 <sup>1</sup> / <sub>2</sub>	Inoculate W 2 <sup>1</sup> / <sub>2</sub>	Inoculate E 2 <sup>1</sup> / <sub>2</sub>
0.07	SEED Z	SEED H
0.07 <sup>1</sup> / <sub>2</sub>	Inoculate X 2 <sup>1</sup> / <sub>2</sub>	Inoculate F 2 <sup>1</sup> / <sub>2</sub>
0.08	SEED I	SEED I
0.08 <sup>1</sup> / <sub>2</sub>	Inoculate Y 2 <sup>1</sup> / <sub>2</sub>	Inoculate G 2 <sup>1</sup> / <sub>2</sub>
0.09	.....	SEED J
0.09 <sup>1</sup> / <sub>2</sub>	Inoculate Z 2 <sup>1</sup> / <sub>2</sub>	Inoculate H 2 <sup>1</sup> / <sub>2</sub>
0.10	.....	Inoculate I 2 <sup>1</sup> / <sub>2</sub>
0.10 <sup>1</sup> / <sub>2</sub>	.....	Inoculate J 2 <sup>1</sup> / <sub>2</sub>
0.11	.....	Inoculate A 15
0.11 <sup>1</sup> / <sub>2</sub>	.....	Inoculate B 15
0.15	Inoculate S 15	Inoculate C 15
0.16	Inoculate T 15	Inoculate D 15
0.17	Inoculate U 15	Inoculate E 15
0.18	Inoculate V 15	Inoculate F 15
0.19	Inoculate W 15	Inoculate G 15
0.20	Inoculate X 15	Inoculate H 15
0.21	Inoculate Y 15	Inoculate I 15
0.22	Inoculate Z 15	Inoculate J 15
0.23	.....	.....
0.24	.....	.....

The meaning of the words "seed" and "inoculate" need explanation. "Seed" is used as in the original paper. The tubes containing the various dilutions to be tried are called seeding tubes, so we have used the word "seed" as meaning "to add the culture to the diluted disinfectant." By "inoculate" we mean to transfer a "loop" from the seeding tube to the sub-culture tube at the expiration of the given time; thus, for example, at 2:05 o'clock the culture is added to the dilution in seeding tubes marked X and at 2:07<sup>1</sup>/<sub>2</sub> o'clock a loopful of that mixture is removed and dipped into sub-culture tube marked X 2<sup>1</sup>/<sub>2</sub>.

It seems to us that a time table of this kind is a great help to an operator who is only occasionally doing this work. Also, an ordinary large test-tube rack can be used instead of specially made blocks.

**DILUTIONS**—The making up of the dilutions of the disinfectants brought out the necessity for an interpretation of the meaning of the figures given in the very useful and complete table printed in this pamphlet. The figures are expressed thus: 1:20, 1:25, etc. Not until we gave considerable study to it was it made clear that 1:20 meant 1 to 19 or 1 in 20. It seems to us that a statement to this effect might well have been made, especially as the peculiar situation develops that 1:1 means full strength (no dilution) and 1:2 means 50 per cent.

**TIME**—Further critical study of the details of the method fails to explain why tests are made for 2<sup>1</sup>/<sub>2</sub>, 5, 7<sup>1</sup>/<sub>2</sub>, 10, 12<sup>1</sup>/<sub>2</sub> and 15 minutes, whereas only the

2<sup>1</sup>/<sub>2</sub> and 15-minute figures are used in calculation of results. The only conceivable advantage would be that a single mistake or outside infection could be shown to be irregular and out of place in the table. As probably no one would rest on a single set of tests, this does not seem worth while.

**THE PHENOL**—There are two other substances entering into a series of tests of this character, which might be possible sources of differences in results: one is the phenol and the other the typhoid organism. The original publication states that Merck's "silver label" phenol was used. We had none of this on hand and used (as in Table I) a supply of Powers-Weightman-Rosengarten Co. phenol that we had on hand and which appeared to be in good condition. This was made up 5 per cent by assay as directed. Later we secured a supply of the Merck "silver label" phenol as in Table II.

**THE ORGANISM**—In Bulletin No. 82 no specific reference is made to the source of the typhoid organism used in tests. We had on hand a culture of *B. typhosis* originally from H. K. Mulford Co. We used this in all the work, each series of tests being made with a culture that had been transferred to fresh tubes of broth on three consecutive days and incubated at 37° C. for the 24-hour periods between the transfers.

After this work was about finished we were informed by Lederle Laboratories that the so-called Hopkins strain of *B. typhosis* used by them was the one also used by Anderson and McClintic. There is no statement to that effect in the original paper and our experience is not sufficient to allow us to state that it is necessary to use a certain strain. Perhaps it is sufficient, as required in Bulletin No. 82, that the culture

TABLE I—FIRST TESTS OF "HYGIENIC LABORATORY METHOD" BY JOHNSON AND JOHNSON LABORATORY

ORGANISM.....Typhosis, 24-hr. culture, filtered ORGANIC MATTER—None  
MEDIUM.....Extract 3, peptone 20, water 1000. Reaction +1.5  
CULTURE.....0.1 cc. to 5.0 cc. disinfectant (P.-W.-R. Co. phenol)  
SUBCULTURES.....One 4 mm. loop to 10 cc.  
TEMPERATURES.....Contact 20° C., incubation 37° C.  
RESULTS.....x = growth (not killed). 0 = no growth (killed)

PHENOL Dilutions	Time of contact 2 <sup>1</sup> / <sub>2</sub> min.	15 min.	CAMPHENOL Dilutions	Time of contact 2 <sup>1</sup> / <sub>2</sub> min.	15 min.
1-100	0	0	1-80	0	0
1-110	0	0	1-200	0	0
1-120	0	0	1-225	x	0
1-130	x	0	1-250	x	x
1-140	x	0	1-275	x	x
1-150	x	x	1-300	x	x
1-160	x	x	1-325	x	x
1-180	x	x	1-350	x	x
			1-375	x	x
			1-400	x	x

$$\text{Phenol-coefficient of Camphenol} = \left( \frac{200}{120} + \frac{225}{140} \right) \div 2 = 1.60$$

shall be grown for 24 hours in each of three successive tubes of broth of definite composition. The typhoid organism was specifically selected because of its supposed uniformity, and the Hygienic Laboratory Method would lose some of its value in our opinion, if to the already severe requirements was added the requirement that a specified strain of organism should be used.

**SOURCE OF SAMPLES**—The samples of Camphenol and Synol Soap used by Lederle Laboratories were purchased in the open market from sources unknown to us. The samples used in the Johnson and Johnson tests were taken from the shelves of the regular stock-room at the works.

TABLE II -PHENOL COEFFICIENTS OF CAMPHENOL AND SYNOL BY HYGIENIC LABORATORY METHOD

RESULTS. . . . . x = growth (not killed). 0 = no growth (killed)

JOHNSON and JOHNSON LABORATORY

LEDERLE LABORATORIES

ORGANISM. . . . . Typhosis, 24-hr. culture, filtered

ORGANIC MATTER. . . . . Extract 3, peptone 10, salt 5, water 1000. Reaction +1.5

MEDIUM. . . . . Merck's "Silver Label"

PHENOL. . . . . 0.1 cc. to 5.0 cc.

PROPORTION CULTURE TO DISINFECTANT. . . . . One 4 mm. loop to 10 cc.

SUBCULTURES. . . . . Contact 20° C. Incubation 37° C.

TEMPERATURE. . . . .

ORGANISM. . . . . B typhosis (Hopkins)

ORGANIC MATTER. . . . . None

AGE OF CULTURE. . . . . 24 hrs. at 37° C.

MEDIUM. . . . . Standard beef extract broth

DOSE. . . . . 0.1 cc. of filtered culture to 5 cc. diluted disinfectant

SUBCULTURE. . . . . One 4 mm. loop to 10 cc. of broth

TEMPERATURES. . . . . Medication 20° C. Incubation 37° C. (48 hrs.)

JOHNSON and JOHNSON LABORATORY				LEDERLE LABORATORIES			
PHENOL Dilutions	Time of contact 2 1/2 min. 15 min.	CAMPHENOL Dilutions	Time of contact 2 1/2 min. 15 min.	PHENOL Dilutions	Time of contact 2 1/2 min. 15 min.	CAMPHENOL Dilutions	Time of contact 2 1/2 min. 15 min.
1-100	0	1-180	0	1-80	0	1-250	0
1-110	x	1-200	0	1-90	x	1-275	0
1-120	x	1-225	0	1-100	x	1-300	0
1-130	x	1-250	0	1-110	x	1-325	0
1-140	x	1-275	0	1-120	x	1-350	x
1-150	x	1-300	0	1-130	x	1-375	x
1-160	x	1-325	0	1-140	x	1-400	x
1-180	x	1-350	x	1-150	x		
		1-375	x				
		1-400	x				
Phenol-coefficient of camphenol = $\left(\frac{325}{100} + \frac{375}{120}\right) \div 2 = 3.20$				Phenol-coefficient of camphenol = $\left(\frac{275}{80} + \frac{350}{100}\right) \div 2 = 3.46$			
PHENOL Dilutions	Time of contact 2 1/2 min. 15 min.	SYNOL Dilutions	Time of contact 2 1/2 min. 15 min.	PHENOL Dilutions	Time of contact 2 1/2 min. 15 min.	SYNOL Dilutions	Time of contact 2 1/2 min. 15 min.
1-90	0	1-30	0	1-80	0	1-25	0
1-100	x	1-35	0	1-90	x	1-30	0
1-110	x	1-40	0	1-100	x	1-35	0
1-120	x	1-45	x	1-110	x	1-40	0
1-130	x	1-50	x	1-120	x	1-45	x
1-140	x	1-55	x	1-130	x	1-50	x
1-150	x	1-60	x	1-140	x	1-55	x
1-160	x	1-65	x	1-150	x	1-60	x
		1-70	x			1-65	x
		1-80	x			1-70	x
Phenol-coefficient of synol = $\left(\frac{40}{90} + \frac{60}{120}\right) \div 2 = 0.47$				Phenol-coefficient of synol = $\left(\frac{30}{80} + \frac{45}{100}\right) \div 2 = 0.41 +$			

RESULTS

In reference to the results given here, all were checked by duplicate series, both in the Johnson and Johnson and the Lederle Laboratories. The results were considered sufficiently concordant and the tables are the ones considered most accurate.

Table I gives the results of our original work on camphenol. Knowing the composition of this preparation, it seemed incredible that the results should be so low (1.60). The receipt of information from Lederle Laboratories that their results showed it to have a coefficient of 3.46 (see Table II) indicated at once that there was need of comparison of methods pursued in the manipulation. A conference on the subject developed the fact that Lederle Laboratories were using a broth containing sodium chloride and only 10 grams peptone, instead of 20, to each 1000 cc. Following up the statement of Lederle Laboratories that theirs was the correct formula for this work, we addressed a letter to Dr. Anderson in Washington asking for the formula used in his original work and received a reply that the broth contained Liebig's extract 3, Witte's peptone 10, salt 5, water 1000. In other words, we had reasoned wrongly so we made up new broth and in the meantime, having secured some Merck's "silver label" phenol, used that also in all future work. Table II gives the results on camphenol; we consider the 3.20 to be sufficiently concordant with the Lederle result of 3.46.

We are unable to offer any rational explanation in the results on camphenol of the great difference between the tests when salt is used in and omitted from the broth. It seems hardly possible that the minute amount in 0.1 cc. of the culture used in contact with the 5.0 cc. of diluted camphenol should produce such difference on account of chemical reaction with the camphenol. Also, such reaction would seem likely to consist in a certain amount of camphenol being

removed from active participation in germ-destruction and hence would reduce, not increase, the figures. Sodium chloride, in common with many other salts, we of course know, throws out of broth, etc., certain organic constituents of animal fluids, but this suggestion, in view of the small amount of broth used, does not supply a satisfactory explanation. However, such action, removing as it would a certain quantity of organic matter from the broth, would seem to tend toward the increase in the figures. The use of less peptone might also influence the results in that direction. As to phenol, we think it hardly possible that the clean crystallized chemical could be held accountable for such widely divergent results.

We regret that we have not found time to thoroughly check up these factors. That the camphenol result in Table II is exactly double that in Table I is merely a coincidence—not a mathematical error.

DISCUSSION

In considering these results we must always remember that the high accuracy of a chemical analysis cannot be expected because we are dealing with a living organism under conditions that are as well controlled as the state of the science permits but yet may be relatively quite variable. Also the two laboratories were using different samples of the disinfectants and different strains of the typhoid organism both of which may or may not have a slight effect upon the result. On the whole, these results are probably as nearly concordant as any two operators could secure in tests of this kind.

As to the Hygienic Laboratory Method we feel fairly well satisfied with the results and with the method except for the unfortunate omissions referred to above. We see no reason why this method should not continue to be satisfactory and of sufficient accuracy to remain as a standard American method for determining the phenol-coefficient of disinfectants.

JOHNSON and JOHNSON LABORATORIES  
NEW BRUNSWICK, N. J.



# THE HYDROCHLORIDE METHOD FOR THE DETERMINATION OF ALKALOIDS<sup>1</sup>

BY GEO. D. BEAL AND ST. ELMO BRADY

The present research was undertaken in the hope of securing a method for the precipitation of alkaloids which might be used as a combined gravimetric and volumetric analytical method, each end point serving as a check on the other. The method, in brief, consists in the extraction of the alkaloid with ether, precipitation from this solution as the hydrochloride by passing in dry, gaseous, hydrochloric acid, evaporating off the ether and weighing the salt, then dissolving the hydrochloride in water and titrating the hydrochloric acid with standard alkali, using phenolphthalein as indicator. The results obtained have been checked in each case by a standard method already in use, that of the U. S. P. VIII being used wherever available.

The first sample used consisted of conium seeds from the grounds of the College of Pharmacy building in Scio, Ohio. These were ground to No. 60 powder and extracted with a mixture of ether, alcohol and ammonia. The extract was shaken out with  $N/1$  sulfuric acid to free the alkaloid from coloring and fat. The acid solution, which contains the alkaloids, was made alkaline with ammonia and the freed alkaloids extracted with ether.

The ether extract, colorless and free from fat, was saturated with gaseous hydrochloric acid, which had been dried by passing through concentrated sulfuric acid. On this treatment, the hydrochloride of the alkaloids separated, partly as a crystalline solid and partly as an oil. When the ether was evaporated on the water bath crystalline coniine hydrochloride was left behind, which was weighed and the percentage of coniine calculated for the drug. The salt was then dissolved in water and the solution titrated with standard alkali to the phenolphthalein end point, and the result calculated on the assumption that the salt formed was the monohydrochloride.

PER CENT CONIINE	Sample A <sub>1</sub>	Sample A <sub>2</sub>	Sample A <sub>3</sub>
By weight.....	1.74	1.72	1.725
By titration.....	1.67	1.67	1.70

To test the accuracy of the above results the seeds were then analyzed by the U. S. P. method, in which

the ether extract is evaporated with an excess of aqueous hydrochloric acid and the dry salt weighed, with the additional step added that this U. S. P. residue was dissolved and titrated as above described.

PER CENT CONIINE	Sample B <sub>1</sub>	Sample B <sub>2</sub>	Sample B <sub>3</sub>
By weight.....	1.74	1.72	1.74
By titration.....	1.70	1.705	1.69

Some redistilled coniine was dissolved in ether, precipitated, weighed and titrated as above described.

GRAMS CONIINE	Sample C <sub>1</sub>	Sample C <sub>2</sub>
Theoretical.....	0.125	0.030
By weight.....	0.12525	0.03006
By titration.....		0.02887

Sample C<sub>2</sub> was treated with silver nitrate in the presence of nitric acid and the silver chloride formed weighed and calculated for the monohydrochloride of coniine.

GRAMS AgCl	Theory, 0.0084	Found, 0.0085
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These last results serve to confirm the nature of the precipitate obtained.

Because of our success in this work we determined to extend the field, and have applied the method to the analysis of tobacco and colchicum root. The extraction followed was practically the same as in the case of the coniine. In each case the oil was observed, as well as the crystalline salt, on the addition of the gaseous HCl.

PER CENT ALKALOID by method	COLCHICUM ROOT		TOBACCO	
	Sample D <sub>1</sub>	Sample D <sub>2</sub>	Sample E <sub>1</sub>	Sample E <sub>2</sub>
NEW { Gravimetric.....	2.22	2.30	2.65	2.61
{ Volumetric.....	2.19	2.28	2.66	2.49
Standard (U. S. P.).....	2.25	2.28	(Kisslings) 2.64	2.67

This work is being continued on other alkaloidal drugs, and in addition the nature of the insoluble oil is being investigated. From some recent work on the nature of some oils obtained with amines, it appears that it is simply a higher hydrochloride, as some of the latter have been obtained carrying as many as ten molecules of HCl. If the oil be washed with cold ether until it is free from free HCl, it still fumes in moist air, and if it be placed in a vacuum desiccator with some stick potassium hydroxide, it is converted to the monohydrochloride, and the alkali becomes encrusted with potassium chloride.

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## LABORATORY AND PLANT

### EXTRACTION AND RECOVERY OF RADIUM, URANIUM AND VANADIUM FROM CARNOTITE<sup>2</sup>

BY CHARLES L. PARSONS, R. B. MOORE, S. C. LIND, O. C. SCHAEFER  
Received Dec. 15, 1915

The work of the Bureau of Mines on radium began in the fall of 1912. A preliminary report published in the summer of 1913<sup>3</sup> outlined the conditions of mining and the wastes involved in the carnotite ore

<sup>1</sup> Presented at the 50th Meeting of the American Chemical Society, New Orleans, March 31 to April 3, 1915.

<sup>2</sup> Authors' abstract from *Bull.* 104, U. S. Bureau of Mines. The bulletin contains complete detail descriptions of operations with full drawings both of floor plan and sections of the radium plant, as well as half-tones of plant and apparatus.

<sup>3</sup> *Bull.* 70, Prel. Rept., "Uranium, Radium and Vanadium," by R. B. Moore and K. L. Kithil.

region of the West. As a result of this investigation, Dr. Howard A. Kelly, of Baltimore, and Dr. James Douglas, of New York City, were interested, and they incorporated the National Radium Institute. This institute leased certain carnotite claims in Long Park, Col., with the right to extract 1,000 tons of carnotite ore therefrom. The National Radium Institute arranged with the Bureau of Mines for a cooperative investigation of the methods of extracting radium from this ore and the saving of the wastes by the concentration of the low-grade ore formerly thrown on the dump.

Sufficient funds were furnished to be expended under the direction of the Director of the Bureau of

Mines, and the first plant was built in the spring of 1914, beginning production on an experimental basis in June, 1914. The result of the preliminary investigation was so successful that the institute authorized the construction of a second and larger plant which began operations in February, 1915; the two plants have been run continuously since that time.

The object of the investigation was to procure an adequate supply of radium for the treatment of cancer in the two hospitals connected with the Radium Institute and to develop methods of extraction whereby the miners might obtain a more adequate return for their ore, which, before this investigation began, had been sold largely to foreign manufacturers. Incidentally, methods have been developed for the preparation of sodium uranate, uranium oxide, and iron vanadate—by-products from the extraction of carnotite ore. Before the Bureau's operations began, several methods, the details of some of which have been kept secret, had been devised, for the extraction of radium from pitchblende and from carnotite.



FIG. 1—RADIUM PLANT: NATIONAL RADIUM INSTITUTE

These involved (1) the use of an acid leach; (2) the use of an alkaline leach followed by acid; and (3) fusing the ore with some material that would make extraction of the valuable contents possible. The acid leaches had been extensively used abroad and had shown an extraction of not over 70 per cent and probably little over 50 per cent of the radium content, owing to the fact that the ores contain sulfates, and any radium sulfate present was not removed under these conditions. The alkaline leach followed by an acid leach would probably remove more radium but involves such grave difficulties of filtration that it seemingly has not been put into commercial use. Fusing the ore with sodium sulfate was long employed on pitchblende<sup>1</sup> and has been used in Australia by Radcliffe in treating carnotite that is obtained at Olary, South Australia. This carnotite, being mixed with ilmenite, is very different from the American carnotite. Fusion with sodium carbonate has also

been employed in this country on carnotite ores but has the great disadvantage that it carries a large part if not all of the silica into solution. This adds greatly to the cost of operation and tends to give radium-barium sulfates of a rather high degree of impurity which require special treatment. From the best accounts available, it appears that this method does not successfully extract more than 70 per cent of the radium present in the ore.

#### METHOD OF ORE TREATMENT

The method devised by the Bureau of Mines is based upon the fact that strong, hot nitric or sulfuric acid dissolves radium-barium sulfates in considerable quantities, as well as the other soluble constituents of the ore. Hence the radium-barium sulfate left behind when dilute acids are used for leaching is obtained in solution and recovered. The use of strong, hot nitric acid, although it presented many difficult problems of chemical engineering, was chosen because the radium-barium sulfate could be precipitated at once in a remarkably pure form and the nitric acid

could be largely recovered in the form of sodium nitrate and used again. Accordingly a nitric acid plant was built in connection with the radium plant and has been regularly operating since February, 1915.

In the Bureau of Mines method, the ore, pulverized to 20 mesh, is fed into an earthenware boiling kettle containing 38 per cent nitric acid. The nitric acid (121 lbs.  $\text{HNO}_3$  diluted to 38 per cent) is brought nearly to boiling by means of steam passed through a glass tube. When the boiling point has been nearly reached the ore is added a shovelful at a time and the whole stirred, heating being continued. After the ore has all been added, heating is continued for 15 minutes when the mass is run on to an earthenware filter and the nitric acid separated from the ore by suction. The ore is re-treated with hot nitric acid of one-third the original strength, and is then washed with hot water. This treatment brings into solution nearly all of the uranium, about 50 per cent of the vanadium, and practically all of the radium present in the carnotite. The residue is discarded. The filtered solution is stirred, and sodium hydroxide is run in slowly with the object of reaching as nearly as possible the neutral point without forming a precipitate. If too much sodium hydroxide is added, both iron and vanadium are precipitated, discoloring the radium-barium sulfate. On the other hand, if not enough sodium hydroxide is added, the acid remains too strong and the solvent action of the nitric acid on the radium-barium sulfate is not sufficiently decreased. By a little practice the right point is easily obtained. Barium chloride is then added in the proportion of 2 lbs. of  $\text{BaCl}_2$  to 1 ton of ore and is thor-

<sup>1</sup> Haitinger, Luding and Ulrich, *Bericht, über die Bearbeitung der Pechblend-Rückstände*, K. K. Akad. Wissenschaft., 117 (1908), 619.



oughly stirred in, and 15 lbs. of sulfuric acid to 1 ton of ore are then added. As the ore contains some barium it is necessary to add only a comparatively small amount of this material to accumulate the radium. The whole mass is vigorously stirred for 1 hour; the solution is then elevated to conical tanks where it is allowed to settle, usually for 3 to 4 days. The supernatant liquid is siphoned off for the recovery of uranium and vanadium and the radium-barium sulfates are collected on an earthenware filter, washed, treated with dilute sodium hydroxide, and dried.

#### RADIUM REFINING

One of the most important features of the Bureau of Mines method is that the radium-barium sulfates first precipitated are of high grade, comparatively free from impurity, and are ready for immediate conversion into chlorides without further purification.



FIG. II—EXTRACTION POTS FOR CARNOTITE ORE

The amount of radium in these sulfates has averaged about 1 mg. of radium element per kilogram of material. It was early found in the work of the bureau that the older methods of converting radium-barium sulfate into soluble form were unnecessarily tedious for the material produced. Accordingly other methods of reduction were tried and it was finally determined that the best method to use is reduction with carbon in graphite crucibles. For this purpose the purest possible charcoal is used, about one-fifth the weight of the total sulfates being taken. The charcoal is mixed with the sulfates in a ball mill and is then transferred to a No. 100 graphite crucible and heated for 7 to 8 hours to a temperature around 800° C. Reduction takes place readily, the carbon monoxide burning out at the spout of the crucible. Three crucibles are heated in the same furnace. A reduc-

tion of over 90 per cent is usually obtained. The radium-barium sulfide is dissolved in pure hydrochloric acid and the residue of unconverted sulfate is re-treated in like manner. The solution should, of course, be performed out doors or under a hood with a good draft, especially as the hydrogen sulfide sometimes catches fire spontaneously; the danger is minimized if the residue is slowly added to the acid in an open vessel. In the re-treatment of the residues a third residue is also obtained. As there is a tendency to an accumulation of lead and other impurities in these residues, it is advisable to fuse the third residue with sodium carbonate rather than to attempt to reduce in the ordinary way with carbon. As the weight of the second residue is only 1 or 2 per cent of the original radium-barium sulfate treated, this special treatment is required only once or twice



FIG. III—STONEWARE FILTERS FOR FILTERING HOT NITRIC ACID SOLUTIONS

a year. The acid filtrate from the radium-barium sulfate is an almost saturated solution of radium-barium chloride and is ready for fractionation. Fractionation takes place much more rapidly in strong hydrochloric acid solution than it does if the solution is nearly neutral. However, the obtaining of containers that will withstand hot solutions of hydrochloric acid is difficult. Ware sufficiently resistant has been found in the silica-lined, acid-proof apparatus made by the Danto Rogeat Company, Lyons, France, and steam-jacketed kettles made of this ware have now been in use for over a year with almost no evidence of erosion.

For the first crystallization, steam-jacketed kettles of 250 liters capacity are preferable although in a series of five the capacity of the last two need not exceed 200 liters. The evaporators are placed under hoods in order to remove acid fumes, and the evapora-

tion is so conducted that the crystals move in one direction and the mother liquors in the other, the crystals from a given evaporation being dissolved in the mother liquors from the kettle second preceding. The crystallization factor of hydrochloric acid solutions averages between 1.5 and 1.6, *i. e.*, if 50 per cent of the barium chloride is removed there will be 50 per cent more radium in the crystals remaining, or if 50 per cent of the barium chloride is crystallized out there will be 50 per cent more radium in the crystals than in the liquor left behind. In a short time, therefore, the crystals in these larger kettles can be brought to a strength of 4 to 10 parts of radium per million; at this stage the crystals are taken from the plant to the laboratory for crystallization in smaller apparatus of the same general type.

The salts of most metals such as iron, aluminum, and vanadium that may occur with the radium-barium solutions as impurities pass into the mother liquors and give no difficulty in the richer radium fractionations. Lead is, however, an exception and

water, the solution is made neutral with ammonia, and the lead is precipitated with ammonium sulfide. The solution is then filtered, and powdered ammonium carbonate is added until all of the barium has been precipitated as carbonate. The precipitate, of course, also contains radium as carbonate. It is washed and dissolved in chemically pure hydrobromic acid, after which crystallization proceeds, an excess of hydrobromic acid also being desirable for the rapid separation of radium from barium. Usually 10 or 12 fractionations are required in the form of bromides to bring the radium up to a strength of from 1 to 4 per cent radium bromide, the factor of concentration for each step in the hydrobromic acid solution being about 2 to 2.2. This makes rapid crystallization possible. Every two or three days the strong crystals are placed aside until the end of the month when they are mixed together in one lot and crystallized in hydrobromic acid solution to high concentration. Three or four crystallizations only are necessary to bring the major part of the radium to a concentration of 60 to 80 per cent radium bromide. One of the surprises of the radium work has been the ease with which separation of radium from barium is brought about. The crystallization is rapid and no difficulty whatever has been experienced in obtaining a high-grade material.

The bromide can be easily converted again into the chloride by one or two evaporations with hydrochloric acid and in this form can be sealed in small glass tubes for transportation. The recovery of radium from carnotite shows so high an efficiency that over 90 per cent of the radium present in the ore may be recovered.

#### SEPARATION AND PURIFICATION OF URANIUM

The acid solution from which the radium-barium sulfate has been precipitated is run directly from the settling tanks into large vats containing an excess of boiling sodium carbonate solution. Under these conditions the uranium and vanadium go into solution as sodium uranyl carbonate and sodium vanadate. For a solution from an ore containing 2.5 to 3 per cent uranium oxide, 250 lbs. of sodium carbonate in excess of that necessary to neutralize the acid originally used is required. This means about 650 lbs. sodium carbonate per ton of ore. It is important that the sodium carbonate solution be hot and be vigorously stirred; that the acid solution be added slowly; and that the boiling be continued for some time. Only in this way will the solution of uranium and vanadium obtained be anywhere near complete. Of course at the same time iron, aluminum, and calcium present in the solution are precipitated, and these are filtered off in filter presses, washed, and thrown away. The filtrate from the iron, aluminum, and calcium precipitate carrying uranium and vanadium, is partly neutral

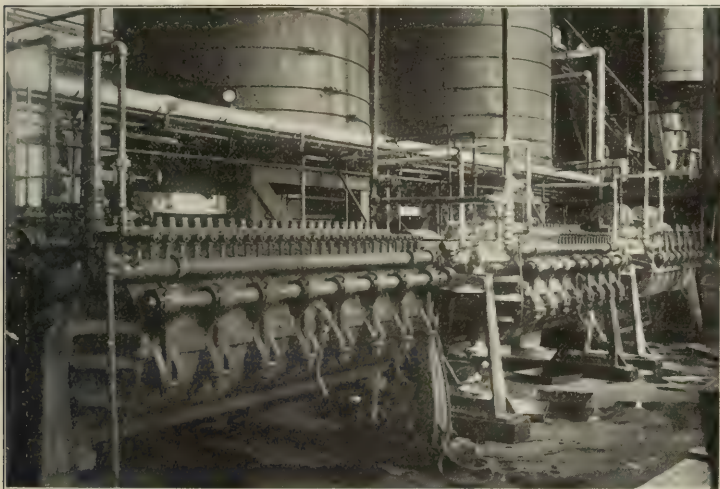


FIG. IV—VIEW IN NEW PLANT SHOWING FILTER PRESSES

requires special treatment although it might be expected that when the radium-barium sulfide is dissolved in hydrochloric acid, the copious evolution of hydrogen sulfide would remove the lead as lead sulfide. This does not occur owing to the high concentration of barium chloride and the lead can be completely removed only after neutralization with ammonia when the addition of ammonium sulfide causes it to be thrown down in an insoluble condition.

The crude radium-barium chloride containing 4 to 10 parts radium element per million is brought from the plant to the laboratory where it is dissolved in water in large porcelain dishes, and hydrochloric acid is added. After the solution has stood over night it is filtered to remove the small part of lead that has been separated as chloride, and to remove whatever carbon and barium sulfate may have escaped previous filtration. After three or four recrystallizations of the chloride, the chloride crystals are dissolved in



ized with nitric acid until a yellow precipitate just begins to form. At this point sodium hydroxide is added to the hot liquid until uranium is completely precipitated as sodium uranate. The sodium uranate at this point generally carries 7 to 9 per cent vanadic oxide, and must be precisely treated to remove the vanadium therefrom. This is best done by fusing

described practically all of the uranium is dissolved in the nitric acid, only a small part (averaging 2.3 per cent) remaining in the insoluble residue because of incomplete washings. The loss of uranium in the iron-calcium precipitate runs usually from 10 to 15 per cent of the material originally present in the ore. The recovery of uranium as sodium uranate has varied

between 75 to 94 per cent of the uranium present in the ore, the average on the last 10 carload lots treated being 84.4 per cent.

**VANADIUM**—The conditions making for the highest recovery of radium, which is the real value of the ore, do not generally coincide with the conditions necessary for the highest recovery of vanadium. It has accordingly been necessary to sacrifice the vanadium in order to get large recoveries of the more valuable element. Strong nitric acid tends to cause separation of vanadium from the solution, even after it has been dissolved, and this separated vanadium is filtered with difficulty and tends to decrease the radium extraction.

More prolonged treatment with nitric acid would dissolve more vanadium but this is not desirable and it has been found best to use just as short a treatment with nitric acid as will insure the



FIG. V—OIL FURNACE FOR REDUCTION OF BARIUM SULFATE AND PURIFICATION OF SODIUM URANATE

the sodium uranate with salt in large, wrought-iron or steel crucibles. When the salt is dissolved in water it carries the vanadium in solution as sodium vanadate and leaves behind a practically pure sodium uranate.

#### RECOVERY OF VANADIUM

The filtrate from the sodium uranate together with any sodium vanadate dissolved out of the sodium uranate by fusion with salt is brought to the boiling point and neutralized with nitric acid, the boiling being continued long enough to eliminate carbon dioxide. At this point a solution of ferrous sulfate is run into the hot solution while under agitation by means of compressed air. As a rule about 75 lbs. of ferrous sulfate are required per ton of ore treated. The heating of the solution is stopped before the addition of the ferrous sulfate is complete, for if heating is continued longer a complete precipitation of the vanadium is not obtained. Iron vanadate obtained under these conditions usually contains 32 to 33 per cent  $V_2O_5$ . If the solution is slightly alkaline the percentage of  $V_2O_5$  diminishes, while on the other hand if the solution is slightly acid when precipitation begins, a much richer product can be obtained. This is accompanied, however, by a loss of vanadium, as some of it passes into the filtrate and causes difficulty in subsequent operations.

#### NITRATE RECOVERY

After precipitation and filtration of the iron vanadate, the solution remaining contains chiefly sodium nitrate with small amounts of sodium chloride and sodium sulfate. It is evaporated to dryness, the sodium nitrate being crystallized out in crystallizing pans and used again for the production of nitric acid.

#### RECOVERY AVERAGES

**URANIUM**—In the extraction process previously



FIG. VI—NITRIC ACID PLANT

complete extraction of the uranium. Fifteen minutes' heating in the extraction apparatus after complete addition of the ore is all that is necessary. Under these conditions, however, scarcely 50 per cent of the vanadium goes into the filtrate and 15 to 20

per cent is lost in the iron calcium precipitate. Accordingly the total average recovery of vanadium, including that from the sodium uranate, has been a little less than 30 per cent of that present in the ore. The recovery of vanadium has barely covered the expense incident thereto.

**SODIUM NITRATE**—By using nitric acid for neutralization throughout the process, a large proportion of the nitric acid used both for the solution of the original ore and for the neutralization of the alkaline solutions is recovered in the form of sodium nitrate. During the months of May, June, and July, for which full figures are available, the average recovery was 87.5 per cent (minimum 84.87 and maximum 90.4). This high recovery has of course greatly decreased the expense of the nitric acid used in the operations as a nitric acid plant was built to work up the recovered nitrate. During May, June, and July, 1915, the expenditure for nitric acid was only 2.411 cents per lb. of 100 per cent acid.

**RADIUM**—When an element exists in an ore in the proportion of 1 part to 200,000,000, its extraction and recovery present difficulties not ordinarily encountered in metallurgy. A recovery of 60 to 70 per cent, or even 50 per cent might, under such conditions, appear to be satisfactory. A much larger recovery than 70 per cent is undoubtedly exceptional. The unusually high recovery of 90 per cent and over of the radium present gives the nitric acid method its real value.

#### COST DATA

In figuring the total costs of the first 4,258 mgs. of radium element produced, the uranium and vanadium products may be either included or excluded. By subtracting the actual costs connected with the production of the uranium and vanadium compounds from the total cost, a close approximation of the cost of radium, provided the uranium and vanadium were not recovered, will be obtained, but such a figure will not be exact, as under the changed conditions various factors would enter in, the effects of which can only be estimated. On this basis the average cost of 1 gram of radium element, including the more expensive early treatment, is as follows:

#### COST OF RADIUM PRODUCTION TO AUG. 1, 1915

Operating costs to Aug. 1:	
Total expenditures.....	\$129,907.42
Construction and equipment.....	52,453.60
	<hr/>
Cost of ore treated.....	\$ 77,453.82
Amortization of plant and equipment at 20 per cent per annum.....	69,767.99
Cost of U. S. Bureau of Mines cooperation (plant dept.)...	9,065.90
Cost of refining 2611.44 mgs. radium element (est.)....	13,628.38
	<hr/>
	\$ 5,353.00
	<hr/>
Less costs in connection with the production of the uranium and vanadium compounds.....	\$175,269.09
	<hr/>
TOTAL COST OF 4,258 MGS. RADIUM ELEMENT.....	19,947.00
	<hr/>
	\$155,322.09

As already stated, refining losses have almost certainly been less than 2 per cent and probably less than 1 per cent. In order, however, to be on the safe side, an allowance of 3 per cent is made for such losses; 4,258 mgs. less 3 per cent is 4,131 mgs., which represents the radium fully recovered as high-grade salts. The average cost of 1 gram of radium element has therefore been \$37,599. It should be remembered that this

cost included the proportionally much higher operating costs of the smaller experimental plant and that the first 2 grams of radium extracted cost considerably more per gram than the last 3 grams; also there have been extracted 31,650 lbs. of uranium oxide and 11,528 lbs. of vanadium oxide. This material has all been contracted for and in part delivered. The returns from its sale will considerably more than cover the cost of its production, and this profit, together with other credits, will ultimately lower by several thousand dollars the cost per gram of radium.

As the price of ore is variable, the question will naturally arise as to the influence of the price of ore on the figures given above. A simple calculation will show at once that the cost of extracting radium, exclusive of the cost of the ore, has been \$20,710 per gram. The ore included in the figure of \$69,767.99 cited for the cost of ore used in the investigation herein outlined was partly purchased before the war and partly mined by the National Radium Institute at Long Park, Col. As 723.97 tons were used, the average cost was \$96.36 per ton. If the ore had cost \$120 per ton, the cost of radium would have been \$41,742 per gram, and for every additional amount of \$20 per ton above these figures the cost of radium would increase approximately \$4,000 per gram.

U. S. BUREAU OF MINES, WASHINGTON

#### A METHOD FOR THE DETERMINATION OF THE STRENGTH AND BAKING QUALITIES OF WHEAT FLOUR

By C. H. BAILEY

Received June 28, 1915

It is quite generally recognized that some form of practical test is necessary in determining the baking quality of wheat flour. Chemical analyses are of value, but the relation between composition and quality is not perfectly understood despite the great amount of research which is directed toward the solution of this problem. It is also probable that if infallible chemical tests were announced which would serve to indicate the relative baking value of flour, they would be too numerous, and require too much time and technical skill to make their use possible on the extended scale necessary in the flour trade. In other words, there are so many factors involved in the chemistry of baking strength, and the determination of all of these would, in most instances, be so difficult that actual baking tests would probably be resorted to in the majority of cases where rapid and voluminous work must be disposed of. For these reasons the development of methods for conducting careful and accurate measurements of flour quality in a practical way are justifiable and necessary.

In developing practical flour tests, a comprehension of the purposes for which the flour is to be used, and of the manner in which it is ordinarily treated in trade practices, are essential. At the present time flours of good baking "strength," color, absorption, flavor and odor are in greatest demand by the bread-making trade. The term "strength" has been used rather loosely at times, although the definition of Humphries



and Biffin<sup>1</sup> has been quite generally adopted. They state that "a strong wheat is one which yields flour capable of making large, well-piled loaves." The rather general terms in which this is stated render it difficult of interpretation at times. The writer has preferred to state it in somewhat more definite, though necessarily technical terms, as follows: *the strength of flour is determined by the ratio between the rate of production of CO<sub>2</sub> in, and the rate of loss of CO<sub>2</sub> from, the fermenting mass of dough.* The defense of this definition, and the application of the principles involved will be made the subject of another paper. The general truth of the assertion will be apparent to those familiar with the production of yeast-leavened bread. Assuming the accuracy of this definition of flour strength, it is evident that some practical, and at the same time accurate, means of determining the extent of production, and retention of carbon dioxide is desirable. This is what is commonly attempted in baking tests in which the dough is allowed to expand to the maximum before being placed in the oven. In such tests the volume of the loaf thus produced is taken as an expression of the relative strength of the flour. In other cases, in which the dough is not raised to such an extent, the texture of the crumb—the "well-piled" condition referred to in the definition of Humphries and Biffin—is used as indicating the strength, in connection with the volume of the loaf. Such tests are of considerable value and are widely used, but certain criticisms may be made of each of them which indicate the desirability of more accurate methods.

#### CRITICISMS OF THE USUAL METHODS

In the case of the expansion of dough to the maximum before baking, the element of judgment enters in to a considerable extent. If the dough be placed in the oven too soon its expansion will be arrested by the inactivation of the yeast and its enzymes, and the fixation of the dough which constitutes the most important phenomenon of baking. The resulting loaf will not be as large as it might have been had it raised longer in the dough stage. If on the other hand the dough stands too long, it will fall in the oven and not only will the volume of bread be reduced, but the texture of the crumb will be impaired as well. The gas pockets will be large and uneven, and the crumb will lack that soft, velvety feeling characteristic of the "well-piled" loaf. It will render the judging of color more difficult as well, owing to the increased expanse and depth of shadow cast by the walls of the large gas pockets.

These criticisms do not apply to those methods in which the masses of dough are placed in the oven as soon as they have expanded to a fixed and uniform volume. In following such methods the expansion in the oven, known to the baker as the "spring" of the dough, and the texture of the crumb of the baked loaf, are taken as indications of the strength of the flour. The element of judgment enters into the scoring of crumb texture, however, and the relative differences between the various flour samples compared may not

be apparent from the reports of the tests. This is particularly true when it is desired that the test serve as a basis for indicating the proportions in which several different flours may be blended to produce a mixture of a certain standard.

#### ADVANTAGES OF THE USUAL METHODS

These tests have certain commendable features, however, and it was with a view toward eliminating the objectionable features of each, while including the desirable ones, that this study was undertaken. First of all the value of the determination of the volume occupied by a dough raised to the maximum must be recognized. While doughs are not usually so raised in either commercial or household practices, it seems to be well established that those flours from which doughs can be produced in which gas production and gas retention are so related as to yield large volumes per unit of weight when tested, will make the most satisfactory bread when treated in the ordinary manner. This is particularly true if the bread is to be baked in pans with relatively high sides, such as are commonly employed in making white bread in the United States. The support afforded by the high sides prevents part of the difficulty experienced by Scottish and English bakers in controlling the shape of their round "cottage" loaves which are baked in shallow pans. Moreover, those doughs which raise well, as evidenced by this test of maximum expansion, will usually stand more rough treatment in the process of fermentation and baking than will weaker, less elastic doughs. The development of a method for the determination of the rate and extent of expansion was accordingly undertaken.

#### GENERAL PRINCIPLES OF THE PROPOSED METHOD

The expansion of an ordinary dough in a graduated cylinder is often employed by flour chemists. This necessitates careful watching, however, in order that the greatest volume occupied by the mass may be noted before it falls. If the observer finds it necessary to leave his post for a few moments, the dough may have collapsed and fallen during his absence, and the record is thus lost. An apparatus was accordingly designed which would automatically measure the extent of expansion. In its design the simplest means commensurate with the requisite accuracy were aimed at. A cylinder was constructed which would hold a dough made from 150 grams of a strong flour if expanded to the maximum by the method followed. It was 7 cm. in diameter at the bottom, tapering to 9 cm. in diameter at a height of 8.2 cm. and continuing at this diameter to a total height of 23.8 cm. A disk was suspended in the cylinder and attached by a cord to a counterpoise weight, the cord being passed over a light-running pulley. This pulley was fastened to the top of a board, the face of which was provided with the calibrated scale shown in Fig. 2. The disk, while resting lightly on the surface of the dough, exerted no pressure because of the counterpoise. To the cord was attached a device provided with a needle which moves along the face of the scale and shows the extent of expansion. A circle of heavy linen paper was

<sup>1</sup> A. E. Humphries and R. H. Biffin, "The Improvement of English Wheat," *Jour. Agr. Sci.*, 2 (1907), 1-16 (note p. 4).

inserted between the top of the dough and the disk so that the latter did not stick, and it was accordingly left at the highest point which it reached during the course of the expansion. The relation of the several parts of this device, which has been termed the expansimeter, is shown in cross-section in Fig. 1.

In arranging the position of the needle on the cord which passes across the calibrated scale, due allowance was made for the curved form of the surface of the dough. This was done by allowing a mass of dough to expand in a glass cylinder of the same diameter, and measuring the segment of the circle described

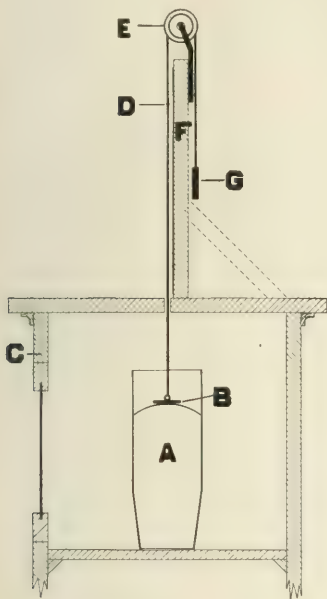


Fig. 1

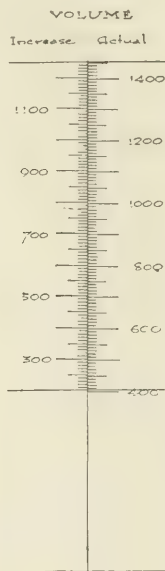


Fig. 2

by the dough surface. The volume of this dome-shaped mass was then calculated and the needle attached to the cord at the proper point.

It was recognized that such an expansion test would serve to show only one factor in the determination of flour quality, *viz.*, the expansibility of the dough. Other items such as color and appearance of the crust and crumb of the baked loaf, and its odor, flavor, etc., are important. To afford a test of these, a dough was made from 450 grams of flour, and at the close of the initial fermentation period it was divided into two portions, one of which was twice the weight of the other, and accordingly represented 300 grams of flour. It was raised and baked in a black iron baking pan, and the cooled loaf on cutting was scored for color and texture, and the flavor and odor noted.

#### DETAILED DESCRIPTION OF THE METHOD

A straight dough was employed which was prepared much as are similar white-bread doughs made in many commercial bakeries. The formula was as follows:

Flour	Yeast	Salt	Sugar	Water
450 g.	5.5 g.	6.75 g.	11.25 g.	Sufficient

No lard was used, since preliminary tests had shown

that the relative quality of the loaves was not altered when it was included.

These ingredients were thoroughly mixed in the small motor-propelled mixing machine illustrated on page 14 of Minnesota Experiment Station Bulletin No. 131.<sup>1</sup> Machine mixing was preferred to hand mixing because it had been found that more uniform results could be obtained in this manner. Moreover, it was not necessary to determine the water-absorbing capacity of the flour first, since this could be done to the best possible advantage during the course of the mixing. The salt and sugar were added in solution in 200 cc. of water. A stock solution consisting of somewhat more than sufficient salt and sugar for the day's work, with water in the proper proportions, was made up and aliquots taken for each test. It had been determined that a solution of 6.75 grams of salt and 11.25 grams of sugar in 200 cc. of water occupied a volume of 208.5 cc., and this quantity was used in each case. A stock yeast suspension was also made up in the proportions of 1 gram of yeast to 1,786 cc. of water (usually 50 grams of yeast were suspended in 89.5 cc. of water): 15 cc. of this suspension, after thorough mixing, were added to the salt-sugar solution from a volumetric pipette. That quantity of yeast suspension represented 5.5 grams of yeast and a trifle more than 9.8 cc. of water, since 5.5 grams of yeast in a water suspension displace 5.17 cc. The mixture of yeast, salt, sugar, and water was placed in the mixing machine together with the flour, and additional water added during the course of the mixing until the dough attained the proper consistency. The quantity of this additional water was noted on the record sheet. A table was arranged showing in parallel columns this added water, and the total water used reduced to terms of cubic centimeters per 100 grams of flour, in which manner these data were reported.

It is recognized that the proportions of yeast and sugar employed in these tests were much less than are commonly used in commercial flour testing. This was partly because the use of such large quantities of yeast and yeast food, with the resulting abnormally large and rather coarse-textured loaf of bread, had been criticized by practical bakers. While their objections were not well founded in every particular, our experience with the formula and method proposed has shown it to give as satisfactory results as the use of such formulae as are used in commercial flour laboratories. The crumb of the resulting bread resembled closely the appearance and flavor of baker's and household bread of good quality; it was a palatable product when made from good flour.

The dough was mixed in the machine until the slow blade of the latter had made 200 revolutions. It was then removed from the machine and placed in a half-gallon stoneware jar. This was covered and set in an electrically heated and controlled thermostat or fermentation cabinet. The temperature was maintained at 28° C. (82.4° F.), which is about the temperature at which the fermentation is conducted

<sup>1</sup> C. H. Bailey, "Minnesota Wheat Investigations: Series I, Milling and Baking Tests, Crop of 1911," *Minn. Exp. Sta. Bull.*, **131**, 1913.



in most large bakeries. The length of the fermentation period was varied somewhat, being reduced by as much as 30 minutes in the case of doughs made from weak flours. Strong flour doughs were allowed to ferment 150 minutes before being broken down, followed by successive light kneadings at the end of 60, 45, and 15 minutes. The total time from kneading to molding the loaf was thus 270 minutes or 4½ hours. At the end of the last 15-minute interval the dough was removed from the jar and kneaded vigorously on a board. The entire quantity was weighed and divided as previously mentioned into two portions representing ⅔, or 300 grams of flour, and ⅓, or 150 grams of flour, respectively. The former was placed in a lightly greased baking pan, the latter in the expansimeter cylinder similarly greased.

The black iron baking pans employed were similar to those used in many flour-mill control laboratories in the United States. They are 14 cm. deep, 7.5 × 14 cm. at the bottom, and 9 × 16.5 cm. at the top. While some other form of pan might be satisfactory, this style was preferred because on cutting the loaf lengthwise a large area of cross-section was afforded for scoring the color and texture. Tall, round pans would do the same but on trying them it was found that the crumb texture was impaired over the lower part of the area because of the pressure of the tall mass of dough. Ordinary bakers' pans were not found desirable, as so large a surface area was not afforded on longisectioning the loaves baked in them.

The dough in the pan was allowed to expand in a thermostat at a temperature of 34° C. (93.2° F.) until that portion in the expansimeter cylinder occupied a volume of 710 cc. This was 3½ times the volume of the unfermented dough, and about 3 times the volume of the dough when placed in the pan. It was then placed in an electric oven which had previously been heated to 200° C., and baked at that temperature until well browned. The time of baking was about 45 minutes. An effort was made to keep the air in the oven as nearly saturated as possible by the introduction of water vapor. This is a factor of considerable importance if it is desired to insure the greatest possible expansion or "spring" in the oven.

The smaller portion of dough, representing 150 grams of flour, was molded and placed in the round cylinder shown in Fig. 1, care being taken to exclude all air bubbles from below and around the mass. A small circle of paper was placed on the top of the dough, and the cylinder set in the proper location in the thermostat, which was maintained at 32° C. The disk was lowered into position, after which this apparatus required no further attention until the dough had fallen, when the maximum expansion which it had attained was read on the scale.

#### RECORDING THE RESULTS OF THE TEST

The expansion of the dough in the cylinder was stated in terms of the increase in volume in cubic centimeters, rather than the total volume of the fermented dough. The initial volume of a dough made from 150 grams of flour was found to be 203 cc. A scale (Fig. 2) was accordingly prepared for use with

the cylinders, on the left side of which the increase in volume due to retention of carbon dioxide was shown, while the right side of the same scale showed the total volume occupied by the mass. This means of expressing expansibility was preferred because the difference between flours is evidenced even more strikingly than it would be by a statement of the total volume. Thus two flours, the first of which occupied a maximum total volume of 600 cc., and the second of 720 cc., on this basis showed differences of only 20 per cent, while as a matter of fact the second sample had actually expanded over 30 per cent more than the first. Since it is this expansion, due to the production and retention of carbon dioxide, with which we are concerned, the expression of the results in that manner which best served to accentuate the relative differences seemed to be desirable.

The baked loaf was cooled, and the volume in cubic centimeters determined by displacement in flax seed. The apparatus used for this purpose is illustrated on page 16 of Bulletin No. 131.<sup>1</sup> It was then cut lengthwise and the crumb scored for color and texture. The lightest shades of color were scored the highest, a score of 100 being given to those loaves having the shade of color possessed by the crumb of loaves baked from the average Minneapolis mill patents. The completed record contains 6 items: (1) the maximum expansion of the dough in the cylinder; (2) the volume of the baked loaf; (3) absorption of water in making the dough, stated in terms of cc. of water at 28° C. per 100 grams of flour; (4) color of crumb; (5) crumb texture; and (6) remarks concerning the flavor and odor. If the latter was not out of the ordinary it was merely recorded as normal; if musty, sour, or otherwise abnormal a brief notation was made concerning its character. It is believed that such a record contains all of the data necessary to a satisfactory evaluation of the flours which are to be compared.

A control baking should be included in each day's work. The dough is made preferably from a strong patent flour which has aged for about 8 weeks before using it for this purpose. The change from day to day is less great in a flour aged to this extent and it may be discarded and another control employed after 6 or 8 weeks' time. The new control should always be tested at least twice in comparison with the old before the latter is discarded. It is only by referring all results back to the control that the results of such empirical tests made on different days can be compared. This is particularly true with regard to the volume of loaf, and the dough expansion in the cylinder. Thus, when the volume and expansion of the control fall below the average, the similar data for all the other samples in that series must be increased in the proper proportion. The control flour need not be regarded as a "standard," but may simply serve as a check on the quality and activity of the yeast, and other conditions.

Table I shows the results of the tests by this method of five flours of widely differing qualities. Sample A was a strong patent flour milled from hard spring wheat; B a rather weak patent milled from Washing-

<sup>1</sup> Loc. cit.

ton Bluestem; C a very weak Western Club wheat patent; D a strong First Clear milled from hard spring wheat; and E an unusually strong, hard spring wheat Second Clear. It will be noted that while the flours stand in the same order with respect to volume of loaf and maximum expansion in the expansimeter, the latter accentuates the differences much more distinctly than does the volume of the loaf. The relative texture of the loaf also serves as a check on the expansimeter test. Thus, while the loaves baked from flours B and C were practically the same in volume, the difference in texture was very striking, and paralleled the test of maximum expansion. Sample E, while strong and capable of yielding loaves of reasonably good texture, was found to be very dark in color. The same was true of D, although to a lesser extent.

TABLE I—RESULTS OF TESTS OF FIVE FLOUR SAMPLES

Sample	Maximum expansion in cylinder cc.	Volume of loaf cc.	Absorption of water per 100 g. of flour	Color score	Texture
A	930	1,480	64.0	101	100
B	720	1,320	60.2	98	90
C	600	1,310	54.4	97	70
D	910	1,430	65.6	85	94
E	990	1,560	64.7	55	92

## SUMMARY

The method outlined is believed to eliminate the personal equation so far as is practicable in making actual baking and expansion tests. The use of a machine for mixing, the automatic recording of maximum expansion in the cylinder, and the raising of the dough to a fixed height before baking all tend to render the element of judgment less prominent than has heretofore been the case with most methods. Automatic regulation of the temperature in the fermentation cabinet also contributes to the ease of making the tests. The use of such appliances and methods tends to render the making of baking and expansion tests less an art and more a science.

CEREAL AND FLOUR LABORATORY  
DIVISION OF AGRICULTURAL CHEMISTRY  
MINNESOTA AGRICULTURAL EXPERIMENT STATION  
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## A CHECK VALVE FOR SUCTION FLASKS

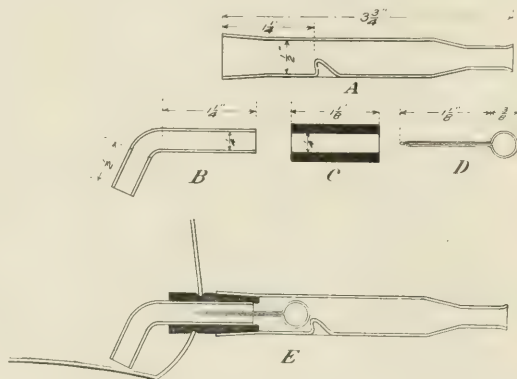
By G. P. WALTON<sup>1</sup>

Received July 14, 1915

In those determinations involving filtration through a Gooch crucible where rejection of the filtrate is permissible, it is a frequent practice to filter in sets of from ten to fifty. Often the time allowable for filtering a set is limited. This requires not only rapid filtering, but the shortest possible interval between successive filtrations. Under such conditions the frequent interruptions occasioned by the necessity for disconnecting and emptying the suction flasks are a source of no little inconvenience. To obviate this the writer has devised a form of ball check valve which may be readily fitted to any of the usual types of suction flask.

The valve shown in detail in the figure has been used in this laboratory for several months and has satisfied all requirements. It consists of a glass tube (A) having an indentation or other check for the

ball-valve; a glass ball valve with guide (D) blown from a piece of capillary tube; an inner glass tube (B); and the valve-seat (C), a short piece of smooth heavy rubber tubing with square cut ends. The parts are shown assembled and fitted to the usual form of suction flask (E). A drain tube, not shown,



completes the apparatus. It is obvious that when a Gooch crucible is placed in the holder in the top of the flask and suction applied, the ball (D) will be drawn tight against the rubber valve-seat. Upon releasing the vacuum to remove the crucible, the height of the column of filtrate in the flask will immediately cause the ball to be forced out, allowing the liquid to be completely drained off. It has been found that comparatively slight suction is sufficient to close the valve perfectly, while upon releasing the suction, a column of liquid in the flask a fraction of an inch above the valve is ample to start the outflow.

The several parts of the valve are readily made and quite durable, the rubber valve-seat lasting for several months with constant use in this laboratory.

While to have the valve made wholly of glass would appear to be advantageous, it has been found difficult to construct one in which the ball will always seat itself so as to make the ground joint air-tight, and yet not be liable to stick in the valve-seat upon releasing the vacuum.

In the form of suction-flask not provided with an outlet at the bottom, a suitable vent may be drilled using a short section of copper tube in a drill press with carborundum and water for abrasive. To adjust the valve, force the rubber (C) through the vent, moisten the inner tube (B) and push it through the rubber making a tight joint between the latter and the wall of the flask; place the ball (D) in position and force the outer tube (A) over the rubber. The rubber should project about  $1/16$ " in. beyond the end of the inner glass tube, which serves merely as a siphon and brace for the valve-seat.

A check valve of the form described has proved a great convenience and time saver when making the final filtrations in such determinations as those of crude fiber, reducing sugars, pentosans and any others wherein filtrate and washings are rejected.

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## THE GAUGING OF STORAGE TANKS

By R. L. OGDEN

Received December 10, 1915

One of the problems which often confronts the chemical engineer is the accurate gauging of storage tanks. When these are merely of upright cylindrical shape, the solution is very simple, but when the cylinder has dished ends and lies on its side, it becomes a rather complicated problem, as there are two variables to be considered, that is, the cylinder and the spherical segments at the ends.

It is the purpose of this article to present a method of solution which, while rather easy of application, yet yields accurate results.

The usual method of constructing these tanks is to make the diameter of the cylinder the radius of the sphere of which the end is a segment.

The depth of the segment can better be calculated than measured; if  $d$  equals depth of dish,  $R$  = radius of sphere and  $r$  = radius of cylinder, then  $d = R - \sqrt{R^2 - r^2}$ : in this case  $R = 2r$  because of the method of tank construction.

The arc of the dished end being only one-sixth of a circle, it may, for all practical purposes, be considered as the curve of a parabola, inasmuch as the curve of a circle and of a parabola for this distance very nearly coincide, and the spherical segment may be considered as a paraboloid. That this assumption yields sufficiently accurate results will be shown by a special example later on.

The volume of the cylinder may be estimated for each inch by integral calculus, but a far simpler method consists in the use of geometry and trigonometry. The first inch is calculated by finding the area of the sector whose segment has a depth of one inch and subtracting the area of the enclosed triangle. This multiplied by the length of the cylinder gives the volume of the first inch of the cylinder.

In Fig. 1,  $\sqrt{r^2 - (r-1)^2} = \frac{1}{2}$  base of triangle  $\times r - 1$  = area triangle.

Sine  $\frac{1}{2} O : \frac{1}{2}$  base triangle ::  $r : r$

Having found the angle  $O$  we may easily compute the area of the sector, since angle  $O : 360^\circ ::$  area sector : area circle. By subtracting the area of the triangle from that of the sector we obtain the area of the segment.

This same method may be applied for every inch and, of course, yields an absolute value, but it involves far less work and is sufficiently accurate for all purposes to find the length of the medial line of each one inch segment of the circle. This may be done by the ordinary methods of geometry. Thus to find the area of the second segment, that is, that lying between the first and second inch, we have:

$$\frac{1}{2} \text{ medial line} = \sqrt{r^2 - (r - 1\frac{1}{2})^2}$$

This result doubled gives the length of the medial line which in linear measure very closely approximates to the area of the one inch section in square inches. It rarely happens that the average inside diameter is expressed in even inches. In this case it is neces-

sary to consider the inch section at the center as composed of two parts divided by the diameter, calculate each separately and add the two together.

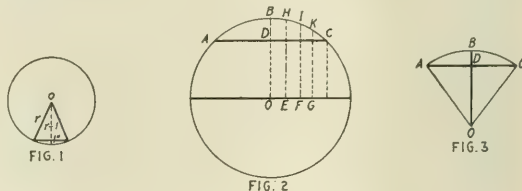
The second half of the circular section is computed in the same manner until one comes to the top segment, which is calculated as shown for the first inch.

By adding together the values of each one inch section successively, the areas of the circular segments are found for each successive inch of depth. These areas multiplied by the length of the cylinder give the volumes of the cylinder for each inch of depth.

The volumes of the spherical segments at the ends are computed for each inch in somewhat the same manner, assuming the segments are those of a paraboloid instead of a sphere.

The area of the medial plane of a one inch section of a paraboloid in square inches very closely expresses the volume of the section in cubic inches. The area of a parabola is approximately the product of the base by two-thirds of the altitude.

The base line of the medial plane of each one inch section has already been ascertained as it is identical with the medial line of each one inch section of the cylinder. If the altitudes of these planes are known it is a simple matter to compute the areas of the medial planes and consequently the volumes of the one inch sections.



In Fig. 2 the lines  $OB, EH, FI$ , represent the medial planes of each one inch segment, supposing the segment to be continued to form a sphere. The radius  $OB$ , as stated, is nearly always the diameter of the cylinder  $AC$ . The depth of the dished end,  $DB$ , having been found by the formula  $d = R - \sqrt{R^2 - r^2}$ , this is subtracted from the radius  $OB$  to find the length of  $DO$ . This value  $DO$ , common to all the planes, added to the height of each one inch segment, gives the radius of each circular medial plane.

Fig. 3 represents a side view of such a plane passing through  $OB, HE, IF$ .

The radius  $OA$  or  $OB$  is  $\sqrt{OD^2 + AD^2}$ .  $OD$  is common to all the planes and  $AD$  is one-half the length of each medial line found previously in the cylindrical section.  $OB - DO = BD$  which is the height of the segment  $ABC$ .

By now assuming that  $ABC$  is a parabola,  $AC \times \frac{2}{3} BD = \text{area } ABC$ , and expresses very closely the volume in cubic inches of the one inch section of which  $ABC$  is the medial plane.

By adding together successively the volumes of these one inch sections on the two ends and adding to the corresponding volumes of the cylindrical part

Depth of Segment	Medial Line <sup>2</sup> $2(N^2 - [r - (y-1, z)]^2)$	Area Whole Segment	Volume Cylindrical Segment Length $\times$ Area	Length AB $\frac{1}{2}$ Medial Line	$AB^2 + 41.57^2$	$AB^2 + 41.57^2$	Height of Segment	$\frac{1}{2}$ Height of Segment $\times$ Medial Line	Total	Gallons
1	9.19	9.19	1103	4.60	1749.22	41.83	0.26	1.59	1106	5
2	16.70	25.89	3107	8.35	1797.78	42.40	0.83	9.24	3128	14
3	21.32	47.21	5665	10.66	1841.70	42.92	1.35	19.19	5724	25
4	24.96	72.17	8660	12.48	1883.81	43.40	1.83	30.45	8780	38
5	27.98	100.15	12018	13.99	1923.78	43.86	2.29	42.72	12223	53
6	30.58	130.73	15688	15.29	1961.84	44.29	2.72	55.45	16004	69
7	32.86	163.59	19631	16.43	1998.00	44.70	3.13	68.57	20084	87
8	34.86	198.45	23814	17.43	2031.86	45.07	3.50	81.34	24430	106
9	36.64	235.09	28211	18.32	2063.68	45.43	3.86	94.29	29016	126
10	38.24	273.33	32800	19.12	2093.63	45.76	4.19	106.80	33819	146
11	39.68	313.01	37561	19.84	2121.69	46.06	4.49	118.80	38818	168
12	40.98	353.99	42480	20.49	2147.90	46.34	4.77	130.30	43998	191
13	42.14	396.13	47536	21.07	2172.00	46.61	5.04	141.60	49337	214
14	43.16	439.29	52715	21.58	2193.76	46.84	5.27	151.60	54819	237
15	44.08	483.37	58004	22.04	2133.82	47.05	5.48	161.00	60430	262
16	44.88	528.25	63390	22.44	2311.61	47.24	5.67	169.70	66155	286
17	45.60	573.85	68862	22.80	2477.90	47.41	5.84	177.50	71982	312
18	46.26	620.05	74406	23.10	2261.67	47.56	5.99	184.50	77895	337
19	46.72	666.77	80012	23.36	2273.75	47.68	6.11	190.30	83882	363
20	47.04	713.91	85669	23.57	2283.60	47.79	6.22	195.50	89930	389
21	47.48	761.39	91367	23.74	2291.65	47.87	6.30	199.40	96027	416
22	47.74	809.13	97096	23.87	2297.84	47.94	6.37	202.70	102161	442
23	47.90	857.03	102844	23.95	2301.66	47.98	6.41	204.70	108318	469
24	48.00	905.03	108604	24.00	2304.06	48.00	6.43	205.80	114490	496

we obtain the total volumes of the tank for each successive inch of depth.

The volume of the first inch of the spherical segments is almost negligible and may be found by assuming it to be a pyramid and calculating in the usual way.

The foregoing remarks are set forth in a tabulated form of calculation which it might be found convenient to adopt. In this case the inside diameter of the cylinder is 48 inches and the length 120 inches. The depth of dish by calculation is 6.43 inches. The inside diameter, being in even inches, it is necessary only to calculate the volumes of each section for one-half the diameter and obtain the others by simple subtraction of each segment from the total volume of the cylinder.

It will be noted in the above summary that the total volume of the tank by this method of calculation is:

$$2 \times 114,490 = 228,980 \text{ cu. in.}$$

The absolute volume of the cylindrical part is,  $\pi r^2 l$  or 217,150 cu. in.

The absolute volume of the dished ends is,

$$2(\frac{1}{2} \pi R^2 h + \frac{1}{6} \pi h^3) = 1194 \text{ cu. in.}$$

Total absolute volume..... 229,064 cubic inches.

Total calculated volume..... 228,980 cubic inches.

Difference..... 84 cubic inches.

This difference of 84 cubic inches, or about one-third of a gallon in the total, between the calculated and the absolute becomes correspondingly less for the smaller gauges and is negligible for all practical purposes.

133 MILTON AVENUE, RAHWAY, N. J.

## THE UNIVERSITIES AND THE INDUSTRIES

Addresses before the New York Section of the AMERICAN CHEMICAL SOCIETY in joint session with the New York Section of the SOCIETY OF CHEMICAL INDUSTRY and the AMERICAN ELECTROCHEMICAL SOCIETY, Chemists' Club, December 10, 1915

### UNIVERSITIES AND INDUSTRIES

By RICHARD C. MACLAURIN

President of Massachusetts Institute of Technology

The title of this address may give rise to some comment as to the place of the Massachusetts Institute of Technology in the general series of discussions that are being carried on by this Society. It can hardly be necessary, however, to say to an audience such as this that the fact that the M. I. T. is not called a university is merely an accident of names and does not touch the substance. For if you examine the matter at all closely you will see that in everything but name what is sometimes unhappily called "the Boston Tech" is a university. The institution of the university, like much else that is potent in our midst to-day, has roots that go deep into the past and when you look back to the early days of the university you see clearly what was the fundamental idea that underlay that medieval name. The idea was not, as has sometimes been supposed, without the slightest support from history, that a university is a place where all subjects are studied. Fundamentally, it was a place to which men came from all parts to study. The

medieval phrase was "university of persons" or "university of nations" and the first test of a university was whether it drew its students from a limited region or from many lands or many sections of one country. The Massachusetts Institute of Technology is as national and international in its scope as any of the so-called universities. It has long drawn men in large numbers from all states in the Union and has a very large proportion of foreign students to-day, nearly twice as many, I am told, as any other institution of higher learning in the country. The other tests were two: *first*, the character of the subjects taught—were they elementary or did they represent what were called the higher faculties; and *second* the character of the teachers—were they men of high standing, the practical test coming to be were they graduates of a recognized university. In the course of ages, a fourth test has been added, one that has long been inherent in the idea of a university, the test of investigation—whether the institution concerns itself merely with imparting knowledge or whether it endeavors to extend its bounds. I need not speak to you of the distinction of the three hundred men who form the instructing staff of the Institute of Technology



to day nor remind you of the great contributions to the advancement of knowledge made by them or their predecessors both in pure and applied science. A fifth test might be suggested, but it is implied in the first—freedom from local prejudices, the recognition of the universality of intellectual pursuits and the appreciation of the great work that others are doing. If I speak mainly of the M. I. T., it is merely because I suppose that on this occasion I am expected so to do, and with a full appreciation of the splendid work being done by other institutions.

The necessity of intimate coöperation between the universities and industry has been discussed so much as to have become very commonplace, but the subject must remain a commonplace of discussion until it sinks so deeply into the consciousness of the people as to be no longer worth talking about. To a select audience such as this, however, it is scarcely necessary to say what might be appropriate to a more general gathering, for you know quite as well as I that the industries of this country will never flourish as they ought until they are permeated with the spirit of the university and especially with the spirit of science, which insists on looking at nothing but the facts, on resting everything on the solid ground of truth, on approaching all problems with an open mind, and on marshalling all the knowledge that is available so as to bring it to bear effectively on the particular problem in hand. I might add that the universities will never rise to their proper level unless they too are affected by something of the active and alert spirit of industry. On every ground it is desirable to bring the universities and industry into close coöperation and nowhere more urgently than in the field of chemistry.

The growing importance of the chemical industry in the United States has been a matter of comment for years and has been reflected within the universities. During the last ten years, for example, the number of students following the course of Chemical Engineering at the Massachusetts Institute of Technology has been increased threefold and the total number to-day in that institution preparing for the profession of the chemist, including the electro-chemist, is about 350, *i. e.*, between one-fifth and one-sixth of the whole school. (I need hardly say that I do not include here those who are taking courses in chemistry for other purposes than to train themselves for the profession of the chemist.) Chemical industry has been growing steadily but quietly in recent years and suddenly has found itself a place in the sun of public opinion.

The war has revealed to every one what was known years before by all who were interested, namely, that this country is almost wholly dependent on foreign sources for the supply of many of its chemicals. This revelation naturally raises the question whether we are wise in being so dependent. It raises among other things the old question of the expediency of higher protection, the old question of the relative importance of home and foreign trade, and many other grave political questions, hoary with antiquity and yet ever new in the disagreements that are revealed in their discussion. These questions, if answered at all, must be answered by political action and if the schools of applied science are to contribute to the solution of the problem it must be mainly along other lines than these. They should give their support to the organization of industry so as to meet the needs of the nation as a whole, but their main contribution here as elsewhere must be in the supplying of men properly trained for the task. With exceptional students exceptional results can be obtained, but with the great majority the most that can be expected is to give them three things: *first*, a knowledge of the fundamentals; *second*, the method of attack; and *third*, the spirit of industry and alertness for improvements.

To this end various courses have been laid out at the Massachusetts Institute of Technology, in one of which, for example,

in a course of four years, the time devoted to chemistry in the first year is one-fourth of the whole, in the second year more than one-half, in the third more than three-fourths and in the fourth year practically the whole. I need hardly say that the laboratory method is generally recognized as essential and in the new buildings of the Institute more than two acres of floor space are devoted to the chemical department, most of this space being for laboratories. These include well-equipped laboratories for research and provide for those sections of the main departments of chemistry that have been organized for research in physical and industrial chemistry. The staff consists to-day of forty-one men—twenty-three instructors and assistants, and eighteen professors on the active list. They include a number of men of eminence in their profession; indeed, as regards the number of such men "the Massachusetts Institute of Technology stands clearly first" among educational institutions of the United States according to the impartial estimate of "American Men of Science." The Institute has been specially fortunate in having on its board of trustees men closely associated with chemical industries, and the advice and coöperation of these men have proved of great value in shaping the chemical courses. To interest the students in the problems of industry, not only is their attention directed to the achievements of the past and the great possibilities of the present and of the future, by the regular members of the instructing staff and by men actively engaged in chemical industry, but the students in their later years are set to attack industrial problems in the research laboratories, and the range of their vision is further enlarged by regular visits to industrial plants under the guidance of professors.

But I must not weary you with a further description of what is more or less familiar to most of you. The real question is "Are the universities doing enough?" or, "Can more be done under the actual conditions that prevail or can those conditions be changed?" Just as in business so in education we are blocked in many lines of advance through lack of funds. This has unhappily become a commonplace of presidential utterances, but commonplace or not, it is of vital importance. Let us consider for a moment some of the suggestions that have been made as to the more that we might do. First it is said we should have better professors, more men of eminence in the profession, more that are thoroughly alive to the needs and possibilities of industry. Men of eminence there happily are, but of course it would be better if there were more. Can we expect, however, a very large number of men alive to the possibilities of industry and capable of meeting its needs to make the great financial sacrifices involved in accepting a teaching position at a salary of a few thousand dollars? The success of the industries demands that we should have a higher level of salaries in our schools of applied science and that we should be in a position to pay a few men at least a reasonable fraction of what they could earn in business.

It is said that we should have better students and there is some complaint that the ablest and brightest men within the universities choose other branches of engineering than the chemical. In so far as this is true it is partly because the possibilities of the chemical industry are not fully realized, the field being relatively new. An important factor, however, is the unfortunate feeling that the chemist will always remain an employee and a rather low-priced one at that. For its own good, industry must be prepared to pay capable men better salaries if it wants to attract the abler students and it should give these men opportunities to develop if they show any capacity for other work than the mere routine operations of analytical chemistry.

It is said that we should have closer contact with industry. Undoubtedly this would be a great advantage in every field of academic activity that affects our departments of chemistry.

It would be a great advantage to the undergraduates after having laid the foundations of chemical knowledge to have more opportunity of getting in direct touch with the methods and problems of industry. This soon resolves itself into a question of dollars and cents, and if the necessary money be forthcoming much more will undoubtedly be done in this direction. It would be a great advantage for the professors were they in closer contact with industry. Here it would surely be well to follow the example of Germany and employ a larger number of professors in attacking the special problems of business that require a thorough knowledge of chemistry. Do not let the industries neglect the professor of "pure" science. Our great problem is to organize our knowledge and to organize it in such a way as to make it as effective as possible in industry. An enormous amount of valuable material is locked up in various ways and not the least of it is locked in the brains of professors of "pure" chemistry. The universities are striving hard to break down the unfortunate barriers, many of them artificial, but none the less effective, between pure and applied science, but the most effective agent in this respect should be the industries themselves. They should take more active means to interest individual professors in the special problems that confront them.

There is, of course, much that has not yet been done, much that has not even been attempted, but after all perhaps our greatest problem is to make the most of what we already have: certainly we do not do this to-day. Take the matter of knowledge. We rightly lay stress on the importance of research and the advancement of knowledge. We can not keep this before us too prominently because the spirit of research is the very basis of progress. We must not overlook the fact, however, that too often we treat shamefully the knowledge that has already been garnered. Thousands of useful results are obtained every year that would be helpful to industry were an effective effort made to make them widely known. We are hurt here by the prevalence of the spirit of trade secrecy. Of course, we must recognize the facts and treat human nature as it is and not as we think it should be, but a large part of what is thought of as "secret" is really widely known and there is much knowledge of value that could be disclosed without any detriment whatever to the revealer. Even the knowledge that is in the text books and that is accessible to everybody is not really used. If we could apply one-tenth of such knowledge fortunes would be made every year. Here industry must help itself. Its attitude towards scientifically trained men must be improved. There is still with us too much of the spirit of the pre-scientific days and too much reliance on "rule of thumb." Old-fashioned superintendents are still constantly employed who have no knowledge of science and little faith in it. Practical men must not be so scornful of what is obvious to men of science. We must remember that in times of peace Germany became rich by having faith in the *obvious* just as in times of war she has won success by realizing that guns and ammunition are useful adjuncts in that terrible form of competition. In the field of chemistry Germany has not shown any special genius for scientific advancement, but she has taken her knowledge seriously and displayed a real and a saving faith in the formulae of the text books. England accepted them as a matter of logic but didn't really believe in them, and America has occupied an uncomfortable middle ground. She must come out of it.

We must have more faith in ourselves. Not all the conditions are against us and in spite of the fierceness of foreign competition there is much wherein we can hold our own. When the war is over the conditions of competition will be peculiarly severe, but the war should have given our chemical industries a new start and a fresh impetus, and if our range of vision is long and our enterprise does not fail, the future of chemical industry in this country should be bright indeed. The uni-

versities are animated by the spirit of service and anxious to do all that they can to help. Let the industries tell us clearly what they want.

## THE UNIVERSITIES AND THE INDUSTRIES

By HENRY P. TALBOT

Professor of Inorganic Chemistry, Massachusetts Institute of Technology

Among the various types of service which the industries may reasonably demand from our educational institutions, there is obviously none of more vital importance than the training of those young men who constitute, in increasing measure, the rank and file of intelligent workers, and who should develop into leaders in the industrial field. It has fallen to my share to discuss briefly this phase of university service, particularly with reference to a possible increase in coöperation, both in spirit and deed. There will be time for the consideration of only a few aspects of this service, and I shall eliminate at once any discussion of the advisability of the support and encouragement of laboratories devoted to investigations in abstract science (so often abstract for the moment only), assuming that all will agree that whatever really extends the boundaries of our knowledge must ultimately redound to the benefit of applied science. It is certainly true that no institution can hold itself free from criticism which does not endeavor to contribute its share to the common fund.

With a problem so complex as that of the education and training of successful industrial workers, it must always be true that the attainment at any particular period will fall short of what is regarded as desirable. Indeed, every advance seems to create new demands. There have been abundant evidences of dissatisfaction in recent years, and this has occasioned much private and public discussion, as is shown by the "Bibliography on the Training and Education of the Chemist and Chemical Engineer" published in the March issue of *THIS JOURNAL* for the current year. This bibliography contains about seventy titles of papers, most of which have appeared within the last six years, and can be commended to the attention of all interested in reviewing the educational aspects of our subject.

If we search this literature to find the nature of the existing dissatisfaction, with a view to the application of remedies, we encounter mainly generalizations. An effort has, however, been made to arrive at some concrete conclusions through the appointment of a joint committee to study engineering education in this country. This committee was formed at the suggestion of the Society for the Promotion of Engineering Education, and is made up of representatives chosen by that Society, and by the prominent national engineering societies, including our own American Chemical Society. It has been my privilege to serve upon this committee, with Mr. Clifford Richardson, as a representative of our Society.

### STUDY OF PRESENT STATUS OF ENGINEERING EDUCATION BY CARNEGIE FOUNDATION

At the request of this joint committee, the Carnegie Foundation for the Advancement of Teaching has undertaken an exhaustive study of the present status of engineering education, and Professor C. R. Mann is devoting his entire time to it, studying, for the present, mainly the longer-established courses in civil, mechanical and electrical engineering. After much preliminary discussion and consultation Professor Mann sent out letters of inquiry, mainly to the members of the engineering societies representing the three branches just named, through which he sought particularly to learn the factors which the engineers regard as contributing most certainly to success in professional work, and also to learn the opinions of the same men as to the efficiency of our educational institutions at the present time with respect to these same factors. He received fourteen hundred replies, and these he has correlated in his report of progress made to the joint committee, under eighteen groups,



some of which we shall consider. While it is true that comparatively few of these letters of inquiry were sent to chemists or chemical engineers, it seems to me fair to assume that the collective verdict of this large number of engineers does not differ materially from that which would be reached in our own profession, and there seems to be something to be learned from these returns.

#### IMPORTANT FACTORS IN PROFESSIONAL SUCCESS

If we assume, as Professor Mann does, that those factors may be deemed most important for professional success which are mentioned by the largest numbers of engineers, then the first place must be allotted to those traits which fall under the grouping "Character." The group includes, beside the general term "character," integrity and honesty, and personality. Self-Reliance and Decision (including, among other traits, Responsibility and Perseverance) occupies the second place in the esteem of the writers, and is followed by Ability to Understand and Handle Men. The fourth place is given to Engineering Spirit (including aptitude and innate ability), and the fifth place to Independence (including initiative and resourcefulness). Technical Knowledge, Scientific Attitude, Accuracy, Efficiency and Business Sense occupy the eighth to the twelfth places, inclusive, and Application of Theory to Practice the seventeenth place.

If we now consider the verdict with respect to the present efficiency of our institutions, the figures are scarcely flattering to the vanity of those of us who are engaged in instructional work. In the case of only three of the groups is there an actual majority of opinion that the factors involved are successfully inculcated. These groups are: Technical Knowledge (by a large majority), Scientific Attitude (by a fair majority), and Ambition or Enthusiasm (by a mere majority). The vote is about even with respect to Self-Reliance, Industry, Character and Efficiency. The verdict is successively more unfavorable with respect to the development of Engineering Spirit, Independence, Accuracy, Understanding of Men, Application of Theory to Practice, and most severe of all with respect to Business Sense.

It may be objected that any such grouping as this involves obvious confusion of terms and that the whole is somewhat artificial. But, granting some imperfections, are there not some useful conclusions to be drawn from this preliminary skirmish in the effort to better conditions?

Let us note first that the most conspicuous among the individual factors which make up the first five groups which are seemingly considered most vital for professional success, are the following personal traits: character, personality, innate ability, perseverance, temperament, leadership, aims—for self or work. Now these are exactly the factors over which the universities have the least influence, and are, indeed, those which are almost entirely determined by a presumably all-wise Providence before the universities receive their students as raw material. It is, therefore, not strange that we find these factors, for the most part, well down in the efficiency list representing university attainment.

Again, there are factors which are themselves, or which involve, traits which are largely God-given but can also be fostered by the universities. Such, for example, are integrity and honesty, tact, ability to cooperate, resourcefulness, power of expression, ability to understand and deal with men, and, in particular, the cultivation of engineering spirit. An examination of the university efficiency list again indicates that our present achievements win comparatively slight approval.

There still remain such factors as grounding in fundamental principles and theories, teaching of fundamental facts, familiarity with authoritative sources of information, power of logical thinking and development of reasoning power, which naturally win higher approval, since they constitute the unavoidable duty of the educational institutions. But these are, oddly

enough, found in the middle or in the lower half of the factors most esteemed by engineers.

If, then, we may assume that Professor Mann's correlation has at least some quantitative significance, does it not show that the consumers of the products of our universities may be a bit unreasonable in their expectations, in that they overlook the fact that so much of what they chiefly desire to find in the young graduate is essentially a question of natural gift? The university may, and should, catalyze the latent powers which Nature has bestowed (using due care to avoid negative catalysis, which is far more likely to occur in the educational than the chemical field), but the university is practically unable to create such powers. In his paper, read at your November meeting, Professor Whitaker referred to our present difficulties in the selection of raw material. In view of the great influx of young men into our educational institutions, many of whom, although without most of these desirable natural traits, still find their way into the chemical and other engineering professions, it may not be unreasonable that the industries should demand cooperation from the universities in an attempt to find better methods for the selection of men, and a more rigid exclusion of the obviously unfit. It is interesting to note, in passing, that experiments are now said to be under way, in connection with the study which Professor Mann is making, with a novel type of tests to determine the fitness of an individual to undertake scientific or engineering work. It is hoped that these tests may usefully supplement our present disappointing method. The results are not yet sufficiently numerous to warrant general conclusions.

#### TECHNICAL GRADUATES LACK ENGINEER'S VIEW-POINT

But after making due allowance for demands which are possibly beyond the power or the function of the universities to meet, there still remains serious criticism, and it seems to me that it can be summed up in the statement that the graduates from our educational institutions fail to catch what may perhaps be termed an engineer's view-point, as applied to chemical industries. In the opinion of their employers they lack constructive imagination; they do not appreciate how diversified are the factors which enter into commercial operations, nor the complexity of the human relationships and agencies involved; they have little business sense. I have avoided the mention of controversial matters which have to do with details of curricula, etc., because these must be eliminated from this brief discussion. The arraignment is sufficiently impressive as it stands, and there can be no question of the sincerity of those who make it.

The answer is not easy or simple. I can, however, point out one particular in which it seems to me that our institutions, not excepting our technological and polytechnic institutes, are at fault, namely this: that they have not sufficiently required, or even encouraged, those of their staff who claim that they are fitting men for the industries to take adequate pains to acquaint themselves with the conditions under which those industries exist and prosper. It has been aptly said that the efficient teacher must have his knowledge in the "contagious form." It must be at least as true that the instructor who is to be capable of equipping his pupils to grapple with industrial problems in the broad sense, must have acquired the engineer's view-point, as I have called it, before he can impart it. I believe that we can attain the best results only when every instructor concerned with undergraduate courses has made such an acquisition—not merely one or two members of a staff whose particular business it happens to be to give courses labeled "Industrial Chemistry" or "Chemical Engineering." The effect must be cumulative, and when it has become so there should be a distinct improvement in the power of our graduates to grapple with industrial conditions.

## INSTRUCTORS SHOULD HAVE REAL CONTACT WITH INDUSTRIAL PROCESSES

It may be objected by some that what has just now been advocated would mean the introduction of too much of what has been called the "dollar coordinate" into our instruction; that it exalts industrial chemistry above the more academic phases of the science. But it does neither of these things, if rightly interpreted. We often marvel at the more intelligent and receptive attitude noted in students who for one cause or another have been obliged to spend a year, or even a summer, in some industry before or during their student career. On the part of a teacher who has had some industrial experience there is a similar increase in resourcefulness, especially in the matter of illustration of principles, which vitalizes his instruction. This surely need not commercialize his instruction; it does tend to enrich it and to give the more academic phases of it, which must always be the backbone of the training, greater vitality. Every lecturer knows that there is an accentuated attention on the part of his students the moment that he cites as illustrative material some incident drawn from his own experience with affairs outside of the university walls. I believe, then, that one of the greatest services which the universities could render to the chemical industries would be the placing of a premium upon, or, when practicable, demanding of its instructing staff some sort of real contact with industrial processes. Even a round of visits among operating plants, of a fortnight's duration, is a wonderful education in itself, and I should be sorry indeed for the instructor who could say, after such a trip (as some who have never made the trip have said), that they have little to learn from the industries. An occasional summer vacation spent at a manufacturing plant would, of course, be better, and a half year better yet, and there are other agencies which may be utilized to the same end, the discussion of which would encroach upon material to be presented by other speakers.

It is, of course, easily possible to carry industrial contact so far, in individual cases, as to seriously hamper instructional efficiency, but this can be safeguarded. There seems to be no valid reason why, if the industries will cooperate, it should not be possible to bring about a desirable degree of contact, but it obviously involves such cooperation.

An incidental, but important, advantage would be the lessening of what seems to be a difficulty in arousing professional interest among students of chemistry. I have heard it alleged that very few chemists could talk intelligently about the larger achievements in their science, and that this was especially true of its teachers. Now, it is relatively seldom that we chemists build ourselves monuments, and when we do, they are apt to become sadly soiled and unattractive, and we all know that it is the rare mind that thrills at the thought of an atom, a principle, or a differential equation, however much of a scientific triumph each may represent. It is the chemistry of daily life and of our national industries which makes the most effective appeal, and this can be more clearly recognized in our instruction and in the writing of our text-books, without any loss of scientific caste. To avoid any misunderstanding, let me add that nothing which has been said should be interpreted as advocating the teaching of details of industrial processes, except in a few typical cases.

One of the most frequent criticisms of the young graduate relates to his inability to understand, or make himself understood by, other men; to his failures to cooperate with others, or to direct the work of others, even though the latter are less intelligent than himself. It is quite possible that our schemes of instruction for chemists and chemical engineers, as they have actually taken form, do tend toward more individualism and less of concerted action than is true in the case of other engineering professions, where students are much more likely

to work in squads. This matter deserves and is receiving consideration in some of our institutions.

Every institution is, I think, endeavoring in some way to promote such general intercourse among students as will tend toward more intelligent appreciation of what it means to "get on well" with one's associates, and to give and receive the best to be had. But not much can be accomplished through mere preaching. It would be a very great help toward the attainment of the results desired, especially with respect to the handling of men, if our students could obtain even simple employment in manufacturing plants in the summer. There is an enormous loss of available energy at present, and I cannot help thinking that the industries would, in the end, be greatly the gainers if they would systematically arrange to take on at least a few of the better men each year, upon recommendation from the universities. The fact that such men show a marked increase in appreciation of later instruction has already been alluded to.

## ABLE MEN SHOULD SERVE BOTH INDUSTRIES AND UNIVERSITIES

Undoubtedly the greatest service which the universities could render the industries in the training of young men would be to increase the proportion of large-minded, mature teachers. Unhappily those entrusted with administrative duties realize that it is increasingly difficult (especially in chemistry to-day) to attract and hold such men (especially young men) in competition with the attractions in the technical field. This is not alone because of the increased emolument which they offer: it is quite as much because of the opportunities for tangible achievement. It is, of course, too much to ask of the industries that they should refrain from securing the services of such men, but it seems very desirable to make an effort to devise some plan of cooperation which will, in a considerable number of cases, permit able men to serve the industries, without severing their connections with the educational institutions.

The fact that financial assistance from the industries which could be used to increase the resources of the universities available for the payment of salaries would be a most helpful form of cooperation, is so obvious as not to require further discussion.

Finally, it is essential, I think, that the industries should remember that the principal thing that the young chemist can bring to his elder colleagues is a fresh knowledge of facts, principles and theories. Someone has said that he "should enter the works with a head full of theory and a soul full of humility." He cannot hope to contribute at once those factors which are necessarily the product of experience and maturity of judgment. Let those who receive these young men into the chemical industries exercise reasonable patience, remembering the statement of Mr. Herreshoff that "chemical engineering necessitates a greater variety of engineering than all other branches of engineering combined," and the further statement of Dr. Nichols that "it should be remembered that a college course is simply a foundation on which further education is to be built in after life—for it is not possible to furnish the thoroughly educated man in four or even in five years."

## THE UNIVERSITY AND INDUSTRY

By WM. H. WALKER

Professor of Chemical Engineering, Massachusetts Institute of Technology

At the opening meeting of this series, President Wagner, with clear conviction, pointed out the fact that there does not exist to-day in the United States that close cooperation between the universities and the industries which has existed for years in Germany; and to which is due that commercial success which is so envied by other nations, and which is now enabling Germany to carry on practically unaided a gigantic war. President Butler at the same meeting stated that it is now time "to see whether a democracy, without departing from the principle of individual initiative, without giving up civil liberty for a bureaucracy, can of its own accord and because of its own con-



victions organize its resources in the public interest as well as any other nation or any other form of government that exists in the world." Realizing as we do that the university—and for the purpose of this discussion we shall use this term to designate all high-grade scientific institutions of learning—is not in that active cooperation with the industrial life of the country which makes for the greatest national efficiency and prosperity, we ask ourselves the question what are the factors which prevent this closer relationship; or conversely, what must be done by both the university and the industries to insure this desired cooperation?

The speakers who have preceded me have discussed the important phases of the last part of this question with reference to the university, and have pointed out what the educational institutions are doing and can do in the future, to more nearly meet the demands of the industries in the way of supplying trained men with whom to build up their organizations, and in furnishing opportunities for research with which to perfect their processes and their products. It is only after much hesitation that I attempt, even in a measure, to answer the first part of the question; but we can at least make a start. With your permission, therefore, I shall devote the time at my disposal to discussing very briefly some of the ways in which, from the university man's point of view, the industries have not fully taken their part in meeting this demand for more efficient cooperation. I do this in the hope that what I shall try to make constructive criticism of the industries may elicit corresponding criticism of the university, when the industries, as I understand it to be the case, are given their inning. In this way let us hope we may get closer together on this question which is of such imminent and national importance.

#### INDUSTRIES DO NOT DISCLOSE PROBLEMS

The first criticism of the industries which you will note, is their failure to make known to the university what their troubles and problems are. This proposition is simple in its statement, but fundamental in its importance and far-reaching in its results. The university can never realize the manifold opportunities in which it can be of service to the industries if such opportunities are never disclosed; it must remain in ignorance of the many problems crying for solution, if these problems remain pigeonholed in rolftopped desks, or hidden behind factory walls.

One reason for this condition of things is, when reduced to its simplest terms, that the industries have too little faith in the university as a source of help. A manufacturer consults the professional man and soon discovers that he does not know the details of his plant or his process or his product. He at once concludes that however able and learned the professor may be, he is too ignorant of the subject in hand to be of service. Here is where the manufacturer goes wrong; and it is at just this point that the industries make a fundamental mistake. It is not only unnecessary, but as a rule undesirable, that the university professor should know the detail of the problem which is so familiar to the manufacturer. Cooperation signifies the combined striving of two people towards the same end. When the manufacturer contributes the practical details of the problem, and to this the university man adds a broad knowledge of the facts and principles of science, with a training and experience in the application of these facts and principles, there is created a team which will produce results to satisfy the most exacting. This is what cooperation means; and it is this combination of science and industry that has made Germany the power she is to-day.

A second reason is, that there is a lack of frankness and a want of confidence on the part of the industries when dealing with the university man, which so far as I know is not merited by him, and which too often makes efficient cooperation impossible. The university man, being ignorant of the details

of the process and possibly never having been interested in the line of work involved, can aid efficiently and intelligently only when he is in possession of all the facts. If the scientist is not worthy of being entrusted with the whole story, he is a dangerous man to be in possession of any part of it. Nothing is more discouraging than to expend a lot of time and energy on a problem only to find later that one was kept in ignorance of conditions which make the results of earlier work useless. If the scientific man cannot be a confidential man, his usefulness to the manufacturer has vanished.

#### SCIENTIFIC DATA OBTAINED IN INDUSTRIAL RESEARCH SHOULD BE MADE PUBLIC

The next matter in which the industries are at fault, is in not assuming a more liberal attitude towards the publication of the results of research work done for the industries by the universities and their graduates. There is a feeling on the part of the president or manager of the company that if the university man be generously reimbursed for his time and trouble he should be satisfied. No scientific man should be, and few scientific men are, satisfied with a purely monetary return for their labor. They appreciate that they are under an obligation to contribute their share towards the development of their science; and when they have completed a piece of work which includes scientific data of value, they feel that such data should be published for the upbuilding of the science. I do not mean that the results of the investigation for which the company has paid a generous sum should be spread abroad for the use of its competitors: such would be manifestly unjust. But I maintain that in every piece of research work there are results which could be published in a perfectly impersonal way, so to speak, that would enrich science, and do the industries no harm. I dare say that there is not a man present who interests himself in the application of science to industry, who cannot think at once of a dozen reports he has written for corporations which contain a wealth of valuable data that could be published in an unapplied form without doing the corporation any injury, but which remain buried in the oblivion of secrecy.

#### "PURE" AND "APPLIED" RESEARCH CAN BE EQUALLY SCIENTIFIC

The unfortunate use of the terms "Pure" and "Applied" research has led to the almost unconscious assumption that the only motive behind pure research is to enrich science, while the sole motive actuating applied research is to enrich the investigator or the organization financing the investigation. This latter assumption is unwarranted. Because an investigation is to be utilized, is no reason why the work should not be done with the thoroughness and accuracy which produces the best of scientific results. If published as scientific data in this non-applied form, the cause of pure science is advanced just as though the work had been undertaken and carried out as a piece of pure research, and the demand of the industries is at the same time satisfied.

As Prof. Gies pointed out, everything which Pasteur accomplished in science was done from a distinctly industrial standpoint. A problem appealed to Pasteur in proportion to its utility. But he did his work with such a breadth of view, with such attention to thoroughness and accuracy that upon the results of his industrial research is founded the science of bacteriology. Had the industries which profited by Pasteur's work been able to lock up in their archives the results of his researches, not only would the industries themselves have been poorer thereby, but they would have deprived Pasteur of the glory of his achievements and science of his epoch-making contributions. To take an example nearer home, consider the splendid research carried on by Whitney and Langmuir on the behavior of gases at very high temperatures. It is immaterial whether you consider this the finest type of pure research, from which the commercially valuable gas-filled tungsten lamp re-

sulted, or an exceedingly profitable piece of industrial research, in which purely scientific results of great value and interest were obtained, and given to the world. The goal towards which we should strive is to conduct our investigations so that the only distinction which can be drawn between pure and applied research is the interval which will probably elapse between the time when the results are obtained, and the time when they become of service to the community.

#### "TECHNICAL DIRECTORS" NEEDED IN OUR INDUSTRIES

A fundamental difficulty which presents itself when we in America attempt to introduce science into industry as compared to the ease with which the same thing is done in Germany, is occasioned by the absence of the equivalent of the German "technical director." Every university professor who has followed his students into the industries knows well how often they all but fail solely on account of a lack of appreciation of the nature of their work by the directing head of the organization. This officer may have all the training necessary to be the son of the owner, or the representative of the majority stockholders, or of the banking syndicate which financed the industry; but he lacks the training which enables him to appreciate the atmosphere which must surround research work, or in fact scientific work of any kind, if it is to be successful.

The infinite patience of the German investigator is made possible and profitable only by a corresponding infinite appreciation and sympathy on the part of the managing director. We may talk until the crack of doom about the miraculous results of Germany, but so long as we continue to draw the technical directors of our industries, the men on whom decision as to development work depends, from the purely commercial side of the organization rather than from those men with a scientific training, just so long shall we continue, notwithstanding our great natural resources, to cry for a protective tariff, more favorable patent laws, and other wholly temporary and superficial aids.

#### UNIVERSITIES MUST SUPPLY INTELLIGENT FOREMEN

Finally we come to that factor in which the industries are most woefully lacking, and to remedy which the university has done almost nothing, namely, the supply of intelligent foremen. It is not necessary for me to develop this fact because everybody knows it. Anyone who has tried to carry scientific work into the industries realizes the difficulties introduced by unsympathetic and frequently hostile foremen, or even superintendents. Clearly it is foolish to think of dispensing with the hard-headed old superintendent, with his wealth of knowledge and his years of experience; or the young foreman with his jealously guarded secrets of the batch, or the mix, or what not. But while science forced into an organization from on top is most helpful, some science introduced at the bottom is also necessary. The younger men now in our industries must be educated; must be shown that a man to attain the greatest success must keep up to his job, that as he grows, his job will grow. Here is a golden opportunity for the university, using this term always in the broad sense already stated, and the industries, to cooperate as they have never done before. All through the long summer the industrial and chemical engineering laboratories of our large institutions are empty. Why should this expensive equipment be idle when there are so many anxious to use it?

Time does not suffice to outline in detail a plan which we are developing at the Institute of Technology, to present to young foremen and superintendents the principles of physics and chemistry on which their chosen industry depends. We propose to assemble each summer in our chemical engineering laboratory, apparatus designed to present one specific industry. We shall invite that industry to send to us their more promising and ambitious men, in order that they may learn the scientific

principles upon which the control of the raw materials, the process and the product depend. There are grave difficulties in such a plan, I admit, but cooperation can solve them. The objection met most frequently is that the industries cannot spare a good foreman for so long a time as six weeks. I can only say, that the foreman does not exist who may not at any time be taken out of the factory for six weeks by pneumonia, or typhoid fever, and yet the factory would not stop, nor the foreman lose his position. No more promising field exists, nor one fraught with greater possibilities for the industrial progress of this country than the opportunity which this problem presents for cooperation between the university and industry. The foremen are anxious to learn; the industries are anxious to have them know; the university is anxious to teach. Let's get together.

#### THE UNIVERSITY AND BUSINESS

By ARTHUR D. LITTLE

Member of Corporation, Massachusetts Institute of Technology

The more obvious function of the university is that of training and developing the students who resort to it at the most plastic period of their lives. Its broader purpose is coextensive with that set forth in the splendid phrase of Smithson "the increase and diffusion of knowledge among men." If knowledge is power anywhere it is certainly so in business and yet we find that business suffers everywhere from lack of knowledge, which it is within the power and province of the university to supply.

It is, for example, a platitude to say before an audience like this that there is a great need at the present time on the part of bankers, capitalists, men of affairs, and directors of industry, and in no less degree on the part of superintendents, foremen, work people and the public generally, for a better appreciation of the part which science plays in furthering industrial development, increasing the efficiency of production, raising the scale of wages, and insuring preparedness, whether for peace or war.

#### BUSINESS MEN IGNORANT OF SCIENTIFIC POINT OF VIEW

This need arises from the fact that men of affairs, and especially financiers, have seldom received a scientific training or acquired a working knowledge of the scientific method or fully understood the scientific point of view. They consequently often fail to realize the intrinsic merit of industrial propositions which are based essentially upon new applications of applied science, and to gauge with accuracy their chances of success.

They can—it is true—employ specialists, as in fact they should do in any case, but they often cannot weigh the validity of expert reports because of ignorance of the scientific method and suspicion of the value of its deductions. As a result of these too common limitations in financial circles the development of large and ultimately highly profitable industrial undertakings is often postponed for years.

The directors of industry—though happily with many notable exceptions, especially among those to whom have been entrusted the affairs of our largest corporations—frequently ignore science. Wilfully or unconsciously, they cut themselves off from that great accumulation of coordinated knowledge and organized common sense which has been painfully built up by thousands of the best minds in every land during the last hundred years.

Proposals based on the scientific study of a problem or situation are, therefore, often rejected by these gentlemen as "theoretical" because the man who prides himself on being "practical" either cannot absorb the data, or does not dare to trust himself to the conclusions. Thus, antiquated methods persist, avoidable wastes continue, and dividends decline.

The attitude of superintendents and foremen and of the industrial workers generally to the innovations and betterments proposed by science is far too commonly one of militant scepti-



cism or hostile suspicion. The superintendent trained in the rule of thumb and ignorant of the wealth of information which the laboratory, lecture room and scientific library has made available to his technically trained competitors, may easily become a direct obstacle to industrial progress. Since he is largely instrumental in determining the selection of the means and methods of production he is often a greater drag upon prosperity than the engineer who puts sand in the cylinder because the oil has been changed or the workman who indulges in sabotage because he objects to motion studies or the increased production of a new machine or process.

Now all these individuals are social units who, with many other interdependents and mutually reacting units, together constitute the public at large.

One may therefore fairly claim that our universities, great technical schools and colleges cannot serve business better than by directing some considerable part of their immense collective resources and influence toward creating in the public mind that mental atmosphere in which alone business can truly flourish.

#### EFFICIENCY IN GOVERNMENT A GREAT NECESSITY OF BUSINESS

The first great necessity of business, as it seems to me, is a wiser, less recklessly extravagant and more generally efficient government of nation, state and municipality, and, as a corollary, a higher respect for law in the community. The second urgent need of business is that of establishing in the public mind as axioms the broad facts and principles without the general acceptance of which business cannot be carried on at high efficiency anywhere.

Business for example suffers much from the notion prevalent in certain quarters that all wealth is produced by labor and none by brains. It is likely to suffer still more from the idea that the productive capacity of all should be limited by that of the least capable. So, again, is business hampered by the general ignorance of workers and superintendents as to what research is and what it can do for them.

A study of the effect of the invention of the telephone upon the scale of wages of young women would be informing. So would one upon the relation which the development of special steels bears to the output of automobiles and the wages of machinists. No economist in these days raises his voice to call attention to the advantages of great fortunes. Yet, however selfishly administered, they have advantages which are obvious to some of us and which should be easily demonstrable to all.

The University of Wisconsin has done much to raise the standard of government in Wisconsin. Other universities everywhere are doing something, but could do much more, to combat the influence of pernicious ideas and enlighten obstructive ignorance.

#### STUDENTS SHOULD LEAVE UNIVERSITY WITH A DEFINITE TREND IN SOME INDUSTRIAL DIRECTION

To those of us who come in contact in considerable numbers with recent university graduates, one of the most shocking defects in the educational system of which they are the product is found in the pitiful lack of decision exhibited by the majority of these young men concerning the work and place in the world for which they are best fitted. One gains the impression that all too often the educational processes to which they have been subjected have been akin to the Strassburg process of stuffing by which geese are fattened. Or, they have been taught as Dr. Johnson said books were made, as an apothecary puts up a prescription, by pouring a little from many large bottles into one small bottle. It is not surprising that both the Strassburg process and that of the apothecary should have failed to draw out and develop the native capacities and latent possibilities of the student or that they should leave him with no well defined directive impulse.

Such a state of affairs is happily not true of our technical

schools and it ought not to be true of our universities. At some time during the university course of every student his attention should be drawn to the range of opportunity which the business world affords, and a clear notion should be conveyed to him of the promise and limitations of these opportunities and the qualities of mind which they demand. He should leave the university knowing something of himself and with a definite trend, if not a permanent set, in some industrial direction.

#### PREVALENT IGNORANCE OF ORDINARY SCIENTIFIC PHENOMENA

Those of us who have received the benefit of any sort of scientific training are constantly amazed at the ignorance of cultivated men and women, business men and work people, regarding the simplest phenomena by which they are surrounded. To a deplorably large proportion of the community the striking of a match, the lighting of a fire, the freezing of water, the fall of snow, the sending of a telegram or a talk by telephone, the operation of a steam engine, or the turning on of an electric light, involve mysteries as far beyond their range of thought as the cause of gravitation or the rotation of the nebulae.

Since business involves at every point contact with natural phenomena and since the proper understanding of these phenomena, or at least some realization of what underlies them, often determines the measure of success attained in business, the university might well establish a compulsory elementary course in general science. This should be designed to give the student at least a rudimentary knowledge of the field covered by the different sciences, the relation of their subject matter to natural phenomena in the affairs of every-day life and those of business, the interdependence of the sciences, and, above all, a clear idea of the scientific method. Such a course could not fail to prove an immense stimulus to any intelligent mind. It would open out new horizons for thought and put an altogether different and more interesting aspect on the world in which we live and in which we must do business.

#### ENGLISH LANGUAGE NEGLECTED AS A BUSINESS TOOL

The business man seldom has at his disposal any more potentially efficient tool than the English language, but in his hands it is a tool which is often rusty and very seldom so keen and highly tempered as to be capable of rendering its highest service. The fault for this is largely with our universities, and the remedy, so far at least as their own students are concerned, is in their hands. Our great institutions of learning are every day disgraced by the inability of their recent graduates to make a concise and convincing oral statement of a series of facts, to prepare a well organized and adequate report, or even to write a graceful and informing letter.

#### STUDY OF SPECIAL INDUSTRIES BY SMALLER COLLEGES

There is, finally, a very definite field in which our smaller colleges can do much for business, and that is by offering specialized courses in the science and technology of those particular industries which are highly developed in their locality. Ohio State University, for example, has for years specialized in this way regarding coal, and the University of Maine is now instituting courses in paper-making. Other colleges and universities are favorably situated as to particular industries, in such numbers and with such variety of opportunity that, were these opportunities utilized in even moderate measure, the young man who desired to prepare himself for any line of industrial activity would have within his reach the means of realizing his ambition.

The result would be the constant accession to the ranks of business of annual quotas of young men not blindly groping into an unknown world like the modern graduate, but advancing eagerly with open eyes toward responsibilities which they know that they can meet.

## ADDRESSES

### THE NAVAL CONSULTING BOARD OF THE UNITED STATES<sup>1</sup>

By L. H. BAEKELAND  
Member of the Board

Modern war, whether it be for robbing, plundering and subjugating other nations, or for legitimate self-defense, has become primarily dependent upon exact knowledge, good scientific engineering, and, to a large extent, applied chemistry.

#### MODERN WAR DEPENDS ON APPLIED SCIENCE

Napoleon used to say that the Lord was on the side of the armies with the biggest artillery and the best ammunition; if this seemed true in his time, it sounds almost like an axiom to-day, when physical training, personal valor, bravery, or courage, appear to count for little if efficient technical equipment, based on sound scientific knowledge, is lacking.

Germany, with her enormous and well-drilled army, with her 42-centimeter guns, and other formidable equipment, would be hopelessly paralyzed, did she not find in modern chemical processes of synthetic nitric acid from the air, the source of supply of this indispensable chemical. How, otherwise, could she manufacture smokeless powder and explosives, since England succeeded in shutting her off from the general source of supply of nitrates from Chile?

#### FRANCE FOLLOWS SECRETARY DANIELS' EXAMPLE

Secretary Daniels seemed to be imbued with these facts, when by organizing the Naval Consulting Board of the United States, he desired to give to our Navy the benefit of the scientific and technical talent of this country. Since then, his example has been followed by the French Republic, who in her hour of danger, has organized a similar civilian board and has even raised it to the dignity of a Ministry: "Le Ministère des Inventions." Great Britain also has enlisted the services of a board of civilian scientists and technologists for her present war operations. As to Germany, we know that long ago, she has abundantly availed herself in her war plans of the advice and coöperation of her scientists, inventors and engineers.

Although general information about the Naval Consulting Board has been more or less available through the daily press, there seems to be a very hazy conception in the mind of the public as to its work and plans. Unfortunately, some published criticisms, emanating mostly from persons who seem to have neither the desire nor the tact to first obtain correct information, have caused a very misleading interpretation of the work of this Board.

#### A BOARD WITHOUT POLITICS

To those whose limits of imagination do not go beyond petty political considerations, it may be well to point out that in the formation of this Board, politics has not had even the most remote influence. Secretary Daniels appointed America's best known inventor, Edison, as Chairman, and applied afterwards to different engineering and scientific societies of the United States, so that each of them should designate two representatives best qualified to serve on the Board, through which our Secretary of the Navy would try, as he expressed it, "to mobilize the inventors and engineering talent of the country in the service of the United States." Until now, Mr. Daniels does not know whether there are any democrats, republicans or progressives on this Board—nor does he care to know. He relieved himself of the responsibility of selecting the members of this Board by putting the matter up to the representative engineering societies of the United States. If any of those

<sup>1</sup> Address presented at the joint meeting of the American Chemical Society and the American Electrochemical Society, Chemists' Club, New York, December 10, 1915.

societies did not make the best possible selection, they alone should bear the blame. In the meantime, it matters little as long as the majority of the Board are men of such ability and personality that they cannot fail to impress their attitude and talent upon the work of the Board.

#### IS THE BOARD TOO CUMBERSOME?

At first it seemed as if a Board of twenty-two men was to be much hampered by cumbersomeness and by long deliberations; but this fear vanished after our first meetings. If any member felt inclined to use unnecessary oratory or rhetoric, he soon changed his mind after he noticed how the other members displayed mutual respect for each other's valuable time, how discussions of secondary importance were eliminated, and how this Board proceeded with unusual directness towards matters of immediate importance.

When the announcement was made that on the first day of our meetings, we were to board the yacht of the President to proceed to the Indian Head Proving Ground, some of us were inclined to think that formalities and social affairs might interfere with the efficient distribution of our time. But this idea also was soon dispelled, as during this entire trip the time was taken up with the discussion of subjects directly related to our work, while becoming acquainted with the other members of the Naval Consulting Board, as well as with the Chiefs of the different departments of the Navy. So little time was given to formalities that even a regular lunch was dispensed with, beyond the distribution of a few sandwiches, while discussing various matters. Our visit to Indian Head gave us an excellent opportunity to get some direct practical information upon matters of ordnance and ammunition. We landed back in Washington after dark, but at half past eight that same evening we were to continue our meeting at Secretary Daniels' office. Although this left us only a few minutes to swallow some supper, none of the members of the Board failed to appear at the appointed time.

#### A JOINT MEETING WITH THE CHIEFS OF THE NAVY

It is not generally known that the Navy has, in itself, an advisory board which is made up as follows:

HON. FRANKLIN D. ROOSEVELT, Assistant Secretary of the Navy  
REAR ADMIRAL W. S. BENSON, Chief of Naval Operations.  
REAR ADMIRAL VICTOR BLUE, Chief of Bureau of Navigation.  
REAR ADMIRAL JOSEPH STRAUSS, Chief of Bureau of Ordnance.  
REAR ADMIRAL R. S. GRIFFIN, Chief of Bureau of Steam Engineering.  
CHIEF CONSTRUCTOR D. W. TAYLOR, Chief of Bureau of Construction and Repair.  
CIVIL ENGINEER H. R. STANFORD, Chief of Bureau of Yards and Docks.  
PAYMASTER-GENERAL SAMUEL MCGOWAN, Chief of Bureau of Supplies and Accounts.  
SURGEON-GENERAL W. C. BRAISTED, Chief of Bureau of Medicine and Surgery.  
MAJOR-GENERAL GEORGE BARNETT, Commandant of the Marine Corps.  
CAPTAIN RIDLEY MCLEAN, Judge Advocate General of the Navy.

All of us were impressed with the concise and business-like way in which each one of these gentlemen described his various responsibilities and presented the details of the subjects on which he desired the advice and assistance of the members of our Board.

#### THE MEN OF OUR NAVY

Not only did they give us the convincing impression that they were sincerely glad to discuss their problems with us, but in doing so, they made us forget that they were the chief officers of the Navy; they appeared to us like so many engineering or business men who, in a simple and direct way, wanted to discuss questions on which they felt their grave responsibilities. To anyone who is acquainted with all the pose and overbearing attitude of European military caste, and who might fear that



this Nation might bear the incubus of militarism, direct acquaintance with men like these would soon dispel this apprehension. Nor did we see, anywhere among them, nor at the Army and Navy Club, nor at the Department of the Navy, as much as one single uniform, except, of course, on board of the "*Mayflower*," where the yacht's officers and crew were in uniform.

Notwithstanding the fact that no time was lost for unnecessary purposes, it was after midnight when the first day's meeting adjourned. Early next morning we met again, this time at the Library of the Navy, and then and there the Board was organized for its future work. Here again, no time was spent upon side matters; everything was transacted in a practical direct way. For instance, when the rules of procedure for further meetings had to be discussed, a sub-committee was immediately organized with instructions to leave the room and report "not later than thirty minutes," so as not to impede other deliberations which were going on; the result was that when at noon we gathered for lunch, all questions of organization and sub-committees had been discussed, sifted and settled until future conditions may make it desirable to introduce any needed changes. But even at lunch, the business meeting went on, and some of us had to interrupt our lunch, and go to a next room to deliberate further in a sub-committee, until a report could be submitted on some matters relating to this particular committee. So when at the end of this second day, the Naval Consulting Board adjourned, a good deal of work had been disposed of. Shortly afterwards, another meeting was held in New York, where the organization of the sub-committees was completed, and where the different chairmen of the sub-committees were appointed.

#### A BOARD THAT RECEIVES NO PAY AND PROVIDES FOR ALL ITS OWN EXPENSES

For those who are accustomed to consider the United States Government as a big "milking cow" for salaries and remunerations, it may be of interest to know that no member of the Naval Consulting Board draws any salary, nor gets any remuneration from the Government. We all pay our own traveling and hotel expenses and each member feels that if he can give his time, free of charge, to the Government, he can still better afford to pay his own expenses. This program is carried out so scrupulously that even the cash for the purchase of stationery and printing is furnished by the members of the Board, who are monthly assessed among themselves.

#### A "SHORT-CUT" BETWEEN THE NAVY AND THE INVENTORS OF THE COUNTRY

The general opinion of the members of the Board is that its scope of usefulness can best be fulfilled by acting as a "go-between" or a "short-cut" to information between the heads of departments of the Navy, and any individual member of the different societies they represent. This carried into practice the idea of "mobilization of inventors and engineering talent" of Mr. Daniels. The Board mainly puts its services at the disposal of the chief officers of the Navy, as fast as the latter feel the necessity of cooperation or advice. For instance, a subject relating to improvements in the manufacture or the composition of a certain explosive, would be referred to the Sub-committee on Chemistry and Physics, as well as to the Sub-committee on Ordnance and Explosives; the matter is discussed in these two committees and the members of these two committees decide whom to select among their fellow members of the chemical or engineering societies who are best qualified to help them in this task, and who, at the same time, are willing to cooperate without any other compensation than the feeling that they are working for the good and the security of our Republic.

It is obvious that in handling all these matters, tact and

discretion are just as indispensable qualifications as talent or knowledge, and this involves no little responsibility for the members of the Consulting Board in selecting suitable collaborators.

As a matter of fact, several important pending problems are now actively before the sub-committees, and, notwithstanding the short time which has elapsed since the first meeting of the Board, some of these questions are already in an encouraging phase towards successful solution.

#### THE SO-CALLED "FIVE-MILLION LABORATORY" OF THE NAVAL CONSULTING BOARD

The so-called "five million laboratory" proposed by the Naval Consulting Board, has been the favorite subject of varied and picturesque criticisms which, as usual, originated more through lack of information than by ill will.

Secretary Daniels requested each member to address to him his personal opinion on the advisability of the creation of a research laboratory where urgent technical matters relating to the needs of our Navy could be studied successfully.

At the second meeting, a special committee was appointed to submit a joint report. On this committee were, besides Mr. Edison, four other members. One of the other members of the committee is a man who has earned a national reputation in organizing and developing one of our largest mechanical industries. The second member is at the head of perhaps the largest and best endowed scientific research institution of the world; another is the chief of one of the most successful chemical and physical industrial research laboratories of this country; the fifth has devoted much of his life to private chemical research.

#### CHEMICAL OR PHYSICAL LABORATORIES ARE RELATIVELY INEXPENSIVE

It was interesting to follow how the five members grouped themselves in accordance with their own point of view, dictated by their daily scope of action. The chemical or purely scientific members of this committee agreed pretty well on the kind of research laboratory they had in view, and although their suggestions had been written independently without consulting each other, their general recommendations as to the organization, equipment, and needed expenditures were fairly similar and relatively modest. But their recommendations were mainly limited to a chemical and physical laboratory; they did not include the study of elaborate mechanical and technical problems which go far beyond the questions which are usually dealt with in chemical and physical research laboratories.

#### MAIN EXPENSE CAUSED BY ENGINEERING RESEARCH AND EXPERIMENTS

The two other members, on the contrary, wanted to prepare thoroughly for engineering problems of immediate importance, the solution of which seems indispensable if the money of the Navy is to be spent to best advantage. They set forth, from their own direct experience, how very expensive such engineering experimental work is likely to be. Edison, for instance, pointed out the millions he spent in developing some of the details of his inventions; another member, identified with the automobile industry, stated that one single automobile concern, here in the United States, had found it necessary to spend half a million dollars in one year for experiments and research. The modest estimate for a merely chemical and physical laboratory was thus snowed under by the irrefutable evidence of the much larger needs for a suitable mechanical or engineering department.

Of course, it was argued that the Navy possesses already several experimental stations at its different Navy yards, and at the Torpedo Station in Newport, aside from the different testing laboratories for the materials used for ordnance or ammunition; that furthermore, the excellent laboratory facilities

of the Bureau of Standards are available. The answer to this was that each and every one of the present institutions were more necessary than ever, but were totally insufficient; furthermore, the full coöperation of all of them is needed; all this in view of the fact that at present, the Navy of this country is facing unusual responsibilities.

EXPERIMENTAL WORK CANNOT BE POSTPONED UNTIL  
IT IS TOO LATE

If it is deemed urgent to be prepared for defense, then this defense involves problems the solution of which cannot be deferred indefinitely. If something has to be done, it must be done immediately—not in five or ten years hence, when it may be too late. In all of our present scientific research laboratories, time seems of relatively little or no account; problems which cannot be solved to-day can be solved to-morrow, or in ten years, or during the next generations; but this is not the case with the problems connected with the contemplated defense of our country; the solution of these problems cannot be postponed. They demand immediate action. Nor is the condition of our Navy similar to that of an industrial concern that can afford to take chances with machinery or equipment which is not strictly 'up to date, and still show some commercial success. For instance, recent events have demonstrated that there is no use building the best and newest fortresses against an enemy who possesses guns strong enough to demolish everything in existence. Nor is there any chance of success in using the very best artillery at anything like equal chances if your adversary can do his scouting and range-finding with aeroplanes provided with reliable engines, while your aeroplanes are equipped with motors which give out at unexpected moments.

UNITED STATES WAS STILL USING OLD BLACK POWDER WHEN ALL  
OTHER NATIONS WERE PROVIDED WITH "SMOKELESS"

In our clumsy war with weak Spain, we went into the field with black powder when all other nations, even Spain, were equipped with smokeless powder. Why? Because we had postponed too long studying the chemistry of the subject. The fact is that if we require a Navy at all, our Navy cannot afford to use anything but the very best and most efficient means of defense. Not to possess the very best might put us in the same absurd condition the wooden navies of the world were in, after our civil war had established the supremacy of the iron-clad vessel.

PRIVATE INDUSTRIAL CONCERNS SPEND MILLIONS FOR RESEARCH

The contemplated outlay for the Navy for the next five years, for new ships, aviation and reserve of munitions, amounts to about \$500,000,000. These tremendous expenditures of money, in order to be of real value, ought to be made as efficient as possible. All doubtful and inferior devices must be eliminated by direct experiment, by research and tests, *before* it is too late to remedy them. This requires accelerated action; in fact Mr. Edison's personal opinion was that research and laboratory work in this instance "should go on night and day without intermission" instead of the usual easy-going short-day plan followed in laboratories. If one single automobile concern in the United States finds it to its advantage to spend in one year half a million dollars on testing, research, or experimentation, how much more important is the business in the United States Navy, where money not spent wisely is better not spent at all, because then at least, we shall not have the illusion that we are equipped for defense, when we have merely lost our money on antiquated devices.

MONEY SPENT ON FLYING MACHINES IS WASTED IF ENGINES  
ARE NOT RELIABLE

Without mentioning any spectacular problems of modern warfare, it might be stated that such a prosaic detail as the corrosion of condenser tubes of our warships, involves an annual direct and indirect damage of about \$2,000,000. If \$1,000,000 were spent

on research on this problem alone, with the result of reducing the damage to one-half, the total outlay would be compensated in a few months' time, aside of the important fact that our fleet would be stronger because less of our ships would be unavailable for service. It was brought out that there was little use in spending so many millions on flying machines as long as there was any doubt on the reliability of their engines, and until an absolutely well tried and standardized engine had been developed. To accomplish this experimental work in a period of a few years, would cost quite some money; but to do this rapidly, within a few months, before order is given to build these flying machines, requires enormous outlays of money, alongside of the indispensable engineering talent.

Another member brought out the fact that even conservative industrial enterprises found it necessary and profitable to spend at least two to five per cent of their sales on research and experiments. At this rate, the contemplated expenditure of \$500,000,000 in five years, would certainly warrant an expenditure of at least five million for research during that period. Money for this purpose wisely used, ought to do so much good to the Navy as to increase its efficiency by the value of several battleships costing considerably more.

THE BOARD SCORNS THE USE OF OLD SUBTERFUGES WITH  
CONGRESS APPROPRIATIONS

In this discussion, everybody seemed to be well in accord with the general idea that whatever expenditures were recommended, the contemplated work should be carried out under immediate supervision of the Navy; that this work should not be started all at once—full blast—but should be extended gradually, as fast as circumstances demand it. In view of all this, two policies were open for obtaining the necessary appropriations—the old time-honored trick of asking from Congress first an appropriation of a few thousand dollars, knowing very well that this would be insufficient, then after awhile, asking an additional appropriation and keeping on nagging and asking at various intervals. But the members of the advisory board thought it a more honest policy to state the facts as they saw them and to confront the Secretary of the Navy with the probable maximum expenses for research and experimentation, commensurate to the five years' Naval building program now under contemplation. The five million dollar budget for experimental work to be expended during those five years, or about one million a year, may strike the uninitiated as needlessly large, although it is only about what some large industrial enterprises have found necessary to spend on their own experimental work.

LET BLUNDERS BE COMMITTED IN A SMALL EXPERIMENTAL WAY  
INSTEAD OF ON A LARGE SCALE

But, if the Nation does not want to go to the expense of developing the latest and most efficient means for defense at the lowest cost by obtaining the necessary information through preliminary experiments, instead of committing mistakes on a large permanent scale; or if our Country wants its Navy to keep on building its ships or other means of defense, such as were good enough in the past, regardless of the fact that modern war requires the very latest and the most efficient available devices, then let us not be astonished if after incomparably more money has been spent for increased armaments, we find that we are loaded with means of defense which have become obsolete in the meantime and are merely good for the junkheap of antiquated equipment.

The foregoing is a brief résumé of various arguments which were submitted by some members of the Board, and this is the first time that this discussion has been reported in public. Let us hope that its publication may help to dispel some of the ideas of the public which imagine that the Board contemplates the immediate erection of a "\$5,000,000 laboratory building,



where the members of the Naval Consulting Board can experiment to their hearts' content in company with long-haired inventors."

As Mr. Edison expressed it picturesquely: "The money should be spent not on buildings, but on a National junkshop," where means of defense can be tried out first, at relatively small cost so as to learn how to get the most and very best for the money, and so as to avoid making expensive and dangerous blunders on a wholesale scale.

ADMIRAL MELVILLE TWELVE YEARS AGO STRONGLY URGED EXPERIMENTAL WORK IN THE NAVY

More than twelve years ago, one of the most distinguished officers of our Navy, Admiral George W. Melville, urged strenuously the necessity of Naval engineering experiments; his well based arguments published in the Proceedings of the Engineers' Club of Philadelphia (Vol. XX, No. 3, July, 1903), brought out the fact that expenditures for experiments are the best means for avoiding expensive mistakes. What he said then sounds even more convincing to-day.

The following quotations are taken from his paper:

"The hulls and machinery of these five battleships will cost approximately \$20,000,000. The armor, armament, and equipment will require an additional outlay of \$15,000,000; so that the actual cost of these battleships will probably be about \$7,000,000 each. The annual depreciation of each of these vessels from the time they are launched, taking into consideration wear and tear as well as loss in fighting value, will be at least 4 per cent of their actual cost. The expense attending the establishment of the proposed experimental station, including its operation for several years, will thus be but little more than the annual loss resulting from corrosion, mishaps, and depreciation of military appliances of two of these floating fighting machines."

"The success of Germany can be accounted for only by recognizing the fact that study, reflection, and research must have been expended in the preparation of plans, in the building up and the organization of the shipyards, and in laying out and carrying on the work of construction. It was the high appreciation of the value of original investigation, coupled with experimental work, that has caused Germany to advance progressively and successfully."

"Where research had not been conducted, disappointment resulted from the construction of vessels which were either faulty in design, ill-suited for the purpose intended, or upon which an inferior quality of work had been expended."

"The problem as to whether or not in-turning screws are detrimental to manoeuvring qualities would have been solved many years ago if the work planned by Mr. Isherwood had been continued. Our increased knowledge of the theory and practice of screw propulsion since the Isherwood experiments is due, however, almost wholly to the work of Froude, conducted for the British Admiralty. This is confirmatory evidence that such important and difficult work can only be undertaken by official or civilian experts who are able to call upon government resources for data and information. It requires government investigation to solve important problems relating to the powering of vessels, since valuable and far-reaching experiments upon this subject require the use of ships as well as the services of a large number of reliable and competent persons to collect the data requisite for the determination of absolute results."

"If it be true that the battleship of one generation is the junkheap of the next, then an economical race like the German is pursuing a wise policy in conducting experimental research and investigation in the direction of finding out how the weak links in the naval chain can be strengthened."

"Experience has shown that the German engineering laboratories are more than a good paying investment for there is not an expert in that empire familiar with the work being done at these laboratories who does not believe that their destruction would be a greater national calamity to the navy and the nation than the loss of one of the battleships of the home squadron. The warship could be replaced in four years. It would take six years to rebuild and put in effective operation the complete installation for conducting experimental research that has been developed and perfected at the Charlottenburg and Dresden technical colleges."

"There is probably not an eminent naval or mechanical engineer in America or England who has given consideration to this question who is not also of the opinion that the establishment of a national experimental laboratory for naval pur-

poses will vastly contribute to military strength. Probably the majority of these experts also believe that such an institution would eventually contribute more to actual naval strength than the building of a battleship. One does not need to possess vivid imagination to realize that much is contributed to the fighting strength of a navy by carrying on research along engineering lines, and thus preventing the design, construction, and installation of appliances that are ill-suited for the purposes intended."

"The cost of maintaining a battleship in commission will approximate \$1000 per day, and warships have been tied up for weeks on account of the corrosion of a few hundred dollars' worth of boiler tubes. It will repay the nation for the cost of an experimental station if the staff of the laboratory will simply cause increased length of life of both boiler and condenser tubes."

YONKERS, NEW YORK

## THE NEED OF A LARGE GOVERNMENT INSTITUTION FOR CHEMICAL RESEARCH

By C. ALFRED JACOBSON  
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The idea embodied in the present paper was born in Germany in 1912, then rocked in a cradle of the deep, nursed under the shadows of the sky scrapers of New York, and finally reared to maturity on the arid sands of Nevada.

Chemistry is one of the basic sciences. It is the foundation upon which countless industries have been built. All other sciences are dependent upon it to a greater or less degree. In short, chemistry is the corner-stone in the edifice we call civilization, and it has given a different meaning to the word *Kultur*. It is needless here to dwell upon the value of this branch of science to our industrial and economic life and even to our existence as an independent nation for this is apparent, even to those who have given the subject but a cursory consideration. There may be those, however, who believe that our present knowledge of chemistry is quite complete and what we need is a better application of the known rather than to be continually striving to acquire more knowledge. To such let me say that, although 200,000 or more definite chemical compounds have been described and thousands of chemical books have been written, the known is still infinitesimal compared to the unknown in this field of science. Graphically speaking, if a tennis ball were thrown into Lake Michigan, the amount of water wetting the ball compared to the rest of the water in the lake would fairly represent our present chemical knowledge compared to that which is still unknown. Whether these estimates are correct or not, matters little. The essential thing is that there are vast riches of knowledge yet uncovered in every field of science, and not the least in chemistry.

Our civilization will advance just in proportion as we are able to push back the frontier, and lay bare the facts of nature, and make them serve our needs. Not until the soldier has had his baptism of fire at the front does he realize or appreciate what war means, and the analogy holds equally well for the scientist. The research men are the ones at the front, and they are in a better position than anyone else to appreciate the economic importance and value of scientific research.

It would seem that no one could read the symposia on the Contributions of the Chemist to American Industries published in the April and November (1915) issues of THIS JOURNAL without being profoundly impressed with the fact that chemistry is after all at the basis of nearly all our industries. Products whose values mount into the billions of dollars annually, are largely conditioned upon the work of the chemist, and the end is not yet.

This branch of science is not only vital to constructive agencies but even more so to the destructive ones, such as those of the army and navy. The present European war teaches us that men and military training are of far less importance to success than a high development of the science of chemistry and it be-

TABLE I—RESEARCH DEPARTMENT SUGGESTED FOR GOVERNMENT RESEARCH INSTITUTION

No.	DEPARTMENT	No.	DEPARTMENT	No.	DEPARTMENT
1	IRON AND STEEL	51	Lichen substances	101	Mordants
2	Copper	52	Saponines	102	EXPLOSIVES
3	Lead	53	Gums and resins	103	GASES
4	Mercury and amalgams	54	Waxes	104	Celluloid and synthetic ivory
5	METALLIC ALLOYS	55	SOAPS AND ETHEREAL SALTS	105	FIXATION OF ATMOSPHERIC NITROGEN
6	Metallic vapors	56	PURINE and PYRIMIDINE BASES	106	Paints
7	Rare elements	57	Nucleo-proteins and nucleic acids	107	Stains and preservatives
8	Radioactive elements and minerals	58	Biliary substances and pigments	108	Corn, sorghum and sugar beet products
9	Inorganic acids	59	Humins and humic acids	109	Grain, rice and potato products
10	Inorganic salts	60	ESSENTIAL OILS	110	Seeds and seed germination
11	METAL PRESERVATION	61	VEGETABLE OILS (DRYING)	111	Hemp, flax, and cordage materials
12	METALLURGY	62	VEGETABLE OILS (NON-DRYING)	112	Paper
13	Metal plating	63	Varnishes and wood preservatives	113	Marine vegetable products
14	Storage BATTERIES and DRY CELLS	64	Organic sulfur derivatives	114	Marine animal products
15	SILICATES	65	Lipoids and phosphatides	115	Forest products
16	GLASS and QUARTZ GLASS	66	VEGETABLE PROTEINS	116	Fruit products
17	INORGANIC COLLOIDS	67	ANIMAL PROTEINS	117	Desert plant products
18	ORGANIC COLLOIDS	68	POLYPEPTIDES	118	TROPICAL PLANT PRODUCTS
19	CARBON and CARBIDES	69	AMINES and AMINO ACIDS	119	Silk and silk by-products
20	ORGANO-METALLIC DERIVATIVES	70	Albinoids	120	Packing house by-products
21	CLAY and CERAMICS	71	Organic halides	121	Sewage utilization
22	PORCELAIN and GLAZING MATERIALS	72	Chlorophylls	122	Fuels and smoke abatement
23	Aliphatic hydrocarbons	73	Vegetable coloring matters	123	Cements and building materials
24	BENZENE and CYCLIC HYDROCARBONS	74	Animal coloring matters	124	Asbestos and mica products
25	PHENOL DERIVATIVES	75	VEGETABLE ALKALOIDS	125	AERONAUTIC MATERIALS
26	ANILINE DERIVATIVES	76	Animal poisons and venoms	126	Fire extinguishers
27	TRAPPENS	77	Tannins and tanning materials	127	Animal metabolism
28	Alcohols	78	Animal fats	128	Catalysis
29	Aldehydes and ketones	79	FISH OILS and FISH PRODUCTS	129	Dental supply products
30	Unsaturated aldehydes	80	RUBBER	130	CHEMICAL CRYSTALLOGRAPHY
31	Organic acids	81	SYNTHETIC RUBBER	131	Photographic materials
32	Cyanogen derivatives	82	Synthetic leather	132	Photographic reproduction
33	ANTHRACENE DERIVATIVES	83	Synthetic dielectrics	133	Color reproduction
34	QUINOLINE DERIVATIVES	84	Uric acid derivatives	134	Chemical dynamics and equilibrium
35	ALIZARINE DERIVATIVES	85	Camphor and synthetic camphor	135	Electrochemistry
36	Indigo derivatives	86	ENZYMES	136	Electrical conductivity
37	PYRIDINE and HETEROCYCLIC COMPOUNDS	87	Antibodies	137	Thermochemistry
38	Pyrene derivatives	88	Bacterial chemistry	138	Odor chemistry
39	DIAZO COMPOUNDS	89	Blood and lymph	139	Low temperature chemistry
40	Monoses and dioses (Sugars)	90	Normal and pathogenic sera	140	High temperature chemistry
41	Polyoses (Sugars)	91	ANIMAL SECRETIONS	141	Water, hydrates and hydration
42	GLUCOSIDES	92	Vegetable exudates	142	Solubilities
43	Starches, dextrans and complex carbohydrates	93	Antiseptics and disinfectants	143	Molecular weights
44	Cyclones	94	Anesthetics	144	Spectral chemistry
45	Pectines	95	MEDICINAL PLANTS	145	Infrared and ultraviolet photography
46	CELLULOSE DERIVATIVES	96	Toxicology	146	Plant metabolism
47	Stearines	97	Dairy products	147	FOODS
48	Nitrogenous glucosides	98	Legumes and grasses	148	DRUGS and PHARMACEUTICAL MATERIALS
49	Bitter principles	99	PETROLEUM	149	Sanitation and disease prevention
50	Vegetable mucilages	100	COAL TAR	150	Atomic morphology and atomic weights

hooves us to learn this lesson quickly lest Belgium's and Russia's fate befall us.

President Wilson's careful interpretation of the signs of the times and of the significance of current developments across the water makes him blow the bugle for preparedness. He is perhaps better able from his exalted position than any other American to peer into the war cloud on the horizon and tell of its foreboding to this country. On the other hand, we could scarcely point to a more ardent supporter of peace on earth and good-will among men than he. It would be well, therefore, at a time like this, to sacrifice political views and prejudices for the one fundamental principle of loyalty to our country.

In the matter of national defense a big step forward has been taken through the creation of the Naval Advisory Board. It is now to be hoped that wise and conservative plans will be made and that the recommendations offered by the Board will receive adequate legislative support. America has gained recognition for the excellence of its chemical work in several different fields, but if we are to compete with Europe and hold a leading place among the nations we must extend this excellence to many more departments; and in order to do that, there must be coordination of the research work and a more intimate coöperation by the manufacturing and commercial interests of the country. Speaking of this coöperation, it should be said that Professor Charles H. Herty, President of the American Chemical Society, has discussed this subject in a very clear and masterful way in the October issue of *The Journal of the American Chemical Society* and it would be well for every chemist, as well as every "captain of industry," to read his article.

#### NEED FOR GOVERNMENT RESEARCH INSTITUTION

As for coördination of chemical research I would say that after several years of thought upon the subject the following hypothetical plans for a large government institution for chemical research have gradually been evolved. By an act of Congress provision should be made for the establishment of an institution

for chemical research composed of 50 major departments and 100 minor departments comprising about 50 buildings, to be located near one of the larger cities of the country. Each of the major departments should be composed of a chief chemist, 4 associate chemists, 8 assistant chemists, 5 laboratory helpers, 2 stenographers; and each of the minor departments of one chief chemist, 2 associate chemists, 4 assistant chemists, 3 laboratory helpers, and 1 stenographer. The total working staff of the institution would then be 150 chief chemists who should constitute the administrative council, 400 associate chemists and 800 assistant chemists. There would also be 550 laboratory helpers, and 200 stenographers, making a total of 2,100 persons, exclusive of the force in the adjunct departments. The character and importance of the work should determine whether it would constitute a major or minor department. Certain lines of work might be started as minor departments and when conditions and results warranted, changed to the major form.

The major and minor departments suggested as a preliminary working basis are listed in Table I, the major departments being printed in capitals. In addition to the research departments there should be the following adjunct departments: a department of supplies, a department of glass-blowing, a department of publications, a department of standards (for weights, measures, thermometers, barometers, etc.), a machine shop and a testing laboratory for chemicals and reagents.

The research departments enumerated may be considered as only tentative suggestions which could be changed and revised by representative committees for that purpose. It is seen that various departments merge into one another and no sharp dividing line can be drawn, but this is true in almost every realm of nature and it therefore becomes necessary to affix certain arbitrary boundaries.

To get an idea of the approximate initial cost of founding an institution of this magnitude the estimates in Table II are given. It is considered that 500 acres of land would suffice;



which could perhaps be obtained for \$1000, or less, per acre. The 100 minor departments would be housed in 25 buildings, making four departments to each building and 25 major department buildings of approximately the same size, each providing for two major departments.

An estimate for the annual running expenses of the institution at maximum salaries is also given in Table II.

TABLE II. INITIAL COST OF FOUNDING INSTITUTION

	Rate	Total
Cost of land		\$ 500,000
Cost of 50 buildings	\$350,000	17,500,000
Equipment of 50 buildings	150,000	7,500,000
Buildings and equipment for adjunct departments		1,500,000
Cost of departmental libraries		1,000,000
		27,500,000

## DEPARTMENT SALARIES

	MAJOR			MINOR		
	Rate	No.	Total	No.	Total	
Chief chemists		1	\$ 6,000	1	\$ 5,000	
Associate chemists	\$2,500	4	10,000	2	5,000	
Assistant chemists	1,500	8	12,000	4	6,000	
Laboratory helpers	900	5	4,500	3	2,700	
Stenographers	1,200	2	2,400	1	1,200	
TOTAL PER DEPARTMENT PER YEAR			\$34,900		\$19,900	

## SUMMARY OF ANNUAL EXPENSES OF INSTITUTION

SALARIES: Director (elected by the council)	\$ 10,000
50 major departments at \$34,000	1,745,000
100 minor departments at \$19,900	1,990,000
50 glass-blowers at \$1,200	60,000
100 other employees at \$1,200	120,000
SUPPLIES AND INCIDENTALS:	
50 major departments at \$15,000	750,000
100 minor departments at \$8,000	800,000
Miscellaneous expenditures	200,000
TOTAL ANNUAL EXPENSES	\$5,675,000

No doubt many of the details of the organization and sources of expense would be encountered that have not been included in this brief summary, but as mentioned before, it is intended only as a basis for something tangible along a more hopeful and promising line of national progress.

The greatest difficulty will be in filling the various research positions, but this would not necessarily have to be done immediately. A good live nucleus would soon build an efficient working force around itself, and an institution of such gigantic proportions would inevitably stimulate research in every other institution in the country and be a source of unprecedented national development for peace as well as for war.

It would be the brain of the chemical nervous system of our body politic, and would coordinate the widely scattered chemical research ganglia. This could be accomplished at an annual cost of less than one-half the cost of a modern battle cruiser. There would be no popular or political influences brought to bear upon such an organization and the sole qualification for every member of the staff would be merit.

The institution would not only discover principles and things in nature but it would discover men,—men whose power would set the elements in commotion, and cause accepted theories to tremble upon their foundations; but who, without such opportunities might never produce a ripple on the placid stream of public consciousness. Each member would have the advantage of expert counsel in practically every other field of chemistry, and the close association and interrelationship of departments would have a stimulating effect upon the personnel and work of the entire organization.

Efficiency and economy could be secured in ways which are impossible of attainment in smaller and widely separated institutions.

No systematic research work is now being carried on in this country in the larger number of the departments here enumerated although every one of them offers a fertile field for investigation. One could not determine in advance which department is likely to yield the most important results. The biggest surprises are likely to come from directions least expected.

One entirely new field for investigation has been suggested, namely, odor chemistry. Since odor particles are so characteristic it would seem possible to study their penetrability

through media, their absorptive or adhesive properties, their deflectibility in electromagnetic and electrostatic fields of force as well as the influence exerted upon them by temperature. Odorless compounds may send out characteristic odor particles that are beyond the range of the olfactory nerve even as there are ether waves beyond the range of the optic nerve and sound waves beyond the auditory nerve. A more rapid system of qualitative analysis might be worked out along this line.

While working upon certain extracts of water hemlock the author has made several startling observations. In drying a small portion of one of these products in a desiccator it suddenly exploded with such violence that the 9 inch Hempel desiccator was blown to dust. Another product from the same plant was found to ignite spontaneously in the air at a slightly elevated temperature, and who is able to say whether these or similar discoveries might not result in commercially valuable products if they could be followed up with that end in view.

Even if a smaller institution than the one here proposed were founded it would doubtless serve a very useful end, and in the course of time develop along the more important lines. It is not improbable that the industrial concerns would recognize the value of such coordination and would endow certain departments of the institution through which they would be directly benefited.

Enough has been said to start the refrain if the idea possesses some intrinsic value. This lump of earth, after being sifted through the press and cupelled by our leading chemists, might leave a residue, which, when alloyed with the proper elements, and then passed through the legislative machines, might produce a filament that will glow and sparkle when a current of American energy and patriotism is passed through it, shedding light into all the world.

UNIVERSITY OF NEVADA, RENO, NEVADA

ON COAL-TAR COLORS, AND THE HALL PROCESS OF MANUFACTURING GASOLINE FROM "GAS OIL"<sup>1</sup>

By C. F. CHANDLER

I have a program here before me and notice that there are five papers to be read to you this evening, so it is eminently proper that I restrain myself, and consequently I am going to say but a very few words to you.

In the first place, I may say that this dyestuff subject has interested me from the very beginning, and when I say from the very beginning I do not speak of the year 1856, when Dr. Perkin discovered mauve. You may remember we gave him the Perkin Gold Medal, created the medal, and gave him the first impression of it, because, as we always say, he discovered the first aniline color, which is quite true; but the first coal-tar color was discovered in 1771, though it was not made from a coal-tar product. It was obtained by a chemist by the name of Woulfe, who treated indigo with nitric acid and obtained picric acid; so this picric acid, which we read so much about just now, is really the first synthetic dyestuff that was ever invented. It was made from indigo. Afterwards it was prepared from several other materials; Laurent, the French chemist, prepared it from the carbolic acid of coal tar in 1841.

My first acquaintance with coal-tar colors was in 1854-5. My fellow student, Evan Pugh, who occupied the table next to me in the laboratory of Friedrich Woehler in Goettingen, was engaged in making investigations on picric acid, and we learned at considerable risk that salts of picric acid were liable to explode, for it happened more than once that solutions of picrates which were left on the sand bath to evaporate, exploded, blew out the doors of the sand bath and scattered the sand all over the laboratory. That was the first experience I ever had with a coal-tar color.

<sup>1</sup> Introductory Remarks by the Acting Chairman at the Symposium on the Dyestuff Situation, New York Section, Society of Chemical Industry, Chemists' Club, October 22, 1915.

Woehler, you may recollect, was a pioneer in synthetic organic chemistry, having prepared artificial urea as long ago as 1828.

Dr. Perkin published the account of his preparation of mauve in 1856; a year or two afterwards, when I first became familiar with it, my assistant prepared a little mauve in the laboratory. Later there were a great many litigations over coal-tar colors and coal-tar drugs in this country. The United States gave a product patent as well as a process patent, and the consequence was that when differences arose among the manufacturers of England, France and Germany, they could bring their lawsuits into this country because we have a distinct and separate patent for a product, "a new composition of matter," and there were a great many such cases.

I think that my experience began more than forty years ago. I remember there were five lawsuits on artificial alizarine. Then Porrier & Co. brought lawsuits here on Rousseau's patents for azo colors derived from sulfanilic acid and naphthionic acid. That was an entirely new type of coal-tar colors; afterwards there were a great many other suits, and the consequence was that I made the acquaintance of several of the leading coal-tar color manufacturers abroad, and when I went to Germany they were extremely civil to me and I spent several days at Elberfeld, and as the guest of Dr. Bettinger, and visited the works several times. I have been at Frankfort and Hamburg as the guest of Dr. Ganz, then director of the works of Cassella & Co., have twice been to the works of the Badische Company, and have visited the works of Meister, Lucius and Brunning at Hoechst, so I have seen a great deal of the coal-tar color industry and have taken a deep interest in it.

Of course, I have read everything that appeared in the newspapers for the last six months on the subject of the dye shortage, a great deal of which interested me, a little of which seemed to be true or plausible, and much—well, that seemed very foolish.

I have thought a great deal about the possibility of making coal-tar colors in this country. Of course, we can do it. We never had any trouble in the laboratory at Columbia in taking any patent, working out the process and producing the dye, but then we did not expect to get our return by selling the product. That is a very different affair.

The growth of the coal-tar color industry has been enormous. In 1876, when we had the Centennial at Philadelphia, there was a superb collection of specimens illustrating the coal-tar color industry. It was shown by Friedrich Bayer & Company of Elberfeld, and I had the good fortune having been in their service in some of their litigations, to secure that collection for the Columbia University museum. Among other things they sent me two or three hundred copies of the catalogue of the exhibit, which are available for any one who will apply at the office of this Club. I think the list contains 160 specimens, including several specimens of coal, tar, etc. Thus the coal-tar industry was exhibited by one of the largest makers in the world in 1875.

I notice here that after describing the great inventions in the coal-tar color industry, they say there is another enormous problem: the artificial manufacture of real indigo. One of these days, they say, it will come; I believe you will see some here tonight. It is manufactured on an enormous scale at the present time. In looking over the catalogue you will see that they equipped their aniline works in 1862; consequently they have had the experience since 1862 to 1915, fifty-three years. The alizarine works were started in 1871, and they have had all those years of experience. In 1875 they had eleven chemists. Ten years ago, when I went through their works, they had three hundred graduates of the University, Doctors of Philosophy, trained chemists, research chemists. That is the way these great German establishments have been built up. The proprietors were willing to pay for knowledge and pay for

science. This catalogue was printed in 1875, and they had 14 in the administration office, they had 16 master foremen, they had 3 engineers, 28 smiths, machinists and firemen, 3 coopers, and 193 workmen. I did not count the coopers ten years ago, but they had 8000 workmen and 300 chemists. They built their original works in Elberfeld, where they are still working, but later they purchased a square mile on the Rhine, and that is covered with the buildings of the present establishment. I cannot help having my little joke. I read in the newspaper two or three days ago that a contract had been made by one of the new great coal-tar color companies in this neighborhood to erect a factory in Long Island City which was to be 40 ft. by 75 ft.

This book I have here is the first edition of Schultz and Julius' Catalogue of Colors, published in 1888, including all the commercial colors that Schultz and Julius could get, which numbered 278. This has gone through a great many editions; five German and three English editions. This is the last German edition, and it contains about 1000 commercial colors. I do not mean to say that that represents all there are. That simply represents the commercial colors of to-day.

Dr. Bogert whispered it in my ear a few minutes ago, that 50,000 different coal-tar colors have been described up to the present time. Several persons have asked me recently where they could get information about coal-tar colors. I referred them to the library at Columbia, and I referred them to the Chemists' Club library upstairs, but there is one book I must mention, which is extremely interesting to anyone who wants to interest himself seriously in coal-tar colors. That is the book published by Friedlander, which represents the progress in the manufacture of coal-tar colors. It gives an account of everything. There are no less than thirteen volumes, which cover the coal-tar color industry from 1877 to 1912 and give either the whole or the essential part of every important patent that has been taken out in that time. There is another work, and I brought it down here for the very reason that I saw by the program that we were to have two distinguished representatives of the United States Government here, and I want to ask them in your presence, in order to make my request more effective, to induce the Census Bureau to reprint No. 210 of the last census, which contains a list of all the chemical patents down to the date of this publication, which is 1902. All the coal-tar color patents, by a curious coincidence, which have expired are contained in this list, so any one going into the business of making coal-tar colors, if he wants to steer clear of patents, can select from these patents a great variety, of every shade of color. If the Government would complete this work down to date, including the whole line of chemical patents, and print enough copies to supply all chemists, and other persons interested, it would greatly aid our chemical industries.

#### HALL'S MOTOR SPIRIT

I feel it a duty, as well as a pleasure, on this occasion when the whole subject of coal-tar dyestuffs in America is to be discussed, to present, in a few words, an account of what William A. Hall, the distinguished inventor, who has his office in this building, has accomplished very quietly in producing motor spirit, benzol and toluol from crude petroleum or petroleum by-product oils.

Dr. Hall called my attention to his work early in 1913 and invited me to visit his experimental plant at Greenpoint. I did this several times and finally conducted some experiments myself to ascertain the nature and results of the new process.

We used, as our raw material, "gas oil" or "petrolite" of the Standard Oil Company, which sold for from  $3\frac{1}{2}$  to 4 cents per gallon. Its specific gravity was 44.5° Beaumé at 11° C., equivalent to sp. gr. 0.800 at 60° F. It boiled at 130° C. The products of the first passage of this material through the apparatus were as follows:



## PRODUCTS FROM 18.97 LITERS

1st—Motor spirit 5.2% Bt. at 11° C. Boils 26° C. (10.60 liters) . . .	55.87
2nd—Light residuum (6 liters) . . .	31.63
3rd—Heavy residuum (0.65 liter) . . .	3.42
Condensed liquids . . .	90.90
4th—Fixed gas . . .	46.5 cubic feet.

The 6 liters of light residuum were passed through the coil again, yielding 2.7 liters motor spirit.

## FINAL RESULTS

	Motor spirit Liters	Per cent
1st run—Motor spirit . . .	10.60	55.87
2nd run . . .	2.70	14.76
Total . . .	13.30	70.63

## EFFICIENCY TEST

Having satisfied myself of the practicability of the process, I then visited the testing laboratory of Mr. Joseph Tracy at Rutherford, New Jersey. Mr. Tracy had set up a White Automobile engine of 30 H. P., mounted on a Sprague Dynamo, with a Stromberg 1 $\frac{1}{4}$  Standard Carburetor not water-jacketed. The air was heated at the intake to facilitate the vaporization of the fuel tested. Each run lasted fifteen minutes. The machine indicates the revolutions per minute. It has a dynamo with an electrical brake. Its field is separately excited with adjustable resistance. The reaction of the casing was met by adjustable weights on a long lever, which measures the "torque," or the pull of the engine in foot pounds from which we calculate horse power and deduce efficiency of the oil as motor fuel.

We ran experiments alternately with Standard Gasoline sp. gr. 0.73 at 52° F. and Hall's Motor Spirit, at three different velocities, 1600, 1400 and 1200 revolutions per minute.

## RESULTS OF 15 MINUTE RUNS—GASOLINE

Revolutions per minute	Load Break	Pounds fuel used	Temperature Average Fahrenheit Water Room	Average horse power	Pounds fuel per horse power hour
1600	22.5–22	5.6	132° 54°	26.97	0.83
1400	25.5	5.57	139° 57.5	27.20	0.81
1200	28	5.54	141° 58	25.60	0.86
HALL'S MOTOR SPIRIT					
1600	21.5–22	4.95	137° 57°	26.51	0.74
1400	26	4.43	136° 57°	27.73	0.64
1200	28	4.21	149° 57°	25.60	0.65

Reducing these results to volume of gasoline and motor spirit efficiency:

At 1600 revolutions per minute, one gallon of Hall's Motor Spirit does the work of 1.18 gallons of gasoline.

At 1400 revolutions per minute, one gallon of Hall's Motor Spirit does the work of 1.34 gallons of gasoline.

At 1200 revolutions per minute, one gallon of Hall's Motor Spirit does the work of 1.31 gallons of gasoline.

There was no noticeable difference in the behavior of these two liquids either in the ease of starting, the absence of black smoke, or the soot deposits in the cylinders.

All that Mr. Hall claimed for his process was justified by the results of the experiments.

This investigation was made before the breaking out of the war on the Continent and consequently the importance of benzol and toluol was not realized and I made no experiments to ascertain what percentages of these substances were contained in the products of Mr. Hall's process.

## MR. HALL'S WORK IN ENGLAND

Owing to the comparative cheapness of Motor Spirit in this country, Mr. Hall concluded that Europe offered him a better field for his invention than did this country, so he went to London and on the 28th of October, 1913, he filed an application for an English patent for his "process for the production of Motor Spirit from heavy hydrocarbons."

The following quotations from his patent will indicate the character of the invention:

"This invention relates to an improved process for the production from heavy hydrocarbons of liquid fuels in the form of

motor spirit suitable for use in the usual carburetors of internal combustion engines."

"I take any cheap hydrocarbon, for instance, a distillate such as gas oil."

"I subject this hydrocarbon to a temperature of about 650° C., under a pressure of about 70 pounds per square inch in a suitable coil of pipe, whereby the oil is cracked and a considerable portion gasified. From this coil of pipe which I term the 'converter' the mixture of oil vapor and gas thus produced is passed through suitable coolers whereby the temperature of the mixture is lowered to about 200° C. and the mixture thus cooled is fractionally condensed in a suitable separator or separators with or without reduction of pressure. Those portions of the mixture nonvolatile at about 200° C., are thus extracted in the liquid state. The gas and the remaining fractions of liquid volatile at the approximate temperature of 200° C., may, if the pressure has not been reduced, be conducted directly through a cooler and condensed under the pressure of the converter, or if the pressure has been reduced in the separator may be re-compressed by means of any suitable mechanical compressor, and then condensed under pressure in the cooler."

## CLAIMS

"1. A process of producing a motor spirit from heavy hydrocarbon oil consisting in cracking the hydrocarbon oil at a temperature upward of 600° C., separating by fractional condensation from the product of the cracking operation, the gases and that portion of the liquid which is volatile at a temperature of approximately 200° C., and condensing together under pressure such vapor and gases to produce a liquid, substantially as described.

"2. Motor Spirit produced substantially as hereinbefore described."

This application was properly considered and the patent was granted on January 28, 1915, No. 24,491. Applications for patents are pending in several other countries.

Very little has appeared in the newspapers or scientific journals with regard to Mr. Hall's invention.

He did, however, on the 18th of February, 1915, read a paper before the Institution of Petroleum Technologists in London, in which he gave an account in brief of his process. A portion of this address was afterwards printed in *Engineering* and re-produced in the *Scientific American Supplement* (May 1, 1915).

The following is a brief summary:

"Hall feeds the oil at a rate exceeding 70 gallons per hour through small tubes of a total of 300 ft. in length, at some 50 to 75 pounds pressure. The apparatus is so worked that the speed of the vapor is over 5000 ft. per minute.

"The oil is first vaporized in a coil preheated in the flue by the waste heat of the products of combustion from the furnace.

"The temperature in the center of the tubular nest is about 550° C.

"The vapors then pass to a vertical pipe about 12 in. internal diameter and 12 ft. high, entering through a very confined space acting as a throttle and impinging upon a baffle. The speed of the vapor flow is thus reduced from nearly 6,000 feet a minute to a nominal rate.

"The temperature rises from 30° C., due to the conversion of the energy of speed into heat, notwithstanding the reduction of pressure from 50 to 75 pounds down to atmospheric pressure.

"Here a large amount of cracking takes place.

"This large tube is filled with small pieces of small tubing upon which any carbon formed is deposited.

"The vapors pass from this receptacle through dephlegmators which separate all fractions boiling above the chosen point of cut.

"The uncondensed vapors and gases pass then to a mechanical compressor working under 70 to 100 pounds pressure per square inch and then through a cooler at this pressure where they are condensed to Motor Spirit, the uncondensable gas being passed on to a holder."

Mr. Hall emphasizes the special advantage of this process for Water Gas Companies, as they would be enabled to employ the permanent gas and the heavy fractions of oil as enrichers, and sell Motor Spirit as a by-product.

## HALL'S PROCESS IN ENGLAND

Soon after Mr. Hall's arrival in England, he set up an experimental plant and caused investigations to be made by several of the most distinguished chemists and engineers in England, among whom were Sir Boverton Redwood, Professor Vivian B.

Lewis, Mr. W. R. Ormandy and J. S. Critchley. These investigations resulted in demonstrating the value of the invention. Mr. Hall then erected a large working plant of a capacity of 6,000 gallons of Motor Spirit per day. This plant was taken over by the English Government and is in full operation, yielding about 6,000 gallons of spirit daily.

Professor Redwood found that the spirit contained over 10 per cent of toluol and 8 per cent of benzol, and on some occasions, much larger percentages of these valuable products have been found.

In May or June last, Mr. Hall contracted to erect a large plant to produce Motor Spirit and toluol for one of the large Light and Coke companies in England.

He is now setting up works in other parts of Great Britain and also a plant for manufacturing 9,000 gallons of spirit per day on the continent.

#### CONCLUSION

Evidently there should be no fear of a shortage of supply of Motor Spirit, benzol or toluol when Mr. Hall can take any crude petroleum or petroleum by-product oil and get these three products on a commercially successful scale.

As you will now listen to several distinguished experts on the question of establishing a permanent coal-tar dye industry in this country, I shall refrain from expressing an opinion on that subject.

COLUMBIA UNIVERSITY, NEW YORK

### THE AMERICAN COTTON INDUSTRY AS SEEN BY THE INDUSTRIAL CHEMIST<sup>1</sup>

By FREDERIC DANNERETH

#### THE COTTON MARKET

On September 28, 1915, the price of raw cotton on the New York Cotton Exchange stood at 12.75 c. per lb., and on October 4th, January cotton sold at 12.87 c. per lb. with the bulls in full control of the market. This is the broker's way of saying that the crop is to be small. The weekly weather report stated that "the picking of the cotton would be favored with good weather. In Oklahoma the crop is ripening slowly and in Texas, the boll weevil is destroying the young bolls, resulting from late growth." On September 30th, it was reported that the Gulf hurricane had destroyed large areas of cotton in Alabama and that the shedding caused by heat and drought had caused heavy damage in the Carolinas, Georgia and Tennessee. On October 1st, the *Giles* cotton report stated that "adverse weather, insect damage, and an early exhaustion of the plant due to lack of fertilizer are causing extensive deterioration." On October 4th, the Crop Reporting Board of the United States Department of Agriculture stated that the yield per acre would be about 168 lbs. and the total production of cotton in our country in 1915 would be about 10,050,000 bales. If this be true it will mean the smallest crop since 1909. Last year the production reached the unprecedented figure of 16,135,000 bales.

In the eastern portion of the cotton belt the crop has been markedly affected by drought, periods of excessive rainfall, cold weather, and poor fertilizers. In the southern belt, September was warm and dry and the picking of the bolls progressed rapidly so that the ginning has advanced remarkably well.

The bumper cotton crop of 1914 together with the curtailment of commerce due to the European struggle, resulted in a complete slump of the cotton market. Producers were glad to get rid of their crop at 8 and 9 c. per lb. And when the surplus threatened to reach the figure of eight or ten million bales, southern congressmen and southern newspapers instituted a most novel campaign. "Buy a bale of cotton" was the phrase

<sup>1</sup> Address before the Connecticut Valley Section of the American Chemical Society, October 9, 1915.

on every lip, and the President of the United States placed his approval on the movement by purchasing a bale at the arbitrary figure of 10 c. per lb. Although the movement started in the mind of one man in Atlanta, Georgia, it spread like wild-fire through the country and the south was saved, fortified and enriched. This movement was the one thing which strengthened the confidence of the producers and disarmed the speculators in 1914. It was universally claimed that the south was planting too much of her land in cotton and farmers were promptly warned that they must reduce their acreage. Bankers were asked to refuse loans to farmers unless they promised to convert part of their cotton area into food crops and cattle raising. One writer suggested that a great cotton spinning industry should be developed around the water power plants of the Blue Ridge mountains. This would require a big selling organization, that had as much scope as its English competitors, to distribute the product of these mills. With such an organization it would be possible to keep our raw cotton at home until we were ready to ship manufactured goods to all the world. We do not at this time possess an effective sales organization for all our mills, and the result is that England is making more profit than we are, off our own raw cotton. England is in fact buying our raw cotton and selling to us the finished cotton goods. She is fighting quite as hard to keep her stranglehold on the cotton market as she is to end militarism in Europe. The opportunity is ripe for the United States to satisfy a world need of cotton goods and find a market for its raw cotton within its own boundaries. To do this more cotton mills must be organized and they must be well organized. The problem does not loom in its full size at first sight. We respond to an apparent necessity but we are incidentally becoming a world power without an effort.

On November 30, 1914, the famous "Cotton Loan Pool" was organized. It provided for loans on middling cotton at the rate of 5 c. per lb. The purpose of the "pool" was to enable the cotton growers to loan money, with cotton as the basis for credit. The pool was organized by the Federal Reserve board and a group of bankers. Its subscriptions reached \$135,000,000. This event, together with the passage of the Cotton Futures Act, are the two notable features of the year 1914 in the marketing of cotton.

On March 15, 1915, the British Government informed the United States Government that it would not permit American cotton to be sold to any country other than England and her allies. This represents one of the most unique experiments in the regulation of our commerce ever tried by a foreign power. Our Secretary of State in a note of protest dated March 30th, stated "this is a practical assertion of unlimited belligerent rights over neutral countries within the whole European area, and an almost unqualified denial of the sovereign rights of the nations now at peace."

In my present paper I am endeavoring to paint for you a picture of the cotton industry of our country and the opportunities which it offers to the industrial chemist. It has been suggested to me because of the partial paralysis of the industry, and I have pointed out to you some of the reasons why it is in this critical condition. It is not our business at this time to say whether or not the regulation of our commerce with neutral countries by a foreign power, is illegitimate.

#### U. S. COTTON TRADE

In the year 1913, the United States exported approximately 10,000,000 bales of cotton of 500 lbs. gross weight, and we imported 250,000 bales. In addition to this we have imported from England immense quantities of spun cotton yarns and cotton fabrics. In other words, we have conceded to foreign spinners the right to spin and weave out cotton for us. This is no arraignment of the English cotton manufacturer for he has



done his work well, and the fact remains that to-day some of the finest yarns and fabrics come to us from English factories. The problem before us is rather this: How can we make our American cotton industry more "self-contained?"

The U. S. Department of Agriculture in 1909 took a step of preëminent importance to the cotton industry. It established standards for the classification of cotton. In years past it had been customary for each cotton exchange to establish and trade on its own standards. The result of this was that such terms as "middling," "middling fair" or "strict middling" had widely different meanings in different trading centers. The Department has also been active in the matter of planting Egyptian cotton in our country. This seed was introduced into the Yuma region of Arizona in 1911 and similar experiments are under way in the Imperial Valley of southern California. After several years of acclimatization and breeding, superior strains have been developed. Excellent crops have been raised and the fiber has brought prices in advance of imported Egyptian cotton. The work which is being done on improving the length and the strength of the fiber will, however, be of little avail until the producers of cotton take care of their product. This means that the uniformity of varieties must be preserved, and furthermore long staple cotton must be kept entirely distinct and apart from the lower grades. The dangers of irregular cross fertilization are too well known to require emphasis at this point.

In 1903 the Mexican cotton boll weevil (*anthonomus*) began to infest our southern cotton fields and to-day this insect pest has extended its fearful work to the very edge of Georgia. In addition to this most important enemy of the cotton plant, the Department has also recognized the cotton boll-worm (*Gelechia*). The boll-worm has in recent years attacked the long staple cotton grown in Egypt, and considerable quantities of this cotton are imported into the United States for conversion into automobile tire fabrics. The Bureau of Plant Industry has decided to keep out this pest at all hazards and with this in mind has decreed that all imported Egyptian cotton must, after Feb. 1, 1916, be sterilized by means of gaseous hydrocyanic acid. As this treatment is to be applied to the cotton while in the bale form, the penetration of the gas is probably incomplete in most cases. But even in those cases where the treatment is effective, there is considerable fear that the strength of the fiber will be permanently affected. When we stop to consider that a factory producing around 5000 automobile tires per day spends over \$1,500,000 per year on cotton tire fabrics, it can readily be seen that these manufacturers have a definite interest in the price and the quality of cotton. In addition to this there are the manufacturers of high pressure hose, and belting for conveying and power transmission. All these products require cotton duck of known strength. And the manufacturer who attempts to use cotton duck for these purposes without previously testing it for strength and moisture and other properties is undermining his own welfare. The production in the United States of long staple cottons having superior strength is to-day one of the principal problems which confronts the cotton grower.

#### THE INDUSTRIAL CHEMIST'S RELATION TO THE COTTON INDUSTRY

This brings us to the principal part of my paper, namely the relation of the industrial chemist to the cotton industry. At the planting end he has studied the soils and the fertilizers necessary to insure the best types of fiber; in the ginney he found the cottonseed and from it produced the oil which bears its name; in the soap industry he has utilized the waste from refining and has recovered the glycerin. He has hydrogenated the refined cottonseed oil and has thus produced a valuable cooking material. Following the seed through the mill he has waylaid the hulls, and has proved them to be valuable as cattle feed. More than this, he has demonstrated their value as

paper stock. Cotton-meal itself is to-day a well recognized feedstuff, and the "oily hogs" which are produced by a strong diet of this material are encountered in every pork-packing plant.

Although I have mentioned many of these achievements by name only, they represent industries which in our present condition are indispensable to us. The cotton oil exports alone in 1913, exceeded 35,000,000 gallons. Starting as waste products, or expensive by-products, they have risen to a commanding position in our national life, as a result of the technical skill developed by American industrial chemists. They have perfected methods for the production of cellulose nitrate (pyroxylin, soluble cotton, guncotton); the Germans have demonstrated to us the methods of producing plastic cellulose acetates; lacquers, photographic films and artificial leather are some of the commercial forms of these products, but the achievement of predominating importance is the production of a continuous filament from cotton linters by the use of chemicals.

This is the industry of "artificial silk" or luster-cellulose. Beginning with Chardonnet's pyroxylin process, manufacturers soon took up the cupro-ammonium process, and a factory using this process was in active operation for a number of years in Pennsylvania. Extensive investigations have been made on the use of cotton linters in this field, and at a price of 4 or 5 c. per lb. it is undoubtedly worth considering. Since about 1909, a plant for the manufacture of artificial silk according to the viscose process has been in active operation at Marcus Hook, Pa. This product is formed by the action of caustic soda and carbon disulfide on pure cellulose. This plant has always been owned and controlled by English capital. The world production of artificial silk is at present approximately 15,000,000 lbs., and this alone is a strong argument for the installation of further plants and the perfection of the process by organized development work.

In this great march of progress, the mother has somehow or other been "lost in the crowd." She has become a kind of chaperon, that which we must have with us in order to appear respectable in public, that which makes us eligible for polite society, the necessity whose choice is determined by our incomes rather than by our aspirations. I refer to the cotton fiber, itself, the fiber which clothes the poor man and warms the heart of the raw-cotton broker. The manufacture of cotton textiles in the United States offers to the industrial chemist opportunities to be compared with those in California in 1849. Our manufacturers have hung out the latch-string and will welcome trained, skilled, aggressive industrial chemists whenever they are willing to pay a call. Numbers of them have gone a step farther. They have trailed the chemist to his cave and demanded his advice and his opinion on the chemical problems of the industry.

#### THE BLEACHING PROCESS

Do you know that raw cotton fiber contains about one-half of 1 per cent of wax and fatty matter? A wax which fuses at about 86° C., and which has caused the cotton bleacher and dyer a lot of trouble? This is the principal reason why all raw cotton is "boiled-out" before it is bleached or dyed in pale shades. If you witness this operation in ten different establishments you will find the operation carried out in ten different ways, very probably. Caustic soda, soda ash, waterglass, Turkey-red oil, rosin, patent medicines and what not, are used. Some foremen use them all while others have specialized on a single one. But the thing which I am trying to impress upon you is this: the choice of the chemical assistants used in the operation is more often the result of chance than of accurate technical observation. The concentration of the liquor, the duration of the treatment, the condition in which the goods are kept during and after the boiling-out operation, the character of the vat in which the goods are boiled-out—all these are in many cases considered problems too technical for serious con-

sideration by a bleacher. Manufacturers of high, low and medium pressure kiers have told him that the particular kier which they make is undoubtedly good because it is used in some works in Europe, and he has purchased the machine. Mind you, the seller of the machine does not pretend to have any knowledge of the process, he simply says: "My machine is the right one for your work." The bleacher accepts this gratuitous technical advice because he considers professional advice too expensive for a plant such as his. He has become the victim of a tradition. Less than a mile from his plant is another bleachery—one operated on a modern basis. At this plant accurate observations are made on the whole operation: time, temperature and concentration of the liquor are carefully checked up. The foreman is instructed to handle his yarn or his fabric in a definite way and he is cautioned about rinsing and storing the finished goods. If we stop to consider that cotton may be bleached in seven different forms we begin to realize that this is a business where haphazard, empirical methods must soon be put away forever. Loose cotton, the sliver, cops and cheeses, yarn, warps, knit goods, and open width piece goods, all require special forms of machinery and special manipulation. The kier used for bleaching the loose fiber is obviously not adapted for treating yarn in skeins or piece goods in the open width, and so it is that the industrial chemist who enters this field must acquire an intimate knowledge of many types of machines. Not only that, he must quickly discover the defects which may be caused by one or the other types of machine. He must know the value of steam pressures and the defects caused by open-head steam. He must know, accurately, the properties of materials and the possible trouble which chemicals cause when brought in contact with cotton and metals—for this is a pronounced example of a chemical process. The fiber, the metals and woods used in constructing apparatus, and the special chemicals used in connection with boiling-out and bleaching, bring with them an endless chain of "troubles." In some cases the defect does not appear until the goods are sold over the counter in the department store. Take for example the case of a person who buys bleached knit undergarments. The goods have been bleached a good white and the "feel" of the garment is soft. It is purchased, worn and then laundered. When the garment comes from the laundry the first or the second time, small holes are observed in many parts of the garment and there is apparently no reason for them. The garment is returned to the store and then to the manufacturer. He in turn hands it to the bleacher for an explanation. The housekeeper, the department store, the manufacturer and the bleacher—all are puzzled. No one can find any obvious cause for the trouble and yet there it is, plain as can be. Finally, as a last resort, the textile chemist is called in by night-telegram. The incident just described is one of very frequent occurrence in our cotton knit goods trade, but it illustrates quite clearly the case of the bleacher who does not use chemical control in his plant. His competitor who is paying a few thousand dollars per year for this control is to all intents and purposes carrying factory and business insurance in order to prevent any sudden cancellation of contracts due to imperfect goods. And our large department stores have now adopted the policy of trading only with manufacturers who stand back of their goods. The responsibility is thrown entirely on the manufacturer.

#### MERCERIZATION

The mercerization process for cotton yarn and fabrics is at present being used by a considerable number of converters in our country. This was made possible by a decision of Judge Lowell, rendered in 1906, whereby the American patents covering the process were rendered null and void. The two essential conditions for mercerizing are that the yarn or fabric be treated with a solution of a caustic alkali and that the treatment take

place while the goods is under tension. With this as the basic principle, various modifications have been introduced for the purpose of producing a silk-like luster on cotton yarns and fabrics. Mercerized cotton batiste 40 in. wide, imported from Europe, is sold in our stores at \$1.25 per yard, while the best grade made in the United States can be had for 25 cents per yard! A similar difference in price is noticed in the case of mercerized embroidery yarns. Here is an opportunity quite equal to that which we noticed in the case of bleached cotton. The production of high-luster mercerized cotton has apparently never been attempted in this country, and at the same time we are importing large quantities of fabrics from Europe and selling them at more than \$1.00 per square yard. The strength of the mercerizing bath, the temperature and duration of treatment, the addition of this or that active substance to the bath, and the amount of tension applied during the treatment—these are some of the factors which should be given attention.

In more recent years, the luster of cotton fabrics has been improved by a process termed "Schreinerizing." This was devised by Dr. Schreiner of Barmen, Germany, and consists in calendaring the fabric by means of finely engraved metal rolls, with the addition of heat and pressure. By combining the processes of Mercer and Schreiner it is possible to produce a very superior luster, but there is still abundant opportunity for more extensive use of these methods.

In the field of printing considerable progress has been made in the United States, and the introduction of laundry-proof dyes has made possible the production of high-grade cotton prints for fine dress goods and men's shirtings. In some cases these colors are so "fast" that their subsequent bleaching in rag paper mills has become a serious problem. Thus we see that the skill and ingenuity displayed by one group of industrial chemists can be developed to the point where it causes another group, temporarily, serious discomfiture. But then, this is the very thing which should spur us on to greater achievements, to higher attainments. The original idea of applying colored designs to fabrics by means of engraved rollers has since been varied in many particulars. "Spray printing" was introduced about ten years ago but has never been used to any extent by us. In this process, sprays of dye solutions are played on the fabric according to a stenciled design. "Metal printing" has been attempted, but has met with limited success, as the powdered metals can not be made to stick to the fabric very tenaciously. The printing of designs on warps previous to weaving has not been used to any extent in the cotton industry. This process was intended to imitate the effect of a woven design, and has been successfully applied in the case of silk fabrics.

#### THE DYEING PROCESS

Finally, I would mention the dyeing process as one in which our industrial chemists have ample opportunity for applying their skill. In the beginning it was always called the dyer's "art" and the aim of the dyer was to make the coloring matter adhere to the fiber by any means available. If he knew of one hundred different substances he would try out one, two, or three of these—dissolve them in water and dip the cotton in this liquor with or without the dye. Sometimes he would keep on adding substances to the bath until the desired coloration was obtained. That being done he sometimes reasoned that all of these substances were necessary for accomplishing his end. And most of the recipes which we have from that period bear abundant evidence of this line of thought. The use of waste animal products was begun at an early date and continued until after the introduction of the coal-tar dyes, in 1870.

Turning to the more recent phases of dyeing, we find that it is to-day distinctly a science and a very important chapter in industrial chemistry. Each substance used in the dye-bath has a definite function, and the amount of each substance used has been very carefully calculated. This point is amply illustrated



in the process of producing insoluble azo dyes directly on the fiber. For example, in the case of New Turkey Red, the proportions of paraunitanilin and beta naphthol and sodium nitrite used in the baths, are based on the molecular weights of these substances.

The perfection of the dyeing process has gone hand in hand with the perfection of dyes. The problem of laundry-proof dyes, sun fast, washable, and weather-proof dyes, has been attacked by our colleagues in Germany with that pertinacity for which they have become famous. When your speaker in 1907 suggested to one large textile manufacturer that we should soon experience a public demand for *sun-fast* dyes, the idea was scoffed at, and yet to-day there are mills which stake their whole reputation on this very thing. The Orinoka Mills in Philadelphia have for a number of years been producing interior decorations which are for all practical purposes fadeless—and washable or laundry-proof shirtings for men are a well known article in high-grade furnishing shops. The sudden demand for “sun-fast” and “laundry-proof” colors on cotton goods has made it necessary to attack this dye problem more persistently than has ever been done before. What we need for this work is chemists with the German university type of training, as experience has shown that American colleges have given more attention to the chemistry of minerals and metals than to instruction in industrial organic research chemistry. This seems almost incredible as the field has been open to us since 1870. At that time the German investors were satisfied with a return of 10 per cent on their investment and in the year 1905 they were getting on an average 30 per cent return. Many American investors have hesitated about encouraging chemical developments as their investment does not yield a return quickly enough. This has been especially true in the dyestuff and textile industries. When the dyestuff stringency became acute I found that one textile manufacturer had been advised that dyes might be extracted from tomatoes, blueberries and pumpkins. It is very unfortunate that such advice is sometimes taken seriously.

#### THE TARIFF AND THE COTTON INDUSTRIES

Our American textile interests are hit by the war, not so much because of a low tariff and the much discussed “dumping” practice, but rather because we have been cut off from the conservative, painstaking, endowed, investigations of European chemists in the field of organic chemistry. A protective tariff frequently makes industrial development work unnecessary, because it eliminates the competition caused by foreign inventive skill. It places an import tax on goods skillfully produced by foreign experts. The Payne tariff bill at the earnest solicitation of American dyestuff manufacturers provided for a duty of 30 per cent on dyes and “intermediates” were admitted free. To-day we know too well the use which was made of this protection. How much money and skill were invested? How many new colors were manufactured since then? The tariff did, however, succeed in raising the price of Direct Cotton Black (an old American dye) from 17 cents to 28 cents per lb. Most of the contemplated increases in dyestuff production in the United States to-day are based on the assumption that the textile manufacturers will pay from five to ten times as much for a dye as they formerly paid. And the defense offered is, “our American industries must be protected.”

It might be well for us to adopt the European idea of making our products as good as any and better than most, instead of incessantly figuring out the possible momentary profits to be made. The “sun-fast” dyes produced abroad were not developed in one or two years—they are the result of 30 years of patient study and close observation.

To-day, opportunity is again rapping at our door, and our cotton manufacturers will soon have to decide whether it is better to plan organized development work now or to let our

competitors abroad keep their strangle hold on the industry. The development of the chemical processes in our American cotton industry will yield us greater dividends and more lasting dividends than any ammunition factory can hope to earn. The laurels to be gained in the pursuit of peaceful arts would seem to be far more enduring.

TEXTILE TRADE LABORATORY  
NEWARK, NEW JERSEY

#### SOME PHASES OF THE CITRUS BY-PRODUCT INDUSTRY IN CALIFORNIA<sup>1</sup>

By R. T. WHILL

Received June 21, 1915

The citrus fruit of California represents an invested capital of \$175,000,000. Annually 38,000 cars of oranges, 6,000 cars of lemons and grape fruit, representing as a total 1,232,000,000 lbs. of citrus fruit are grown and shipped from California to eastern markets. Only the best fruit is selected for the eastern markets and the “cull” fruit is valuable (1) as an insurance for a clean pack and a delivery of fine fruit; and (2) whatever value may be derived from its utilization and manufacture into citrus by-products. Estimates of the amount of fruit available in California for the manufacture of citrus by-products vary from 1 to 5 per cent of the total shipments, *i. e.*, 12,320,000 to 61,600,000 lbs.

Since this fruit is blemished on the surface or skin only, its characteristic qualities are quite the same as the more perfect fruit, which is packed and shipped. Its appearance and susceptibility to the action of mold and decay are the only factors which prevent the shipment of the “culls.”

#### BY-PRODUCTS INDUSTRY NECESSARY

The average returns to the grower of citrus fruit have not been entirely satisfactory. He has seen on one hand a large production in his orchards at times when market prices were very low; and he has also seen the amount of fruit he has taken to the packing house and on his tally sheet the amount of fruit he has been paid for. This difference, amounting to almost five per cent, has not only been a source of loss to the fruit grower, but has also been a source of expense to the packing house in getting rid of the cull fruit.

The first and most natural thought seems to have been to make this cull fruit valuable instead of hauling it to the dump to decay. And again, the first impulse has been to manufacture this fruit into something which would be in demand on the market, *viz.*, marmalade. Marmalade seems to be the least harmful and the most easily manufactured product, being familiar, as we all are, with the English product used to considerable extent in this country. To be sure, the English marmalade is made from bitter Seville oranges, which we do not raise here; but this is quite aside from any calculations; and we proceed to manufacture marmalade by the ton, with the result that the market is soon overflooded with a product that is unfamiliar to the average taste, and which is sweet and not bitter, and demands a price equal to, if not greater than the English product. The average layman and fruit grower has been unfamiliar with the vast number of citrus by-products imported into this country and their financial value. He looks only to the immediate future, and does not examine the details of a possible industry, as we, as chemists, must necessarily do. At this point the chemist and chemical engineer is called in to be confronted with vast quantities of waste fruit to be worked into easily saleable manufactured products.

Commercial manufacture of citrus by-products began in National City (below San Diego), where a rather extensive plant for the manufacture of oil of lemon, citrate of lime, and citric acid was erected, about the year 1899. At the time San Diego

<sup>1</sup> Presented before the Southern California Section of the A. C. S., Los Angeles, March 18, 1915.

and National City were struggling with California's infant lemon industry, but, owing to considerable setbacks in the prices of fruit in eastern markets and foreign competition, they were forced to find other channels and means to market the fruit raised. The National City plant was, in fact, over-complete in many respects, and included a great deal of machinery of an expensive character. After operating for but a short time, the plant was closed for lack of sufficient capital and for certain other reasons, the principal ones of which seem to have been a very poor quality of distilled lemon oil, selling 50 cents below the imported article, an inferior quality of citric acid, and considerable losses in the process of manufacture. Furthermore, the plant was not designed along modern economical lines so that its efficiency was very low, making the initial cost of by-products at the factory too high.

Shortly after this plant closed the newspapers heralded Los Angeles as the coming seat of a tremendous industry—the citrus by-product; the product to be made was lemon juice preserved with all its original characteristics for household and numerous other uses. In fact, one of the most amusing half-hours I have spent was in reading the prospectus and pamphlets of this corporation, setting forth the various applications of lemon juice. I was greatly surprised to learn that lemon juice not only promoted the growth of hair on the head, but also could be used, with the proper mixture of ingredients, as a furniture polish; but as I have never tried either, I am still unable to give any expert opinion as to its merits, for these purposes.

Several car-loads of lemon juice were packed in bottles of various sizes and shipped to eastern points, where it met with considerable favor except for the fact that after a few weeks on the shelves of a store it spoiled, and the promoters of the Company found themselves with thousands of bottles subject to their order at different distributing points, and their capital invested in considerable quantities of worthless machinery.

Although this so-called "Discovery" of the preservation of lemon juice was heralded throughout California over ten years ago, up to this day we have all had to admit defeat in preserving this juice successfully.

The next phase in the development of the industry was the first real step in the right direction. Realizing that over 98 per cent of all the citrus fruit oils used in the United States imported from abroad were made by hand-pressing methods and that these methods were not applicable to the economic production of oils from California citrus fruits owing principally to the lack of cheap hand labor, a corporation was organized in 1902 for manufacturing essential oils by means of a chemical solvent. Pasadena was the seat of this enterprise and from 1903 to 1907 some 5000 lbs. of lemon oil and about 5300 lbs. of orange oil were produced. During this period the National City plant again opened its doors, making the same products as before, but under new management and new chemists, only to close down again on account of lack of finances.

The Pasadena plant used the rind or skin of the fruits only, while the National City plant used the pulp of the lemon principally. Some juice pressed from the lemon pulp ordinarily discarded at Pasadena was shipped to National City for making citrate of lime. No disposition was made of the orange pulp whatever at the Pasadena plant, the sole product being essential oil. Both of these plants were handicapped by the one-sided character of product and a consolidation would have proven a benefit from both sides, in view of the fact that both had certain overhead charges against the products made, greater than selling prices of oils and citrate warranted.

The Pasadena plant finally closed its doors through lack of capital and poor management, and it would seem, considering the excellence of the process employed, that, if this plant had been in the heart of the citrus fruit country, and not in Pasadena, to which all the fruit used in the plant was shipped, it should

have been a success, even though the pulp of the fruit was discarded.

In 1904 a plant of considerable size was developed in Redlands, the center of the orange industry, where marmalade was made in large quantities and packed in individual glass jars. About the same time, in Riverside, a plant for the purpose of manufacturing orange wine was built, and a large quantity was made and stored in the warehouse, where, owing to lack of sale, it was allowed to remain until slowly disposed of. The orange wine plant was never a success owing to the one-sided product made. The rind of the fruit containing the essential oil was discarded, the pulp only being utilized. Again in Riverside, at about the same period, a plant was erected for manufacturing crystallized and candied citrus fruit peel, and after a short period of operation it closed, on account of lack of finances and the capital involved. Various other small plants of practically no consequence were opened up in different parts of Southern California, only to find some considerable drawback in the manufacture of citrus by-products.

The Redlands plant, during all this period and until 1913, continued to operate in a small and indifferent way, although the equipment was large enough to take care of a considerable volume of fruit. The Redlands corporation purchased the Pasadena plant, and moved it to Redlands, where they attempted to round out their production with oil as well as marmalade, using the whole fruit as was the logical course to all appearances.

The National City plant was then again re-opened during this period and failed once more, for the fifth time. It is quite remarkable the persistence of the San Diego people in maintaining what appeared to be a dead issue with them, at some considerable expense. More recently, a plant for manufacturing citrate of lime and lemon oil was erected at Santa Ana, and after a short operation moved to Riverside, where, owing to financial difficulties, it closed its doors.

#### PRESENT STATE OF INDUSTRY

The present situation represents three plants of considerable size: one at National City, one at Riverside, and one at Redlands, with about 5 other minor plants distributed throughout Southern California.

The question now naturally arises why, after almost fifteen years of continual effort in the direction of the perfection of processes and products from the manufacture of citrus by-products, we have not yet a stable and satisfactory industry. There are three reasons: (1) the citrus fruit grower has only recently realized the urgent necessity for utilizing his waste fruit; (2) in all new industries a certain amount of pioneering must be done, and in this process of pioneering many failures must be counted and charged off to profit and loss; (3) inefficiency, in its fullest sense, has been characteristic of all of the attempts made up to this time to utilize the whole culled fruit, which, after all, is the keynote of the matter. Manufacture of the oil of orange or lemon alone is insufficient to support the industry, overhead charges being too great where but a portion of the fruit is utilized.

The successful by-product industry must be founded upon five factors: (1) cheapness of fruit and its accessibility, *i. e.*, proper plant location; (2) economical and efficient machinery for the production of the products on a large scale by efficient processes; (3) complete utilization of the fruit so that there will be no waste; (4) conservative management of the business and ample capital; (5) a stable demand and an easy sale for the manufactured products at a sufficiently large margin of profit.

On one hand we see the Pasadena plant operating a one-sided process and although demonstrating that this could be done, financially the plant was not the success it should have been. We have the National City plant in much the same situation, while the Riverside plant is possibly coming closer to the ideal:



while I realize that many will not agree with me in these contentions, yet it would seem that they were the only logical ones to consider, taking all things into account.

Chemical control has entered into the production of citrus by-products to but a small extent because the promoters of most of the enterprises have thought either that such control was unnecessary, or that the money spent for competent supervision could be more profitably spent in advertising or in some other routine business way.

As Mr. Chase has already put before you in a former meeting characteristic phases of the by-product industry in Italy, I shall not draw any comparison between that industry and the California situation, except to note here the imports of citrus by-products into this country. The imports into the United States for consumption during the year ending June 30, 1913, were as follows:

PRODUCT	POUNDS	VALUE
Orange and lemon peel, candied, dry or preserved.	654,307	\$ 34,435
Oil of lime	13,075	16,025
Oil of orange	79,797	155,199
Oil of lemon	410,003	794,215
Oil of bergamot	64,259	310,135
Citrate of lime	5,526,954	756,309
Citric acid	8,677	2,915
Citron in brine	1,773,187	63,771
Citron and citron peel, candied, dried or preserved	515,686	41,219
Concentrated lemon, orange or lime juice	.....	116,572

These imports represent in actual fruit a total of 165,000,000 lbs., and it is not surprising that our efforts should be directed along the lines of the utilization of our culled fruit. We certainly have a large field to cover and I am looking forward to the time with much pleasure when we may fully realize our hopes for the citrus by-product industry.

One thing that the fruit growers require more now than ever before is a safety valve as an outlet for the fruit produced. So many thousands of acres of oranges and lemons have been planted during the last few years and are rapidly coming into bearing that the volume of fruit sold in the east can hardly grow in proportion to the production. The result seems almost inevitable that we shall have to be content with much lower prices for the fruit or else reduce some factor in the cost of production or shipping. As far as it would appear, the production of citrus by-products from the waste fruit would largely reduce this cost of production, and possibly even reach a point where nothing but the choicest fruit would be shipped east and all second-grade and orchard-run fruit be manufactured into by-products here.

#### GENERAL REQUIREMENTS OF INDUSTRY

Bearing in mind always that the cost of production of citrus by-products must be kept at the lowest possible point, the fruit from which the by-products are made must necessarily be as cheap as possible; placing a limit of possibly \$10 per ton on the fruit, 80,000,000 lbs. of fruit are available for manufacturing purposes. This fruit, as it is received, must first be examined and cleaned. This is best accomplished by means of brushes in the ordinary fruit-cleaning machine, together with such necessary water as the fruit may require, since adhering dirt and scale, while not always detrimental to the manufacture of the product, are not to be desired if they can be avoided.

Upon the condition of the ripeness of the fruit much depends as to the final product, especially in the manufacture of citrus oils. In the manufacture of lemon oil a green fruit gives an oil of the finest characteristics, and any fruit of whatever nature that has been subjected to a sweating process, or to slight decay or ageing, is almost wholly unfit for the manufacture of the finer products.

The next step in operation is to peel the fruit in some suitable manner or separate the pulp from the peel. The outer rind represents roughly from 20 to 25 per cent of the whole weight of the fruit, and contains the oil in a very finely divided condition spread throughout its spongy structure. The oil is separated

either by a chemical solvent or by means of centrifugals. The quantity of oil in the fruit depends on seasonal changes, and it may be interesting to note that during the last ten years the quantity of oil in the fruit has decreased, due, no doubt, to severe climatic conditions and possibly to certain influences of cultivation and irrigation of the trees themselves.

One of the greatest problems that has confronted the manufacture of citrus by-products has been a mechanical method for rapidly and completely separating the pulp from the peel in an efficient manner. Much time and money have been spent upon this phase of the mechanical side of the manufacture of by-products, and, although it has baffled many of us, I am glad to say that at present, at a merely nominal cost, it is possible to install a method of peeling citrus fruits on any scale desired, at a low cost.

To peel citrus fruit by hand requires the expenditure of \$5 per 2000 lbs. of fruit and this only under the most favorable conditions of labor and fruit. None of the older devices for peeling peaches and apples will successfully touch the rind of an orange, particularly if the fruit has wilted so that the skin is leather-like. The Pasadena plant referred to before practiced hand peeling with what is known as the Pomona knife; abroad, where a separation of the pulp and the peel is essential to the production of hand-pressed essential oil, the fruit is first cut into halves and then the pulp scooped out with a specially formed knife. As has been more recently discovered, the peeling of the fruit is not absolutely essential for the production of citrus by-products. The whole fruit is crushed between heavy rollers and then ground to a fine pulp from which the essential oil is extracted and the juice separated from this oil-free pulp by means of centrifugals. Other methods have also been pursued in crushing the fruit roughly and pressing in a hydraulic press; the resulting juice being mixed with a small proportion of oil is then subjected to centrifugal action; an emulsion of oil, juice and a proportion of the pulp not separable by filtering is formed.

#### SOLVENT PROCESS FRUIT OIL

For all purposes, we now have the peel separated from the pulp of the fruit. The peel used for the manufacture of oil is crushed between rollers to a fine pasty consistency, the lemon paste containing approximately 1.9 per cent of oil, and the orange peel containing possibly 2.2 per cent of oil for all practical manufacturing purposes. Theoretically the lemon contains twelve pounds of oil to a ton of fruit, whereas the orange contains sixteen pounds as a maximum. Seasonal changes and conditions of fruit largely govern the oil content. This pasty citrus fruit peel is now mixed with the proper proportions of a solvent, which dissolves out a portion of the contained oil. This solvent is run into suitable stills where the solvent is recovered, the oil remaining behind. A second, third or fourth extraction of the peel may be made, the solvent recovered in each case, until finally a liquid is obtained of a dark reddish color in the case of the orange, or a dark, yellowish green color in the case of the lemon. This is subsequently treated and purified to develop the perfect aroma of the orange and lemon.

For the purpose of comparing with the oil produced by this solvent process that produced by hand-pressing methods, we should note that foreign orange oil contains 93.4 per cent terpenes, limonene, 1.26 per cent of aldehydes, consisting of citral, methyl anthranilate and a crystalline ester melting at 65° C., 5.34 per cent of oleo resinous bodies, sesquiterpenes, while the oil manufactured by the solvent process contains 88.36 per cent terpenes, 1.28 per cent citral and aldehyde, and 10.36 per cent oleo resin.

We note, therefore, that the solvent process oil has five per cent greater weight of resinous bodies than the foreign oil, and





any considerable deterioration. This oil may be easily kept in white bottles, loosely corked in warm situations, and retains for many months its original characteristics. For the production of emulsion it is unsurpassed, giving to the emulsion its characteristic color, quite different from the color produced artificially or artificially added to the emulsions produced from foreign oils.

Another characteristic of these solvent process oils is their fixing quality. As we know, in all perfuming materials, in making mixtures for ultimate consumption, it is absolutely essential that some fixative be employed to prevent the rapid evaporation of more volatile bodies imparting the characteristics to the perfume. The same thing is true in essential oil. When foreign oil is mixed with some food material which is subjected to the action of heat, the final product oftentimes contains very little of the original flavoring body, and in order to produce sufficient flavor in the finished product larger quantities of this foreign oil must be used than is necessary to give the required flavor.

The resinous oils, containing as they do resins of such high melting points, and higher boiling points, tend to fix the flavor and characteristic odor in the finished product, and do not bake out or freeze out with the result that smaller quantities of these oils, compared to foreign, are required to produce the same flavor. These resins also seem to prevent the oxidizing action of the terpene on the aldehyde. In other words, they mask the effect of the reaction of oxygen, with the terpene as well as with the aldehyde, just as the addition of volatile bodies to citrus oils prevent the action of oxygen in a considerable measure.

In addition to the oil made from the peel, the peel is used for the manufacture of alcoholic extracts and tinctures. These tinctures are principally used by manufacturing chemists for mixture with various medicinal compounds. In some cases, the peel is dried, ground and extracted with cold or hot alcohol. In the U. S. P. alcoholic tincture, fresh peel is used; in the household, the essence of orange and lemon is largely used, and this is made principally from the oil.

If the foreign oil or the solvent process oil is subjected to properly regulated distillation, the terpenes may be separated, and we have what is known as the terpeneless oil. This oil is more soluble in dilute alcohol and is used very largely for the manufacture of extracts. The principal bulk of oil imported to this country is made into extracts and is used by the biscuit makers, candy makers and manufacturing chemists.

Next to the flavoring principle vanilla, lemon is perhaps the most widely used of all flavors. It is, therefore, not to be wondered at that some 400,000 lbs. of lemon oil are annually imported to this country, almost wholly for flavoring purposes. In California, unfortunately, as it first appears, the relative planting of oranges to lemons is about five to one; in other words, one acre of lemons to every five of oranges. While this ratio is being somewhat decreased by the more recent planting of citrus fruit, at the same time we are essentially an orange-producing country, and the chemist and chemical engineer must necessarily look to the development of such products as will utilize the bulk of the fruit available, which in our case is oranges.

The orange, on one hand, has far greater uses as a food, whereas the lemon has the greater use as a flavor, and as a condiment. The orange may be manufactured into almost an endless number of various products, while the lemon is necessarily limited to the production of essential oil, citrate of lime and citric acid.

#### PRODUCTS MANUFACTURED FROM CITRUS FRUITS

**ORANGE MARMALADE**—This product, which is most familiar to us in the form of the English marmalade, is essentially a cooked mass of sugar and fruit. In England the marmalade is made

of bitter Seville oranges. These oranges are received from the boat and after the necessary cleaning, the pulp and the peel are separated and the seeds extracted by special highly developed machinery, patented in England. The white pith adhering to the peel and containing bitter bodies, of which aurantium is the principal one, is separated from the peel, and the peel is then placed in large vats and subjected to steaming for a number of hours in order to soften materially and possibly drive off a portion of the essential oil so that the sugar in the after process of cooking may more readily penetrate and produce a transparent finished product. The softened peel is then run through a peel-shredding machine, which automatically cuts the peel into very fine shreds. The pulp meanwhile has been subjected to a thorough grinding process to produce as fine a division of particles as is reasonable and practicable. This pulp is then mixed with a proper proportion of shredded peel and placed in kettles for cooking. Some factories add sugar directly to this prepared mass, while others give a preliminary boiling before the sugar is added with water, in order to permit the sugar more completely to penetrate the peel and the fibrous bodies contained in the pulp. When the mass of orange peel has been subjected to boiling for some time with sugar, and the proper consistency is reached, it is placed in jars and sealed.

The characteristic of the English marmalade is its slight bitterness and its tart flavor; sugar being the cheapest ingredient in it, at approximately 2 cents per pound compared to our sugar at 4 and 5, the product is loaded with sugar in order to reduce the cost of manufacture to as low a point as possible.

We have not available the bitter Seville orange in California, and must content ourselves with the manufacture of so-called marmalade, in reality orange jam, on a large scale by very different methods.

The fruit, if cleaning is required, is cleaned and then sliced with what is known as the kraut cutter, which is simply a revolving disc upon which is screwed semi-circular knives which cut the fruit into slices. These slices are sometimes subjected to a preliminary soaking in water, but are more often placed in kettles with sugar and water immediately, brought to a boil and boiled until a proper consistency is reached. As the fruit is the cheapest ingredient entering into this product, the marmalade is loaded with fruit, although large consumers of this product in bulk usually specify 50 per cent sugar to 50 per cent fruit in the finished product.

The orange jam so made is rather a sweet mass not having many characteristics of the English marmalade. It has, however, certain uses, as in the manufacture of biscuits and the like. One nation-wide concern has used many cars of this orange jam in making a product similar to what we know as the fig newton.

By the proper methods, however, it is merely a matter of handling to produce a marmalade from the sweet orange very similar to the English product. This is accomplished by treating the fruit in the same way and with the addition of some more acid fruit, such as the pomelo or grape fruit, or lemon juice from the lemon.

One of the characteristics of the orange marmalade produced here, and differing from the English marmalade, is the fact that it jells very readily. In other words, it is a solid mass, rather than a syrupy mixture. This is due to the fact that the pectin or jellying body is developed very readily in the orange, whereas the foreign fruit is stripped of the white pith bearing the pectin and pectose body, and these consequently do not always enter into the product as an essential characteristic.

The combination of various fruits have also been made into marmalade, which have their own peculiar pleasant characteristics. The pomelo has also been made into marmalade quite extensively and has found favor as a competitor with the Eng-

lish marmalade on account of its inherent tartness and its slight bitterness.

Here in California, there are some twenty people making marmalade of various sorts, and there are possibly 100 more who make marmalade on a very small scale; these may almost be styled amateur producers.

**ORANGE PASTE**—Another purpose for which the whole orange is used is the manufacture of orange paste. This product is similar to the marmalade except that it contains less water and instead of appearing in slices, it is a ground mass of fruit cooked with sugar. This product seems to show great promise in its large use put up in bulk packages for certain types of biscuits.

**ORANGE JUICE** is a subject alone sufficient for a very lengthy paper, for so much work has been done without any real success up to the present time, that I will cover only the principal factors briefly. The orange juice is produced by two methods, either by squeezing the whole fruit and separating the oil by known methods, or by peeling the fruit and separating the juice from the pulp by intermittent or continuous presses.

For general consideration I will state that the preservation of orange juice has been the subject of research by many able men, notably Dr. Jokichi Takamine. The Department of Agriculture at Washington and the By-Product Experiment Station in this city, also the Experiment Station at Berkeley, have struggled with this problem in all its various phases, and to-day I know of no orange juice preserved in bottles which will remain unaltered in all its characteristics for three months on the shelves of a grocer, except perhaps the product produced by Dr. Takamine's process.

The problems confronting the preserver of the orange juice, are, to say the least, tremendous. In the first place, it is more a question of bacteriology than of chemistry, and it may be for this reason that Dr. Takamine has so far headed the list as a successful inventor of a process.

In my own researches on this subject certain things have been firmly impressed upon me. In my judgment, an orange juice which does not resemble almost identically the characteristic flavor, color and taste of the juice pressed from the fresh fruit, is not an orange juice at all. It is a comparatively easy matter to clarify an orange juice, bottle and preserve it and keep it indefinitely, but such a product is not orange juice in the truest sense, for it has not the color, flavor or taste comparable to that present in the fresh fruit.

I will therefore consider only the juice as a cloudy liquid of a characteristic orange color, and not the clarified juice which, to me, is an entirely different and an insipid product in comparison.

Orange juice as it is pressed from the fruit contains certain albuminous bodies, albuminoids in reality, finely divided portions of the pulp structure itself, sugar, acids, and such mineral salts as the fruit itself contains, together with the necessary water to give a characteristic specific gravity of about 1.03; the ratio of acid to sugar for the juice that tastes the best and is most palatable, to the majority of people, is 8 of sugar to 1 of acid. Here is the first limitation in the successful preservation of Washington naval orange juice, for it must be realized that only the most perfectly ripe fruit (not the least under-ripe or over-ripe) has this acid sugar ratio, and the period over which the fruit in this condition is at the very maximum  $2\frac{1}{2}$  months during the year. This must mean that even with a successful process for the preservation of orange juice, that the bulk of the product must necessarily be put up during this short period. Often this period is but a month, dependent of course upon seasonal conditions and climatic causes beyond reasonable control. But granted that we have unlimited quantities of the juice in the right stage of fruit development, the next step, and the stumbling block, is to preserve it. Pasteurization and

sterilization of this juice so far has proven the only factor controlling its successful keeping quality, and this at best is an extremely delicate operation. Sterilization of the juice by ozone has so far proven disastrous to final finish of product. The addition of sugar to this juice, even though its addition is declared on the bottle, does not necessarily insure its keeping qualities.

Our ideal of a juice is, of course, one to which nothing has been added, from which nothing has been abstracted, and in which nothing has been destroyed. To treat the juice without destroying its colloidal structure is, I believe, the key to its successful preservation.

Treatment with fluorides and ultraviolet rays, gasifying with various gases, the addition of essential oil, fermentation, oxidation and defecation of the juice, are some of the many stages through which the average research worker goes before he discovers that he is on the wrong track and finally gives up in despair.

The sense of taste and smell of many of those attempting to put out a delicate product oftentimes leads them on the wrong track, and gives them a satisfaction in believing that they have finally discovered what has baffled others. This sort of discovery is usually heralded through the papers as epoch-making in the citrus by-product industry. As a matter of fact, I do not believe that orange juice is in any measure a controlling factor in the success of the citrus by-product industry.

In considering the problems confronting us in the successful preservation of orange juice and lemon juice also, it seems fitting that we should emphasize here two things: first, the laughable, and at the same time pitiful, efforts of the more inexperienced chemist with a product; such as, for example, orange juice, produced by some known or secret process without fully and completely testing its merits and qualities. So many eastern brokers and distributors of California citrus by-products complain, and rightly so, that they can place no dependability upon the products they receive, and it is my opinion that the failure of the industry up to this point has been very largely due to this factor. The haste of the chemist to put a product on the market may not necessarily be an inherent quality of the individual, but possibly the anxiety on the part of his backers to get a return for the money invested as quickly as possible. Such methods are, of course, possible in certain well-tried and well-known industries, but where we are dealing with something so entirely complex and new, disastrous results are sure to follow, when tests of products under actual working and selling conditions are not carefully and conscientiously made.

Again, there is so much work that has been done in this field and so little has been published as to the results, that the chemist's observation is often his only guide in the perfection of his product. The capitalist is largely to blame for this reticence on the part of chemists to put before the public such data and information as to inform research workers and chemists in a similar field, that certain steps have been taken and certain conclusions reached. It would almost seem that a clearing-house of ideas or a registry of all important processes be kept by some disinterested organization such as this society, and an abstract of this information issued to those applying, giving perhaps the merest hint as to what has been accomplished, but certainly a real indication of what work has been done.

I find in examining the records of various chemists in the citrus by-product field, that they have covered much ground, and contemplate covering much ground in their schedule of operation, which has perhaps been done by many others. This would seem a needless waste of time and material. The secret process no doubt affords great protection in the actual or prospective capitalization of industries, and yet it seems quite a serious reflection upon us as members of the American Chemical Society to harbor this distrust of our fellow-members.

I fully realize that there are many reasons why the secret



process cannot be abandoned, at least in a reasonably short time. If we could but live up to the ideal of the patent law, we could give information to others in similar fields, feeling perfectly safe that they would not use such information without consent and credit to the original source. This is an ideal which I hope we may realize at some near future time.

The second factor which I would emphasize is certain qualifications of the research chemist. So much has been written regarding the qualifications and specifications, you might say for the industrial and engineering chemist, that I cannot help calling to mind the fact that the research chemist must not only have the ordinary qualifications of analyst, engineer and industrial chemist, but he must be most proficiently awake to a full sense of his responsibility. His judgment must be keen and faultless; he should be a psychologist and philosopher, and more than all else, he should have developed to the very highest degree a sixth sense—*horse sense*; this sixth sense is probably the most valuable developed asset which chemists can have, aside from the uncommon factor of accurate observation.

In stating these qualifications, it is not my intention to picture to you a super-man, but rather to indicate that we are perhaps too prone to specialize and remain in our own little rut. Do we read enough, see enough or hear enough, and finally absorb enough and lay this information away in our minds to be available at some future time? Are we broad enough to make ourselves the dominant and controlling factors in the manufacturing industries of to-day or are we to remain inactive because of the discrediting attitude of these industries?

I emphasize this attitude as characteristic of the research work in citrus by-products in California, and no doubt the same application can be made to an endless number of other industries in this country.

**LEMON JUICE**—To further take up the citrus by-product, lemon juice is the next in order. This juice while similar in characteristics to the orange, contains, of course, less sugar and more acid, and consists essentially of water, citric acid, and some other minor fruit acids, from  $3\frac{1}{2}$  to 7.6 per cent; sugar from 2 to 10 per cent and the usual mineral constituents; the sugar and acid content vary with the quality and characteristics and the ripeness of the fruit.

The squeezing of the lemon juice is carried on in an identical manner with that of the orange, and in efforts to preserve it the same researches have been carried forward, with perhaps more encouraging results, except for the fact that almost in all cases the juice has turned limey. In other words, a portion of the more volatile aromatic principles has oxidized and in some respects has made the juice unfit for the commoner uses.

It has been suggested that possibly the addition of sulfur dioxide in some form and in very minute quantities might be added to check the limey flavor developed on standing in this juice. My own experiments along this line seem to indicate that such large quantities of this gas are required that the use of enough to almost make a weak solution of sulfurous acid in juice, is required before any real effect is felt.

As the process of turning limey is purely one of oxidation, it would seem that any volatile reducing agent, without disrupting a colloidal condition when added in proper quantities, would prevent this change, and no doubt along this line the final solution of the problem will be found. From all angles the possibilities in lemon juice seem greater than in the orange. From the facts that the fruit ripens almost throughout the entire year and that the contents of acid and sugar can be easily controlled in this fruit, it would seem that this field has greater possibilities than orange juice for a consumption as food.

Lemon juice, of course, is the principal source of CITRATE OF LIME. This substance, as we have already noted, is imported in large quantities to this country, to be made into citric acid by eastern chemical manufacturers. The process of manufac-

ture is exceedingly simple. The lemon juice, subjected to rough filtration is run into properly lined vats, where it is heated to the boiling point, and the acidity taken. The proper quantity of calcium carbonate finely ground or in the form of rock or chalk is then added. The ensuing reaction being purely chemical, is tested at various points until a neutrality or a slight excess of calcium carbonate is determined, when the resulting mixture of water and insoluble calcium citrate is filtered by the proper means and dried.

The users of citric acid and the buyers of citrate of lime pay for this chemical on a basis of 64 per cent citric acid with a proportionate allowance for higher or lower tests, with a free chalk test bearing a penalty for every per cent in excess of two per cent.

As citrate of lime is imported into this country at a very low cost, and although its use is wide, for our consideration as a commercial possibility in California, it seems sufficient to state that without the necessary rounding out with other products, the production of this product alone is insufficient to maintain the industry financially, the margin of profit being altogether too small. We are forced to produce oil in connection with the citrate of lime in order that the fruit may bring a reasonable return to the grower.

**CITRUS FRUIT SYRUP** for use at soda fountains as flavors for various soda drinks, is comparatively a simple problem. With the essential oils at hand it merely becomes a question of mixing the proper quantity with the necessary volume of sugar syrup of certain strength, to produce a finished product, one ounce of which may be mixed in an eight ounce glass with the necessary ice cream and soda water. There are certain concentrated syrups, namely, orangeade syrup, which, in addition to having the flavoring of the orange, has its color. It is a curious thing that the home of orangeade is not California, and that the first orangeade was made from California oranges in Rochester, New York, where the manufacture of this product has developed into a considerable industry.

**CITRUS FRUIT PEEL** has been imported from abroad for many years for the purpose of manufacturing crystallized peel. The peel as it comes from abroad is packed in immense hogsheads in brine, from which the peel is taken and soaked in water for a certain period in order to remove the brine and then it is placed in a diluted sugar solution, the concentration of which is increased from day to day until a point is reached where the process of osmosis has been carried to a final point necessary fully to preserve the peel by means of sugar. It is then removed from the heavy sugar syrup and dried as a preliminary step, and is then sometimes dipped in a very heavy syrup, which, upon final drying, leaves a thick crust of crystallized sugar on the surface.

Glucose is often added to the sugar syrup in order that the product in its finished state may not dry out as completely as it would were sugar used alone. The lemon, orange and citron are the principal fruits used for this purpose.

We have in California but very few acres of citron. These are principally in Riverside, and while the production of these groves is prolific, the attempt so far made to manufacture candied citron peel, has not proved altogether a success in competition with the candied citron peel imported from abroad.

If orange juice is fermented under properly regulated conditions, a very excellent quality of vinegar may be produced. If the process of fermentation is arrested at a certain point a very palatable quality of orange juice, free from alcohol, may be preserved; and again, if the juice is subjected to filtration and clarification, before acetic acid fermentation has set in, it may be bottled as an orange wine with characteristic odor and flavor.

**SPECIAL PRODUCTS**—There are certain special products which I have left to the last, as they are really by-products of the by-products made from citrus fruit, bearing in mind that

they are not essential in any sense to the success of the by-product industry, but rather a final refinement of processes to which we must look in the future development of the industry.

PECTIN, pectose, or proto-pectin exists in unripe fruit or barely ripe fruit; but not in over-ripe or rotten fruits. Citrus fruits in general and the orange in particular should be a considerable source of this body. Pectose is converted to pectin by hydrolysis; pectin is in reality parapectin, and forms a colloidal solution in water, from which it may be precipitated by ethyl alcohol. Pectin is the body which causes gelatination when fruit is boiled in water to a certain concentration, and is permitted to cool; this body is not very different from ordinary gelatine, or from the vegetable gelatine, in its action and the body from which it is made, pectose, is almost entirely contained in the rind of the citrus fruit. In the extraction of the oil of the citrus fruit, this body remains, being insoluble either in organic solvents or in water; the exhausted peel when properly handled should give a colloidal solution of pectin, which may be easily concentrated into a solid product. This final product is then available for use as a jellyfier, just as gelatine is used to-day in the household and in certain of the arts.

If we are to charge the cost of production in citrus by-products against the main product, that is, the oil, etc., the cost of producing pectin from the residual waste of oil manufacture would leave a fair marginal profit for its recovery. There have been one or two attempts to exploit a process for recovering pectin from citrus fruit alone, but they have never come to any more than a paper basis, probably for the reason that the overhead charges against pectin, where this body is produced alone from the citrus fruit, are too great to make it a saleable product.

ALCOHOL—Bearing in mind that the average orange contains approximately 10 per cent sugar, in fermentable state, it is astonishing that we have not heard more regarding denatured alcohol as produced from this fruit. As a matter of fact, however, the yield is not sufficiently high to compete with alcohol made from other raw materials, much richer in sugar bases, and as the cost of production must be charged against the final product, alcohol produced alone would not be a financial success. However, it has possibilities, when worked in conjunction with other and more saleable products. In fact the principal scheme possibly to recommend in the case of the production of citrus fruit by-products, from oranges, would be the production of alcohol from the juice of the fruit rather than its preservation as a bottled beverage.

VINEGAR—This product seems to hold considerable possibilities for local consumption, or possibly for shipment to foreign ports, where the question of freight may be reduced to a minimum. The orange juice is very readily made into vinegar when proper regulation of fermentation is made, and it would seem that the lemon vinegar would prove a very satisfactory method of disposing of considerable quantities of waste lemons, in view of the fact that the bottled juice has not yet been placed upon the market as a successful enterprise.

HESPERIDIN, ISOHESPERIDIN, AURANTIAMARIN—Three glucosides exist in the rind of the orange, principally in certain conditions of the ripeness of the fruit. Aurantiumarin is the principle which gives the orange its bitter flavor; it is very similar to quinine in its physiological action and characteristics.

The results of researches and investigations up to the present time may be summarized as follows

#### A—UNCOMPLETED OR FAILURE:

- 1—Production of citric acid in orange juice by means of *Citromyces* mould.
- 2—Preservation of whole citrus fruit juices
- 3—Permanent citrus fruit oil gum emulsions
- 4—Continuous cooking machinery for fruit pulps, etc.
- 5—Aromatic constituents of fruit juices
- 6—Reaction of solvents on containers
- 7—Formation of constituting bodies of lemon and orange oil from terpenes

#### B—THOSE COMPLETED

- 1—Economic production of citrus fruit oils
  - a—By solvent process.
  - b—By centrifugals.
  - c—By water flotation
- 2—Manufacture of citrate of lime
- 3—Quick process for crystallized citrus fruit peel
- 4—Direct oxidation of sugars to alcohols without yeasts
- 5—Economic peeling process for citrus fruits
- 6—Terpeneless citrus fruit oils.
- 7—Soda fountain syrups—orangeade, etc.
- 8—Breaking complex oil emulsions.
- 9—Solid products from orange juice.
- 10—Recovery of pectin.
- 11—Orange paste.
- 12—Fruit stock for cheap jams and jellies
- 13—Imitation English marmalade
- 14—Continuous centrifugals, for fruit pulps and oils
- 15—Essential oil solvents, comparative values.
- 16—Recovery of hesperidin, isohesperidin and aurantiumarin
- 17—Vinegar and wine from orange juice.
- 18—Clarified orange juice, preserved in bottles.
- 19—Canned and dried oranges.
- 20—Purification of citrus oleo-resins and separating constituents.
- 21—Acid and sugar ratio for palatable orange juice.
- 22—Flavoring value and characteristics of coloring matter in citrus fruit peels.
- 23—Natural formation of citrus fruit oils and seasonal changes
- 24—Factors controlling and prevention of oxidation of the terpenes and aromatic bodies in citrus oleo-resins.
- 25—Reaction products of citrus oleo-resins with bases and acids.

So many fields of research have been touched by the investigations in citrus by-products that it is almost impossible to enumerate them all, much less tell of the lines that have been discarded as worthless.

In closing I would draw attention to the fact that in rough estimate there is to-day invested in California in citrus by-product manufacturing plants approximately \$150,000, and somewhere in the neighborhood of \$75,000 has been spent individually and by corporations for the pioneering research work in this field, during the last ten years. Approximately \$120,000 worth of goods have been sold which have been made from citrus fruit into by-products by these California plants during this ten-year period. Many processes and many products and a great deal of special machinery has been developed, and yet to-day there is not one of all the projects started and undertaken which has lived through successful years and has become a financial success.

It is indeed a very pessimistic outlook from some angles, but when we realize that the pioneering has been done, and that we are just about to realize in a full measure the complete success of this industry, the outlook in reality is not as pessimistic as it may appear.

Since the disastrous freeze of 1912 the citrus fruit grower has been confronted with the necessity of finding a reservoir into which he could dump vast volumes of fruit in times of such disaster as he faced during the freeze. The situation is at present in his hands entirely, and in my opinion his salvation rests in amply financing this industry.

To sum up the factors which are potent to such a success I will say that we must have as a basis: (1) liberal coöperation on the part of the fruit grower; (2) accessibility and cheapness of raw material; (3) ample capital; (4) conservative management; (5) adequate chemical and engineering control; (6) a rounded and complete system of processes and products for the manufacture of products which are readily saleable and already well known on the market.

In this ultimate analysis it will be seen that the success of this industry does not depend upon factors different from those in the ordinary course of business, or those of other industries, and as a final word, it is well to consider the fact that up to this time the citrus by-product has been the plaything and the toy



of many dabblers and incompetent people who have not realized even the rudiments of the necessities of business, much less understood the control that the chemist alone can provide in the success of what must be a highly developed manufacturing industry.

There is one thing again which comes to mind and that is the fact that the orange belt is lacking in just the very thing which this industry affords, and that is a manufacturing industry. This industry would act as a tremendous balance wheel for the whole scheme of citrus fruit raising in this section, not only from a moral but also a financial standpoint. We have seen the rise and lowering of values in the citrus grove; also in the study of financial conditions in the citrus industry we have

often noted the difficulty the country banks have in making and keeping a balance of money available for fruit growers at such times as they require it the most. As it is now, the citrus industry is a very one-sided and unbalanced affair. Large volumes of fruit are marketed in a very short time and large amounts of money are thrown back into these communities only to be dissipated in what may be a reckless manner in a few short months leaving financial institutions, while perhaps not in serious difficulties, certainly embarrassed in taking care of reasonable demands. The by-product industry should regulate this in a sufficient and thorough manner.

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## CURRENT INDUSTRIAL NEWS

### PLATINUM SUBSTITUTES IN LAMP MAKING

An incandescent lamp must be hermetically sealed and yet must have current led through its walls to the filament. From the beginning this has been effected by sealing two platinum wires through the red hot glass, all other methods of effecting a permanent seal having been quickly discarded. Of course there have been many patented propositions to effect this seal in some other way, such eminent inventors as Edison, Elihu Thompson, Sir Hiram Maxim, etc., having contributed to the list. Various improvements in lamp-making, however, reduced the amount of platinum necessary in a lamp to two bits of wire each a tenth of an inch long by 6/1000ths of an inch in diameter, making the fraction of the total cost of a lamp due to the platinum in it very small, even with platinum at its present price of \$70 to \$80 per troy ounce. Nevertheless, to such concerns as the General Electric Company, making 100,000,000 lamps per year, even this small amount of platinum per lamp mounts up. Lately, however, sundry substitutes for all-platinum seals invented by Byron E. Eldred, have met with such general success that they have to all intents and purposes displaced the use of platinum. Mr. Eldred made seals which were not only as good as platinum seals but better.

In sealing a wire through glass, two things come into play, one being the cohesion of the metal and the glass or what is termed the "wetting" of the metal by the glass, and the other the relative expansion and contraction of the metal and the glass. Softened or fluid glass "wets" platinum readily; this may in part be due to the specific physical affinity of the molecules of glass for the molecules of the platinum, and may in part be due to the fact that the platinum maintains a metallic surface during the sealing operation.

The expansion of glass, however, is somewhat more than that of platinum, even with the soft glasses which are often used for lamps. The difference is not great but it exists. The net result in cooling a platinum-glass seal from a high temperature to a lower temperature is that the platinum tends to shrink away from the glass. This shrinkage is not great but it is responsible for a little strain: a strain which is resisted by the cohesion of the glass and the platinum. Mr. Eldred conceived the idea of doing away with this condition of tension by making a wire whose expansion was a little less, but not much less, than that of the glass to which it was to be sealed. With a wire of this kind, on sealing and cooling the glass shrinks down on the wire and there is a little compression in the seal. The amount of this compression must not be great, since otherwise dangerous strains might exist; but a little compression there should be. He devised a type of wire having a core of nickel steel of a very low rate of expansion, a jacket of copper on the core and a further jacket of platinum on this copper sheath. The composition of the nickel steel was so chosen that its own expansion, averaged with that of the copper and the platinum, gave the

wire as a whole a little less expansion than that of the glass so that in sealing the desired shrink-on effect or compression seal could be attained. The function of the copper in the combination was not only to give a greater electric conductivity, something which was very much needed in these small gauge leading-in wires, but also to make more regular the expansion of the nickel steel. While nickel-iron alloys can be made to have any expansion within a certain range that may be desired, yet this expansion is not regular through the range of temperature incident to the sealing in. The copper serves to make this curve of expansion more regular.

As soon as this substitute wire for seals was proposed, it met with general adoption and the Commercial-Research Company, which had acquired the Eldred patents, has recently sold the United States patents to the General Electric Company who have adopted the Eldred wire generally in their manufacture of lamps. The Commercial-Research Company, however, retained rights under these patents. The sum paid by the General Electric Company for these patents is said to be the largest ever paid for unlitigated patents.

### MINING PROSPECTS IN SOUTHWEST AFRICA

Now that the German rule in southwest Africa has ceased, says the *Mining World*, it is interesting to know what are the actual mineral possibilities of the country. The following information is taken from official sources and the figures quoted are for the year 1912:

**COPPER AND LEAD**—The high price of copper in September, 1912, enabled the Otavi copper mines to export a quantity of inferior ore in addition to increasing their output. The principal workings are those of Tsumeb mine. The ores are carbonates throughout and rich in copper and lead.

**DIAMONDS**—The largest stones are found in the Pomona territory where a trace of the Kimberley formation exists. In 1912, 902,157 carats were sold for £1,303,092 or an average of £1 8/8 per carat.

**GOLD**—Considerable prospecting has been done for gold, and a number of claims have been pegged off at Kunjas in the Bethany division but no development work has been done.

**IRON**—There are numerous iron beds in the country but these are not worked, owing principally to cost of transport and absence of suitable cheap coal. In Kaokaland, large tracts of iron ore exist.

**TIN**—The tin area lies around the Erongo Mountains and is found in the numerous pegmatic veins which pierce the mica schists. There are also deposits of alluvial tin on which attention is being concentrated. In 1912, tin ore to the value of £470 was exported to Germany.

**WOLFRAM**—At Nakais, a wolfram mine has been opened up where it is stated the quality of the ore is good but none of the metal has yet been exported.

The quality of the crude ores shipped averaged 16 per cent copper, 25 per cent lead and 400 g. silver per ton. The copper matte contained 47 to 48 per cent copper, 25 per cent lead and 400 g. silver per ton. The metallic lead contained 98 per cent lead and 910 g. silver per ton. The number of persons employed in the diamond industry was from 3000 to 4000 and in the copper industry 1000 to 1500. —A. MacMILLEN.

### THE BOOM IN NATURAL INDIGO

Some idea of the effect of the impetus given to the cultivation of natural indigo by the lack of supplies of the synthetic product is obtained from a consideration of the official report from Pondicherry by the Consul, A. H. Drewe. About twenty years ago the exports of indigo from Pondicherry were an important item but with the introduction of synthetic indigo, trade began to decline and the area under cultivation gradually grew less till last year when it was only 448 hectares, an amount barely sufficient for the requirements of the local dyeing industry. The war, however, by curtailing the supply of synthetic dyes has created a demand for the natural product and prices have exactly doubled during the year. This enormous increase has had a corresponding effect in increasing the manufacture of natural indigo and also its cultivation. Whether the price will be maintained or whether the competition of British-made dyes will reduce it after a time cannot, at present, be foreseen. The trade, at any rate, has been revived and considerable interest is being taken in it by growers and dealers.—M.

### WORLD'S BEST SUGAR PRODUCTION

The world's beet sugar industry, according to the West India Committee circular, has materially decreased. In 1912-13 the total beet sugar output was 8,976,277 tons, in 1913-14 8,908,375 tons and in 1914-15 8,156,534 tons. For 1915-16 is estimated at 6,765,000 tons, the war being accountable for the diminution. Thus, the estimated crop of Germany is 1,850,000 tons as against 2,725,000 tons in 1913-14; of Austria-Hungary 1,170,000 tons against 1,672,000 tons; of France 200,000 tons against 230,000 tons; of Russia 1,700,000 tons against 1,731,000 tons or a total deficiency in the countries most concerned of 2,086,000 tons.—M.

### DESTRUCTIVE DISTILLATION OF SEWAGE

In a paper on this subject before the Institute of Sanitary Engineers, London, W. J. Menzies described an apparatus designed to distil sewage destructively. The design is based on the fact that, when the crude material is heated to that point at which the chemically combined water is broken up, only a slightly higher temperature is necessary for decomposition and further that, when in the retort, owing to the immobility of the particles, only that portion which is in contact with the hot surface parts readily with its volatile matter. The apparatus provides for a thin layer of feces being kept in constant agitation on hot plates enclosed in a vessel. The products of distillation are obtained in a useful condition, and the operation is conducted without creating a nuisance. The oil, which distils, contains less than  $\frac{1}{4}$  per cent sulfur and would therefore comply with the standard requirements for a fuel oil, and tests made with it in liquid fuel burners have been satisfactory in every way.

The first fraction is a colorless spirit of specific gravity 0.760 and vaporizes at a little above the normal temperature. From its smell, it seems to contain traces of pyridine bases. The second fraction is a pale burning oil which, however, must be further purified. The intermediate oils are light in color but are not viscous, while the last fraction appears to be a good lubricating oil with good viscosity. The presence of pyridine

bases is regarded as adding value to the oil in connection with its use as a denaturant of alcohol.

Finally ammonia is recovered as liquor.—M.

### SUPERPHOSPHATES

Works for the manufacture of artificial manures, sulfuric acid, sulfates, etc., according to *Engineering*, are about to be erected near Bergen in Norway, cheap power and a suitable site having been secured. The cost is calculated at \$400,000 and the works should be ready to start operations about the end of 1916. Norway is rich in one of the most important raw materials, *viz.*, pyrites, and of apatite there is also plenty, while a sufficiency of nitric acid can be obtained from the large atmospheric nitrogen installations. Cheap power is also available. Norway imports annually some 50,000 tons of phosphate and superphosphate and with the present rate of freights, the cost of these commodities has risen considerably.

The manufacture of superphosphate has assumed large proportions of late years; in Sweden, there are four factories with an aggregate production of 250,000 tons per annum; in Denmark the production amounts to 200,000 tons and in Holland to 300,000 tons, of which half is exported.

The aggregate production in England, Germany, France and Spain amounts to from 3,000,000 to 4,000,000 tons per annum. Among the largest importing countries is Russia.—M.

### PHOSPHATE ORES

M. B. de Rollière, of Paris, whose discovery of a new ore of high phosphorus content was announced in a former issue, now draws attention to another that he has found in quantity in the granites of France. It is a manganese phosphate extracted from a blackish brown rock in cleavable masses and analyzes as follows: phosphoric acid 33 per cent, lime 2.5 per cent, manganese oxide 32.5 per cent, ferric oxide 32 per cent.—M.

### SERBIA'S MINERAL WEALTH

Serbia possesses deposits of antimony, bismuth, chromium, copper, gold, iron pyrites, lead, and mercury besides coal, magnesite, sulfur, marble and other stones for ornamental and building purposes. Antimony ore is principally worked at Krupanj and Zajaca. The coal region lies in the vicinity of the Danube and thus the mineral can be shipped in normal times to districts where fuel is required. Varieties of coal found in the Timok valley are said to be almost as good as the best English coal. Gold is found in alluvial gravel and in quartz veins, especially in the district of the river Timok which forms the frontier of Bulgaria.

Dredging for gold takes place on the River Pek and River Morava.—M.

### JAPANESE GUANO AND PHOSPHATES

H. M. Commercial Attaché at Yokohama reports that artificial manure manufacturers have requested the Japanese Government that the guano deposits on the island of Angaull might be worked again with a view to relieving the difficulties of artificial manufacturers who are suffering from lack of supplies from abroad.

The island of Angaull was owned by the German Government and leased to a German company which had arranged for shipping the phosphate to a British firm in Japan. As a result of the war, the island has been taken over by the Japanese and the working of the phosphate suspended. Supplies of phosphate from Africa and North America have been less than usual, and the Japanese are now making investigations as to whether they can obtain phosphate in Japan itself.—M.



## THE MELTING POINT OF TUNGSTEN

The intrinsic brilliancy of tungsten filament just before melting is, according to Irving Langmuir (*Physical Review*, 1915), 7,200 international candles per square centimeter. This would, in accordance with the constants of Nernst, Parani, Wartenburg, and Coblentz correspond to a melting point for tungsten of  $3540^{\circ}\text{C}$ . absolute, instead of the previously accepted value of  $3200^{\circ}\text{C}$ . As the presence of minute amounts of hydrocarbon vapors (from the vaseline or stop-cock grease) made these determinations somewhat doubtful, Langmuir recently made the redetermination of the melting point of tungsten by two methods. In the first, he determined the black-body melting point of large filaments in nitrogen while estimating the emissivity of helically wound filaments of various sizes in vacuum and in nitrogen. In the second method, he measured the brilliancy of a surface of molten tungsten, simultaneously determining the brilliancy of the image of a second surface of molten tungsten reflected in the first; thus, he directly determined the reflectivity of the molten metal. For this purpose, he made use of an alternating arc between tungsten electrodes in nitrogen. The ends of the two wires formed convex molten surfaces showing multiple reflections of the two electrodes which could be watched for an hour or more. The resulting melting points of three determinations were  $3540^{\circ}$ ,  $3532^{\circ}$ ,  $3566^{\circ}\text{C}$ . absolute, the value  $3540$  being the most probable.—M.

## THE WHALE OIL INDUSTRY

The whale oil industry, according to *Engineering*, is becoming every year more important. In 1914, the world's production amounted to 750,000 barrels, hailing from every part of the globe. At the same time as the production has increased so have the uses to which the oil is put. It is now used for lubricating, often mixed with mineral oil, for the treatment of leather in tanneries, in the iron and steel industry for hardening purposes, in the textile industry for the manufacture of artificial rubber, for lighting purposes and in the soap industries. Large quantities are used in the manufacture of glycerine, whale oil thus being a factor in the production of explosives.—M.

## EXTENSIVE PLATINUM DEPOSITS

According to recent press reports from Madrid, an eminent engineer claims to have discovered platinum-bearing minerals of enormous wealth in the Ronda Mountains of Seville and Granada. The hills are said to be of the same geological formation as that of the Urals, and specimens of platinum exhibited to the Spanish Institute of Engineers have attracted the attention of the Government which is proceeding to make extensive investigations. Optimistic opinions compute the wealth of the platiniferous areas as exceeding even that of the Russian mine fields.—M.

## CEMENT TESTING

According to the *Engineer*, a laboratory for testing cement has now been added to the Technical Research Department of the Imperial Institute of London. In certain countries, such as the Argentine, the Government has adopted an official specification for cement to which all cement intended for use in the construction of public works must conform. The Argentine Government also requires the certification of such cement by a laboratory recognized for that purpose by the Government of the exporting country. H. M. government has now recognized for this purpose the cement testing laboratory of the above Institute where analyses and tests will in future be conducted for British-made cement for contractors, engineers, manufacturers and others desiring to export cement to countries where a government certificate is required.—M.

## BRITISH BOARD OF TRADE

During the months of October and November the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles. Firms who may be able to supply information regarding these things are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall Street, London, E. C.

## INQUIRIES DURING OCTOBER

Butumen, tar and pitch	Bone, good—such as pen sticks
Blanc fixe	Bootlaces, rifle, price about 14/6 per gross
Cardboard boxes	Brackets, small metal, cheap
Crayons, for lumber work	Clay, calcined and raw for glass melting pots and ovens
Cellulose wadding	Display stands for picture postcards
Enameled steel rings	Electric lamps, metal filament
Glass powder or flour	Pero-cerium bones, for automatic lighter
Lactic acid	Fibreboard, vulcanized for suit cases
Lime blue	Mugs, earthenware or porcelain
Needles, knitting machine	Porcelain goods for electrical purposes
Packing materials	Ramic yarn for gas mantles
Picture postcards, cheap	Teapot stands, tile with nickel plated surround
Potato flour	Tins decorated for floor polish
Salicin	Zinc sheets for dry batteries
Thermometers	
Ultramarine blue	

## INQUIRIES DURING NOVEMBER

Agate, rough	Beads, head necklets, cheap plain or colored
Automatic lighters	Charcoal, flake free from dust
Celluloid accumulator boxes	China clay for picture frames
Chemicals	Collar-studs, bone or imitation bone
Aniline oil and salt	Corset-steels
Arsenic, metallic	Electric batteries for pocket lamps
Barium nitrate	Enameled iron shades
Benzol	Glass and glassware
Calcium acetate, pure	Glass, opal
Calcium chloride	Glass wool
Calcium sulfide, luminous	Gum
Carbon disulfide	Harmonium reeds
Diamido phenol	Hooks and eyes, brass
Didymium nitrate	Logwood, for making dyes
$\alpha$ -Naphthylamine	Mantles, incandescent
Formaldehyde	Marbles, glass
Guaiaol	Porcelain for incandescent lamps
Magnesium chloride	Pumice stone
Manganese sulfate	Rubber sponges
Potassium iodide	Stearine flake
Sodium bichromate	Shaving sets
Sodium hydrosulfite	Struts, nickel-plated, to fit on back of leather covered mirrors
Strontium carbonate	Toilet ware
Tetrachlorethane	Tools, trade
Toluol	
Copper sheets, perforated	

## SEARLES LAKE POTASH IN 1916

At the recent annual meeting of the Consolidated Gold Fields of South Africa in London, Lord Harris in reviewing the company's American investments said:

"Of course the interesting question there is, What is the American Trona Corporation going to do? We experimented first of all with a process which proved after a fair trial to be unsuccessful, or, rather, too expensive and wasteful for adoption, and we have now reason to believe that the process which has been substituted will be entirely successful, besides being more economical. It is not a difficult process and has only to be adapted to the special climatic conditions of the country. A very elaborate trial of the brine was carried out during the summer by an independent firm of chemists, and the results have been reported on by capable referees so encouragingly that the company felt justified in ordering the plant, which, I am happy to say, is of a standard type, and at present it is anticipated that potash will be produced next year—the most optimistic hope in the earlier months—when we shall most probably still have the advantage of the high price obtainable for potash at the present moment. All the work necessary to secure the company's title to the area located in accordance with the mining laws of California is being carried out, with a view to obtaining an indefeasible title from the United States authorities. These proceedings necessarily take time, but our legal advisers inform us that they have no doubt that such title will be granted us in due course."

# NOTES AND CORRESPONDENCE

## NOTE ON DUCTILITY TEST OF ASPHALT

In standard specifications, especially for asphaltic cements, where a ductility test is called for, it is usually made by pulling apart, at a speed of 5 cm. per minute, a briquette having at its center a cross section area of 1 sq. cm. Some machines used for this test are only slightly over a meter in length and many asphaltic cements of 60 to 70 penetration will run over 100 cm. The writer has been requested in several cases to compare asphalts supplied on specifications. In most cases specifications call for a ductility test of from 70 to 90 cm. at 5 cm. per minute. With few exceptions this requirement is met, briquettes not breaking under 110 cm., the limit of the writer's apparatus.

Ductility being a measure of surface tension, it is desirable to make the test indicate more sharply the difference between asphalts under examination. It is conceivable that of two asphalts showing a result of 110+ cm., one might run to 200 cm. before breaking, while the other would break below 150 cm. The writer has been using two speeds for some time, namely: 5 cm. per minute and 10 cm. per minute. Results show that the latter speed is still conservative and that no good asphaltic cement of the "pure bitumen" type would be done an injustice by adopting it.

The following results are typical (specifications called for minimum of 90 cm.).

Speed	5 cm. per minute	10 cm. per min.
Sample A.....	90 to 95	65
Sample B.....	110+	110+
Sample C.....	110+	110+

When examined after pulling to 110 cm. at 5 cm. per minute B and C threads appeared about the same size, but at 10 cm. per minute, the thread of C was about the size of a fine hair, while B was two or three times the apparent diameter of C.

318 LAVALLETTE ST. WEST  
MONTREAL, CANADA, July 24, 1915

T. LINSEY CROSSLEY

## THE ESTIMATION OF CARBON DIOXIDE IN THE ASH OF PLANT AND ANIMAL SUBSTANCES

In a recent article by George E. Boltz [THIS JOURNAL, 7 (1915), 859], it has been shown that during the combustion of plant substances for the estimation of ash, the carbon dioxide interacts with the basic oxides of calcium, potassium, sodium, etc., to form the respective carbonates which are not broken completely by further ignition.

While it is essential that some correction be introduced for accurate results, the modification suggested by the above author is rather long and tedious, *i. e.*, boiling the ash with 3.6 per cent hydrochloric acid for half an hour, absorbing the CO<sub>2</sub> evolved in a 4 per cent sodium hydroxide solution, neutralizing the same with normal HCl using phenolphthalein for an indicator; and finally introducing a few drops of methyl orange and titrating with *N*/20 HCl, using the factor 0.0022 g. CO<sub>2</sub> per cc. of *N*/20 HCl.

A much simpler method has been worked out by Gooch and Kuzirian (*Am. J. Sci.*, 31, 497), namely, the use of sodium paratungstate (5 Na<sub>2</sub>O.12WO<sub>3</sub>) which is easily prepared and well suited for the estimation of CO<sub>2</sub> by loss on ignition, when the sample is not required for other determinations. The time required is remarkably short and the results obtained are excellent.

The method of procedure is essentially as follows: Weigh the crude ash accurately, introduce a dry portion of this flux and weigh again, ignite over a low flame (generally a 3- to 5-minute ignition is sufficient), cool and weigh. The loss represents CO<sub>2</sub>.

S. B. KUZIRIAN

IOWA AGRICULTURAL EXPERIMENT STATION  
AMES, IOWA, November 15, 1915

## THE USE OF COBALT NITRATE FOR MARKING ON PORCELAIN

In quantitative work it is very desirable that the porcelain Gooch crucibles used be so marked for identification that the mark will be permanent and will stand a high temperature of ignition.

Ink and soft lead pencil, when burned into the surface of porcelain, leave a light red mark which gradually fades away in use.

Fine results can be obtained by the use of a very dilute solution of cobalt nitrate for this purpose. It has been used in this laboratory for marking on porcelain with success.

The procedure adopted by the author is as follows: The porcelain is gently heated with a low flame, then with the sharp end of a burned taper or a pen, the desired mark is made and the same ignited with a strong flame for about three minutes, when a deep black mark remains. The advantage of a black mark on a white surface is that it enables one to see the mark from outside the desiccator.

S. B. KUZIRIAN

IOWA AGRICULTURAL EXPERIMENT STATION  
AMES, IOWA, November 15, 1915

## THE COST OF ESTIMATING POTASH AS POTASSIUM PLATINIC CHLORIDE

*Editor of the Journal of Industrial and Engineering Chemistry:*

For some time there has been more or less question concerning the loss of platinum in estimating potash as potassium platonic chloride and recovering the platinum. Since there seems to be very little data giving the actual loss in the process of reducing and recovering the platinum and the approximate cost of the process, the following may be of interest:

During a recent fertilizer season (1914), 670 potash determinations, averaging about 0.0300 g. of potash for each determination, were made in this laboratory with a loss of 5.02 g. of platinum not recovered. If platinum is worth \$1.80 per gram, this loss would amount to \$9.04. About one day's labor (which may be valued at \$4.00) was required for the recovery of the platinum saved making a total cost of \$13.04, or of \$0.0194 for each determination.

MICHIGAN AGRICULTURAL EXPERIMENT STATION  
EAST LANSING, MICHIGAN, August 11, 1915

O. B. WINTER

## IRON CARBONYL IN WATER GAS

In the course of some recent experiments a constant easily regulated supply of CO was required. Hydrogen being in no way detrimental, a steel cylinder of compressed water gas was used. The presence of iron in all parts of the apparatus was soon evident and could not be explained by any mechanical introduction in the slow stream of gas. The presence of Fe(CO)<sub>5</sub> seemed to be the most reasonable explanation.

Accordingly, a slow stream of the gas was passed through a glass tube, heated to about 250° C., and a metallic mirror formed almost instantly. It had the appearance of an antimony mirror, but test showed it to be pure iron.

Iron was determined quantitatively by passing a measured volume of the gas through a tube heated in five zones by small flames. Between each zone was a small plug of glass wool. It was found necessary to use these plugs as the iron is formed as a fine dust and is unavoidably carried out of the tube. The decomposition of the iron carbonyl was so complete that the first three plugs contained practically all of the iron not deposited as mirrors. The iron was dissolved in HCl, oxidized with HNO<sub>3</sub> and determined as Fe<sub>2</sub>O<sub>3</sub> gravimetrically. A volume of



gas equivalent to 7850 cc. at standard pressure and temperature, gave 0.087 gram  $\text{Fe}_2\text{O}_3$ . This is equivalent to 5.3 mg.  $\text{Fe}$  per liter of 0.0088 gram  $\text{Fe}_2\text{CO}_3$ . Calculating the weight of the water gas:  $\text{H}_2$  30 per cent,  $\text{CO}$  64 per cent) as about 0.88 gram per liter, the  $\text{Fe}_2\text{CO}_3$  comprises 2.2 per cent by weight, but only 0.214 per cent by volume.

Speculations as to possible equilibrium between a 64 per cent  $\text{CO}$ , cold drawn steel and  $\text{Fe}(\text{CO})_5$  at about 500 lbs. pressure and room temperature are left to the reader. At any rate, water gas compressed in contact with iron should be tested before use in experiments. It has been assumed that the iron carbonyl is  $\text{Fe}(\text{CO})_5$ , although the fact that it was necessarily formed in absence of light might give  $\text{Fe}(\text{CO})$ .

LEONARD M. LIDDLE

MULLIN INSTITUTE OF INDUSTRIAL RESEARCH  
UNIVERSITY OF PITTSBURGH  
PITTSBURGH, October 14, 1915

# AMERICAN INSTITUTE OF CHEMICAL ENGINEERS EIGHTH ANNUAL MEETING BALTIMORE, JANUARY 12-15, 1916

The Eighth Annual Meeting of the American Institute of Chemical Engineers will be held in Baltimore, Maryland, on January 12-15, 1916, with headquarters at the Emerson Hotel. The evening session on January 14th will be a joint meeting at the Johns Hopkins University with the Baltimore Section of the American Chemical Society, following which a smoker will be given at the Johns Hopkins Club by the Maryland Section of the American Chemical Society. The subscription dinner (\$3.00 per plate) will be held at the Emerson Hotel on the 13th.

The members will be welcome at the chemical and physical laboratories of the Johns Hopkins University any day during the meeting between 9 A.M. and 5 P.M.

## PROGRAM OF PAPERS

- The Development of the Manufacture in the United States of Products Derived from Coal. H. W. JORDAN
- The Cracking of Petroleum and Other Hydrocarbons as a Chemical Engineering Problem. W. F. RITTMAN
- Ethyl Alcohol from Wood Waste. A. D. LITTLE
- The Production of Ammonia from Cyanamid. W. S. LANDIS
- The Barium Industry. M. TUCH
- A New Process of Bleaching. S. F. PERKHAM
- Lutes and Cements for Chemical Purposes. S. S. SADDLER
- Ozone Purification of Water. MR. POWELL
- Artificial Daylight. H. E. IVES

## PROGRAM OF EXCURSIONS

[It is understood that Chemical Engineers who are allied with competing companies will not attend these excursions unless they so declare themselves and extend the same courtesy of inspection from their own plants.]

The following plants will be visited: Sewage Disposal Plant of the City of Baltimore; Ozone Water Purification Plant of the Baltimore County Water Co.; Building of the Emerson Drug Co., Manufacturers of Bromo Seltzer; Maryland Glass Co. Plant; Crown Cork and Seal Co. Plant.

*Alternate Excursions*—Plant of American Steel Co., Sparrow's Point; Standard Fertilizer Works; McCalls' Ferry Power Plant of the Pennsylvania Water and Power Co.; Tidewater Portland Cement Co., Union Bridge, Md.

On January 13th a special car will take the members to Annapolis where the Naval Academy Grounds and Buildings, and the Naval Experiment Station will be visited.

## LOCAL COMMITTEE

Richard K. Meade, *Chairman*, J. G. Bailey, W. T. Van Horn, and E. Emmet Reid of the Maryland Section of the American Chemical Society.

## PERSONAL NOTES

The following officers of the American Chemical Society have been elected for the term beginning January 1, 1916: Charles Holmes Herty, *President*; W. R. Whitney, W. D. Bigelow, *Directors*, to serve three years; Geo. D. Rosengarten, W. D. Bigelow, B. C. Hesse, G. N. Lewis, *Councilors at Large*, to serve three years.

The Perkin Medal Committee, consisting of representatives of the Associated Chemical and Electrochemical Societies of America, have awarded the Perkin Medal for 1916 to Dr. L. H. Baekeland for eminence in research in industrial chemistry. The presentation of the medal to Dr. Baekeland will take place at the regular meeting of the New York Section of the Society of Chemical Industry, on January 21, 1916.

The Bureau of Mines and the United States Geological Survey tendered a complimentary banquet at Washington, D. C., on November 20th, to Mr. Van H. Manning, in honor of his recent appointment to the Directorship of the Bureau of Mines. The speakers of the evening were: Mr. George Otis Smith, Director of the Geological Survey; Mr. Sanford, Editor, Bureau of Mines; Senator Thomas J. Walsh, of Montana; Mr. J. F. Callbreath, Secretary of the American Mining Congress; Hon. Franklin K. Lane, Secretary of the Interior; and Mr. Manning.

The Thompson chemical laboratory of Williams College, Williamstown, Mass., a three-story brick structure, was destroyed by fire early on December 7th, with a loss estimated at \$56,500, of which \$47,000 is covered by insurance. According to the college authorities, the fire started in a workroom on the first floor from spontaneous combustion and spread rapidly

through the building. Classes in chemistry have been meeting at the usual times in the Biological Laboratory, the work consisting largely of lectures.

Dr. Walter O. Snelling, of Pittsburgh, has bought land in Long Island City on which he will erect laboratories for chemical research.

T. J. Parker, who was president and treasurer of the Bayonne Chemical Works until it became a part of the General Chemical Company, since which time he has been identified with the latter company in an official capacity, has gone into the chemical business on his own account, specializing in carbolic acid, nitrobenzol, aniline oil, organic and inorganic chemicals. Mr. Parker has been in the chemical business for upwards of thirty-five years.

The Cincinnati Section of the American Chemical Society, originally the Chemical Society of Cincinnati and Vicinity, and in point of time the third section to receive a charter from the parent organization, celebrated its Twenty-Fifth Anniversary on the evenings of December 20th and 21st. Dr. Thomas H. Norton, the first president of the local organization, gave an illustrated lecture on the 20th, upon the Government work in which he is now engaged—an investigation of the status of our chemical industries relative to the European situation. The subject of his lecture was "The Trend of American Technical Chemistry." The Anniversary Banquet was held on the 21st at the Hotel Sinton.

The Chemical Society of Washington held a special meeting on December 8th, through the courtesy of the National Rivers and Harbors Congress; the program consisted of motion

pictures, accompanied by descriptive lectures, illustrating the manufacture and testing of the National Tube Company's steel pipe. The 254th meeting of the society was held on December 16th with the following program: "Some Samples of Metal Failure" (illustrated), by G. K. Burgess, Bureau of Standards; "Chemical Factors Affecting Electrolytic Corrosion in Soils and Reinforced Concrete," by B. McCollum, Bureau of Standards; "The Action of Natural Waters on Boilers," by R. B. Dole, Geological Survey.

Dr. Walter F. Rittman lectured on various phases of the Bureau of Mines study of the cracking of petroleum before the following sections of the A. C. S. during December: St. Louis Section, Chicago Section, Philadelphia Section, Rochester Section.

The following awards have been made by the President and Council of the Royal Society, London: The Copley Medal to Prof. Ivan Petrovitch Pavlov for research in physiology; the Davy Medal to Prof. Paul Sabatier for his research on the action of finely divided metals as catalysts; the Hughes Medal to Prof. Paul Langevin for researches on electrical science.

Prof. Raphael Meldola, F. R. S., of Finsburg Technical College, London, died suddenly on November 16th, at the age of sixty-six. He held, at the time of his death, the position of chairman of the Advisory Council of the Board of British Dyes.

The sixty-eighth meeting of the American Association for the Advancement of Science, and the fourteenth of the "Convocation week" meetings, was held in Columbus, Ohio, from December 27, 1915 to January 1, 1916, with hotel headquarters at the Chittenden. The meetings of the Association and also of the several affiliated scientific societies that held their sessions in Columbus, were at the Ohio State University.

Dr. Frank K. Cameron gave a talk on "American Resources in Fertilizer Materials," at the regular meeting of the Rochester Section of the A. C. S., on December 6th.

Prof. Alan W. C. Menzies, of Princeton University, gave an illustrated lecture, on December 9th, on "Some Applications of the Isoteniscope," before the Gamma Chapter of Phi Lambda Upsilon, at Columbia University.

The thirty-sixth meeting of the Connecticut Valley Section of the A. C. S. was held in Hartford on December 11th with the following program: "Smoking Opium in the United States," by H. L. Thompson; "The Rittman Gasoline Process," by Dr. E. C. Stone; A Symposium on "Substitutes for Gasoline as Motor Fuels." At the October meeting it was voted by the Section to establish a question bureau and a committee was appointed with R. J. Marsh as chairman, to arrange details. The committee have decided on a plan whereby any member or associate member who desires to have any question answered, or subject discussed, can submit such question or subject to the chairman of the question committee and it will be brought up in due course at some future meeting of the Section.

The Buffalo Foundry and Machine Company announce that they have opened an office in New York City, at 1432 Whitehall Building, 17 Battery Place.

The Carbondale Instrument Company has been purchased by the Griebel Instrument Company, Carbondale, Pa., in whose name the future business will be conducted.

The Wilson-Maeulen Company, Inc., manufacturers of pyrometers, announce a change of address to their new factory, laboratory and office located at Wales Avenue and E. 142nd Street, New York City.

The Pittsburgh Section of the A. C. S. held a Gigantic Smoker and Get-Together Meeting on December 2nd. The affair consisted of a four-reel motion picture, shown in the Assembly Hall of the Mellon Institute, of the mining, milling and smelting of copper, followed by a sociable at the Turn Verein.

The *Journal of the American Pharmaceutical Association* has changed its address from 63 Clinton Building, Columbus, Ohio, to c/o Philadelphia Drug Exchange, Bourse Building, Philadelphia. Mr. E. G. Eberle, Editor of the Journal, announces the same change in his address from Dallas, Texas.

The University of Michigan Section of the A. C. S. at the regular meeting on November 23rd, elected the following officers for the coming year: *Chairman*, D. M. Lichty; *Secretary-Treasurer*, H. H. Willard; *Councilor*, W. J. Hale; *Executive Committee*, B. W. Peet, M. Gomberg and W. G. Smeaton. At the December 9th meeting, Mr. R. L. Sessions, of the Vanadium Alloys Steel Company, Latrobe, Pa., addressed the Section on "Ferrotungsten as an Industry."

Mr. A. C. Boylston, of the Mallinckrodt Chemical Works, addressed the December 13th meeting of the St. Louis Section of the A. C. S. on "Some Relations between Chemical Constitution and Physiological Action."

Prof. R. A. Millikan, of the Physics Department of the University of Chicago, spoke on "The Nature of Radiant Energy," before the December 8th meeting of the Wisconsin Section of the A. C. S. Prof. Millikan's paper dealt largely with his own researches in the field of photo-electricity.

The *Plant World* announces the offering of two prizes for the best papers embodying original work in soil physics. The first prize will be \$50 and the second \$25. The conditions governing the award will be similar to those employed in connection with the prizes for papers on the water relations of plants, which were offered in April, 1915. The contesting contributions should be in the hands of the Editor of the *Plant World* by December 1, 1916; the announcement of the award will be made not later than March 1, 1917.

The second meeting of the Ames Section of the A. C. S. was held December 2nd. Prof. Homer F. Staley, of the Iowa State College, spoke on "Peculiarities in the Chemistry and Physics of Silicate Industries."

The Burdett-Oxygen Company announce the completion of the erection of its Fort Worth, Texas, plant, on December 15th. The plant is designed to supply the Texas trade with electrolytic oxygen, and is the ninth plant erected by the Burdett Company in the various industrial centers of the country.

The General Chemical Company has just awarded to John W. Ferguson Company, engineers and contractors, Paterson, N. J., and New York City, a contract for the construction of a manufacturing building at their Hudson River Works, Shady-side, N. J.

Dr. A. G. Worthing, of the Nela Research Laboratory of the General Electric Company, addressed the Cleveland Section of the A. C. S. on December 13th, on "The Electron Theory and Some of its Applications."

Chancellor Samuel Avery, of the University of Nebraska presented an address on "Our National Chemical Industries," before the December 11th meeting of the Nebraska Section of the A. C. S.



# GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

## BUREAU OF MINES

**Determination of Nitrogen in Coal.** A. C. FIELDNER AND CARL A. TAYLOR. Technical Paper 64. 22 pp. "The experiments described in this paper were undertaken in the course of fuel investigations being made by the Bureau of Mines, their purpose being to ascertain which modifications of the Kjeldahl method are best adapted to the determination of nitrogen in coal, and, if possible, to check the results with the Dumas gas-volumetric method. The latter method, although difficult and tedious, is generally regarded as being applicable to almost all classes of organic compounds.

"In determining the nitrogen content of eight different coals by various modifications of the Kjeldahl method, the highest and most concordant results in the shortest time of digestion were obtained by the combined Kjeldahl-Gunning method when both mercury and potassium sulfate were used as proposed by Dyer."<sup>1</sup>

The value and speed of digestion with various nitrogenic agents is described in detail. It is concluded:

"In all determinations, in order to insure a maximum yield of nitrogen, it was necessary to digest coal approximately two hours after the solution became colorless."

**The Explosibility of Acetylene.** GEORGE A. BURRELL AND G. G. OBERFELL. Technical Paper 112. 12 pp. Paper, 5 cents. "In this report are shown the results of experiments made by the Bureau of Mines to determine the limits of complete propagation of flame in mixtures of acetylene and air.

"The term 'limits of complete propagation of flame' is used by the authors to designate the lowest and highest percentages of a combustible gas in mixture with air that permit combustion to spread through the mixture from any given point of ignition. Propagation of flame then takes place from point to point or layer to layer throughout the mixture without any necessity for the continued presence of the source of heat that starts the inflammation.

"The authors' experiments showed that the smallest proportion of acetylene capable of propagating flame in a mixture of acetylene and air was 2.53 per cent.

"The largest proportion of acetylene capable of propagating flame in a mixture of acetylene and air was found to be about 73 per cent.

"Acetylene, not mixed with air, is explosive under a pressure of 3 to 5 atmospheres when an electric spark is passed through the mixture or where a platinum spiral is heated in it.

"The danger connected with the handling of calcium carbide in a mine is remote if reasonable care is observed in handling."

**Notes on the Use of Low-Grade Fuel in Europe.** R. H. FERNALD. Technical Paper 123. 36 pp. Paper, 10 cents. "In order that the true significance of these important commercial problems might be more fully presented to those responsible for the production, transportation, and utilization of fuel in the United States, an attempt was made during the summer of 1914

to procure in Europe, through personal inspection, definite information relating to (a) the utilization of high-ash coals; (b) the use of wood refuse and other similar material; (c) the recovery from fuel of by-products—ammonium sulfate, tar, pitch, etc.; (d) the recent developments in the preparation and use of peat; (e) the results of low-temperature distillation of fuels; (f) the possibilities of the slagging type of gas producer; and (g) the use of powdered fuel."

A number of well illustrated descriptions are given of the various types of non-by-product producer gas plants, wood distillation apparatus, and the slagging gas producer. The character of the fuels, the quantity and quality of the products obtained, and the various uses to which the products are put commercially are discussed fully.

## GEOLOGICAL SURVEY

**Geology and Oil Resources of the West Border of the San Joaquin Valley North of Coalinga, California.** ROBERT ANDERSON AND R. W. PACK. Bulletin 603. 219 pp. "The main purpose of this report is to present the geologic evidences of the existence of the San Joaquin Valley, California, between the Coalinga oil district and Livermore Pass, and to discuss the chances of finding oil in commercial quantity in this region."

**The Phosphate Deposits of Florida.** G. C. MATSON. Bulletin 604. 101 pp. This is a brief summary of the geology of the northern part of the Florida peninsula, followed by a discussion of the mode of occurrence, geologic relations, and origin of the phosphates which occur there and methods of mining them. Numerous halftone plates give views of the deposits and of fossils found in them.

**Bibliography of North American Geology for 1914, with Subject Index.** J. M. NICKLES. Bulletin 617. 167 pp. This gives a list, arranged alphabetically by authors' names, of publications on the geology of the continent of North America and adjacent islands, also Panama and the Hawaiian Islands, issued in 1914. The work is indexed and contains lists of chemical analyses reported, and minerals, rocks, and formations described.

**Statistics of the Pottery Industry in the United States in 1914.** JEFFERSON MIDDLETON. Mineral Resources of U. S., 1914, Part II. Preliminary issue dated August 6. "The tables show the status of the pottery industry in 1913 and 1914 and the production of pottery from 1898 to 1914. Imports are shown from 1886 to 1914, and exports from 1895 to 1914. The figures indicate that the condition of the industry in this country was not so satisfactory in 1914 as it has been in the previous few years.

"The value of all domestic pottery marketed in 1914 was \$35,398,161, a decrease of \$2,594,214, or 6.83 per cent from 1913. The imports decreased even in greater proportion, 17.96 per cent. The actual decrease in value of imports was \$1,828,009.

"In 1914 only one variety—red earthenware—increased in value, the increase being \$59,375, or 5.93 per cent over 1913. Porcelain electrical supplies showed the largest decrease, \$1,607,471 or 28.02 per cent, and china showed the smallest, \$39,374 or 1.62 per cent."

**Gems and Precious Stones in 1914.** DOUGLAS B. STERRETT. Mineral Resources of U. S., 1914, Part II, 307-46. Separate, published October 13. "This report does not deal with the gem-mining industry of the United States during 1914 alone, but follows a plan adopted several years ago by which as many different gem localities as possible are examined and described each year, regardless of whether or not they are worked that year. The aim of this plan is the collection of information for

<sup>1</sup> Dyer, B., "Kjeldahl's Method for the Determination of Nitrogen," *Jour. Chem. Soc.*, 67 (1895), 811-817.

a more complete report on the occurrence of precious stones in the United States at some future date.

"The total production of gems and precious stones in the United States in 1914, as reported to the Survey, amounted to \$124,651. This is a large decrease from the production reported for 1913, which amounted to \$319,454.

"The value of the imports of precious stones into the United States during the calendar year 1914, as reported by the Bureau of Foreign and Domestic Commerce, amounted to \$18,711,084, the smallest since 1908, when it was \$13,700,404. The imports were less by \$26,720,914 in 1914 than in 1913, the greatest proportionate decrease occurring in rough or uncut diamonds." A full summary of the precious stone industry of the period 1882 to 1914 is given. The production for each year for each of the important stones is given and a discussion included of the sources of the gems at different periods.

**The Production of Asphalt, Related Bitumens, and Bituminous Rock in 1914.** JOHN D. NORTHRUP. Mineral Resources of U. S., 1914, Part II, 347-62. Separate published October 18. "The marketed production of natural asphalt in the United States in 1914 aggregated 77,588 short tons, valued at \$630,623, a decline of 15,016 tons in quantity and of \$120,090 in value from the output of 1913. Of the production in 1914 of natural asphalt, 48,771 tons, valued at \$151,122, or \$3.10 a ton, are classed as bituminous rock; 19,148 tons, valued at \$405,966, or \$21.20 a ton, represent the combined output of gilsonite and wurtzilite (eleterite); and 9,669 tons, valued at \$73,535, or \$7.60 a ton, are credited to grahamite. No production of natural soft asphalt, known as maltha or breia, was reported for the year.

"The number of active producers of natural asphalt in the United States declined from 14 in 1913 to 11 in 1914.

"The term natural asphalt is used in this chapter in a generic sense and denotes all commercially utilized types of native bitumens, pyrobitumens, and bitumen impregnated rocks, to which, for statistical convenience, the native paraffin wax, ozokerite, has been added. The term manufactured asphalt is here used to denote only those forms obtained as by-products in the refining of certain asphaltic oils. Mastic, a prepared mixture of bituminous material and mineral matter, and partly treated or refined native bitumens are included under natural asphalt.

"The marketed production of oil asphalt derived from petroleum of domestic origin in 1914 amounted to 360,683 short tons, valued at \$3,016,969, or an average of \$8.36 a ton, a decrease of 75,903 tons in quantity, of \$1,514,688 in value, and of \$2.25 a ton, as compared with the output of 1913. The explanation of this condition lies in the competition of the domestic product with that derived from Mexican petroleum. The quantity of this latter type of oil asphalt manufactured wholly within the United States in 1914 was 313,787 short tons, valued at \$4,131,153, or an average of \$13.16 a ton, as compared with 114,437 short tons, valued at \$1,743,749, or an average of \$15.23 a ton, produced in 1913.

"Of the quantity of oil asphalt produced in 1914, from oils of domestic origin, 171,447 tons, valued at an average price of \$7.83 a ton, found utilization chiefly as road oils or as fluxes for softening harder bitumens, and 189,236 tons, with an average value of \$8.84 a ton, were classed as residual pitches and utilized in the paving industry. Of the quantity produced in this country from oils of Mexican origin, 111,058 tons, valued at an average price of \$11.10 a ton, were classed as road oils and fluxes, and 202,729 tons, valued at an average price of \$14.29 a ton, were classed as residual pitches.

"During the calendar year 1914, the total imports of asphalt or consumption in the United States amounted to 139,057 short tons, valued at \$675,618, or an average of \$4.85 a ton.

"In addition to the imports of raw asphalt in 1914, asphalt

products aggregating \$10,524 in value were imported for consumption during the calendar year.

"The published records of the Bureau of Foreign and Domestic Commerce show that 37,246 long tons of crude asphalt, valued at \$845,838, together with asphalt products valued at \$401,182, were exported from the United States during the calendar year 1914. Compared with the corresponding period in 1913, these data show a decline of 21,304 tons in the exports of crude asphalt and a decrease of \$10,604 in the value of asphalt products sent out."

The conditions and the production in the principal producing states are discussed and considerable information is given as to the imports and production of ozokerite and ichthyol. The substitution of domestic ozokerite and synthetic ichthyol have markedly increased during 1914 because of the interruption of foreign supplies.

**The Production of Lime in 1914.** G. F. LOUGHLIN. Mineral Resources of U. S., 1914, Part II, 363-73. Separate published October 14. "The lime manufactured and sold in the United States in 1914 amounted to 3,380,928 short tons, valued at \$13,247,676. This was a decrease of 214,462 tons, or 5.96 per cent in quantity, and of \$1,400,686, or 9.56 per cent in value, compared with the output for 1913, which was 3,595,390 short tons, valued at \$14,648,362. The value given represents the value of bulk lime f. o. b. at point of shipment, and does not include any weight or cost of barrel or package. Both the quantity and the value for 1914 are less than for any previous year since 1908, and show how severely the lime industry as a whole was affected by the business depression of the year.

"The decrease in average price was not general for the entire country. The States with increase and those with decrease in average price were about equally divided, and the amounts of increase and decrease varied greatly from State to State.

"The total number of plants reporting operations in 1914 was 954, as compared with 1,023 in 1913, 1,017 in 1912, and 1,139 in 1911. The number operating in 1914 was, with the exception of that in 1908, the smallest since record of them was first made in 1906. The decrease was evidently in part temporary, owing to the unfavorable conditions of the year, but in part it marked a continuance of the tendency of the industry toward combination. In contrast to the decrease in number of plants, the number of kilns in operation increased from 2,203 in 1912 to 2,338 in 1913, and to 2,374 in 1914. This increase, however, was in part due to the more complete returns received in successive years."

There is included a discussion of the uses to which quicklime and hydrated lime are put at the present time. Data as to imports and exports and the character and quantity of fuels used in lime burning are also presented.

**The Production of Peat in 1914.** CHARLES A. DAVIS. Mineral Resources of U. S., 1914, Part II, 375-85. Separate published October 9. "In 1914, so far as reported, there were four peat-fuel plants in operation in the entire country, with an estimated production of 1,925 tons of air-dried machine peat. Of these plants one had been operated more or less regularly for several years but on a small scale, employing but three men during the working season of 1914. A second plant was wholly experimental and was in operation only occasionally. One of the other plants was not completed until late in the season, and consequently was in operation only a short time and with an unskilled force. The fourth plant reported a prosperous and satisfactory season.

"The production of peat for fertilizer uses during 1914, as reported, was 37,720 short tons, valued at \$249,899. The selling prices given varied widely according to the grade of the product, the uses to which it was to be put, the quantity and quality of materials added, and the size of the selling unit. In car-load lots the price of sun-dried, untreated peat ranged



from \$3.50 to \$6 a ton. In small lots, shipped in bags or barrels, the prices ran considerably higher. Fertilizer filler, sold at a somewhat uniform price per unit of nitrogen, varied according to the percentage of nitrogen and locality of production from \$4.50 to \$7.50 a short ton, the average price being \$6.02. The quantity of peat sold for fertilizer filler was 22,267 tons, and for fertilizer 14,962 tons.

"Three other uses of peat were reported by producers in 1914, for stock food, for mud baths, and for making paper. As the production for each use was reported by a single firm, the whole output is given under a single heading. This total was 7,439 short tons, valued at \$53,253. The highest price and the lowest production reported for any peat product was that of peat for paper pulp, as the plant producing it was in operation only a small part of the year."

The condition under which peat occurs and its distribution in this country, as well as the methods of utilization of peat in Europe, are discussed.

**The Manufacture of Coke in 1914.** C. E. LESHER. Mineral Resources of U. S., 1914, Part II, 387-442. Separate published October 13. "The production of coke in 1914 was the smallest, except in 1908, in 10 years or since 1905, and amounted to 34,555,914 short tons, valued at \$88,334,217. Compared with 1913, when the production was 46,299,530 short tons, valued at \$128,922,273, the output in 1914 was decreased 11,743,616 short tons, or 25.4 per cent in quantity and \$40,588,056, or 31.5 per cent in value. The value of coke has a marked tendency to follow the rate of production, answering in a general way to the law of supply and demand. Prices in 1914 fell gradually, with slackening demand and decline in output, from the beginning of the year to the end, the result being an average value obtained at the ovens of \$2.56, as compared with \$2.78 in 1913. The decline in value was shared almost equally by beehive and by-product coke, the former declining from \$2.39 to \$2.15, or 10 per cent, and the latter from \$3.82 to \$3.39, or 11 per cent.

"The cost of coal to the manufacturer per ton of coke produced in 1914 was \$2.166, or practically the same as in 1913 (\$2.169), and this fact, considered with the decrease in average value for the coke, indicates that the actual returns to the producers were relatively less in 1914 than in 1913. Of the 34,555,914 tons of coke made in 1914 in the United States, 23,335,971 tons were beehive or oven coke, valued at \$50,254,050, and 11,219,943 tons, valued at \$38,080,167, were by-product or retort coke.

"The decrease in the production of retort coke in 1914 was 1,494,757 short tons, or 11.8 per cent; the beehive output decreased 10,248,859 tons, or 30.5 per cent.

"The tendency to consolidate into large units is exhibited in the manufacture of coke, as in other branches of industry, and the number of coke-making establishments has shown a steady decrease since 1909, when, on December 31, there were 579 coke-making establishments in the United States. At the close of 1910 the number of establishments had decreased to 578, at the close of 1911 to 570, in 1912 to 559, in 1913 to 551, and in 1914 to 536. Although the total number of establishments in the United States decreased 15 in 1914, the number of by-product plants increased 4, whereas the plants using beehive ovens decreased 19. There were 5 establishments with a total of 231 ovens under construction at the close of 1914. Four of the new establishments with a total of 171 ovens were retort oven plants.

"The 5,809 retorts in existence in the United States at the close of 1914 consisted of 1,957 United-Otto, 1,669 Koppers, 1,598 Semet-Solvay, 281 Rothberg, 232 Didier, 27 Kloenne, 27 Gas-Machinery, and 18 Wilputte ovens. At the end of 1914 there were 644 retort ovens in course of construction, of which 388 were Koppers, 150 United-Otto, 91 Semet-Solvay, 12

Roberts Fuelless, and 3 Gas Machinery. The Gas-Machinery retort is a new type, the first installation being in 1914 at the Cambria Steel Company's plant at Johnstown.

"Although not a retort oven the Mitchell or rectangular oven has achieved considerable popularity in the lower Connellsville district of Pennsylvania, where the activity in that kind of construction has been greatest. In the rectangular ovens the process is the same as that of the beehive, but the coking chamber, instead of being round, is, as the name implies, rectangular and oblong, so that the coke may be pushed, as from the retort oven, and does not have to be drawn, as from the beehive. The rectangular oven is therefore included with the beehive type.

"The total value of the coke, gas, tar, ammonia, and other products produced at by-product recovery ovens during 1914 is shown in the following table:

	Quantity	Value
Gas (c) (M. cu. ft.)	61,364,375	\$ 6,009,583
Tar (gals.)	109,901,315	2,867,274
Ammonia—sulfate or reduced to equivalent in sulfate (lbs.)	170,763,906	4,696,590
Ammonia liquor (gals.)	5,938,233	658,497
Anhydrous ammonia (lbs.)	25,370,509(a)	2,300,137(a)
Other by-products		997,007(b)
Total value of by-products		\$17,529,088
Coke (short tons)	11,219,943	38,080,167
Grand total		\$55,609,255

(a) Mainly ammoniacal liquor sold on pound basis of  $\text{NH}_3$ .

(b) Mainly benzol.

(c) The gas included in the foregoing statement is the surplus not consumed in the coking process, which is either used at manufacturing establishments operated in connection with the coke-oven plant or sold.

**The Production of Feldspar in 1914.** FRANK J. KATZ. Mineral Resources of U. S., 1914, Part II, 449-54. Separate published October 15. "The marketed production of feldspar in 1914 was 135,419 short tons, valued at \$629,873. This, the largest recorded annual production of crude feldspar, was an increase over the output of 1913 of 14,464 tons, or 12.15 per cent in quantity and a decrease of \$146,678, or 18.88 per cent in value. The sales of crude spar were 85,905 short tons, valued at \$366,397, a decrease of 26,050 tons, or 34.5 per cent in quantity and of \$261,605, or 41.5 per cent in value, as compared with 1913.

"The average price per ton in 1914 for crude spar was \$3.07, compared with \$3.31 in 1913 and \$3.36 in 1912. The average price per ton in 1914 for ground spar was \$7.40, compared with \$8.31 in 1913 and \$7.18 in 1912. The average price per ton in 1914 for the combined crude and ground output was \$4.77, compared with \$6.49 in 1913 and \$6.01 in 1912. Of the total output, 63.44 per cent was sold by the producer crude and 36.56 per cent was sold ground. Of the total value, the crude represents 41.82 per cent and the ground 58.18 per cent.

"Feldspar is used principally in the manufacture of pottery, enamel ware, enamel brick and tile, and electrical ware. Of these applications the most important is its use in the body and glaze of the various grades of pottery and vitrified sanitary ware, in which it constitutes from 10 to 35 per cent. \* \* \* In glazes the percentage of feldspar used is higher than in the body, running from 30 to 50 per cent. Feldspar of a lower grade than that demanded by the pottery trade is used as a binder in making emery and corundum wheels, in manufacturing opalescent glass, as a pountry grit, as a constituent of roofing material, and for surfacing concrete work. Small quantities of the purest grades of potash feldspar are used in the manufacture of artificial teeth. For this purpose it brings the highest prices, from \$6 to \$8 a barrel of 350 lbs. It is also used in the making of scouring soaps and window wash. Ground feldspar has been used as a fertilizer, but with results of doubtful value. Attempts are being made to extract from feldspar its content of potash. Experiments directed to this end have not yet developed a commercial process, but some of the efforts may yet be successful."

## DEPARTMENT OF AGRICULTURE

**Gossypol, the Toxic Substance in Cottonseed Meal.** W. A. WITHERS AND F. A. CARRUTH. *Journal of Agricultural Research*, 5 (Nov. 15), 261-88. It is shown that cottonseed kernels and cottonseed meal are less toxic when gossypol is partially extracted from them and practically non-toxic with nearly complete extraction.

**Relation of Sulfur Compounds to Plant Nutrition.** E. B. HART AND W. E. TOTTINGHAM. *Journal of Agricultural Research*, 5 (Nov. 8), 233-50. "The data presented from these greenhouse studies with one type of soil indicate that certain plants are measurably increased in their growth by the addition of sulfates. We have emphasized in another place the fact that sulfates have very little effect as compared with soluble phosphates on the soil flora. This difference in action will remove the sulfates from the category of effective fertilizers for all crops. Nevertheless, for certain plants and types of soil they will be beneficial if their only action is as a source of sulfur.

"In general, the calcium sulfate was more effective than the more soluble sodium sulfate. The special influence of sulfates on root development is pointed out.

"The somewhat common observation of the benefit of land plaster to this plant can probably be closely correlated with this special effect of sulfates on root development, as well as its high protein character, which would make special demands for sulfur.

"Whether recorded failures in the use of land plaster are to be correlated with wet seasons, or a high sulfur content normal to the soil under observation, or the variety of plants used is a matter for future observation.

"Application of these results to field practice is reserved until more data on field plots are available."

**An Improved Respiration Calorimeter for Use in Experiments with Man.** C. F. LANGWORTHY AND R. D. MILNER. *Journal of Agricultural Research*, 5 (Nov. 22), 299-348. This is a description of a new model of respiration calorimeter with accessories and includes a discussion of the proper methods of operation and precautions for the work.

**Occurrence of Manganese in Wheat.** WILLIAM P. HEADDEN. *Journal of Agricultural Research*, 5 (Nov. 22), 349-55. It is concluded that manganese is present in approximately the same proportion as iron in the wheat kernel, irrespective of soil or climatic condition or iron content of the soil. It is apparently the proper conclusion, therefore, that it is an essential constituent of the wheat.

**Ash Composition of Upland Rice at Various Stages of Growth.** P. L. GILE AND J. O. CARRERO. *Journal of Agricultural Research*, 5 (Nov. 29), 357-64. Ash analyses of upland rice were made in order to show the variation in composition, especially in regard to iron, from the early stages of growth to complete maturity of the plant.

**Miscellaneous Insecticide Investigations.** E. W. SCOTT AND E. H. SIEGLER. *Department Bulletin* 278. Contribution from the Bureau of Entomology. 47 pp. Paper, 10 cents. This bulletin describes experiments with various chemicals used singly and combined for the destruction of insecticide pests. It is primarily of interest to horticulturists but contains material of value to those engaged in the preparation or analysis of insecticides.

**Our Foreign Trade in Farm and Forest Products.** PERRY ELLIOTT. *Department Bulletin* 296. Contribution from the Bureau of Crop Estimates. 51 pp. Paper, 10 cents. This bulletin is a summary of the leading features of the foreign trade of the United States in farm and forest products. It is intended for general circulation. The following products are discussed and data given as to production and trade conditions:

Live animals, dairy products, packing-house products, other

animal products, cotton, grain and grain products, sugar, coffee and coffee substitutes, cocoa and chocolate, tea, tobacco, oil cake and vegetable oils, nuts, alcoholic liquors, seeds, spices, vegetables, fruits, vegetable fibers, minor agricultural products, logs, lumber and timber, naval stores, gums, and minor forest products.

In discussing these topics data of general chemical interest are given for the following articles not mentioned in the above list: Beef fats and oils, oleomargarine, stearin, oleo stearin, tallow, animal grease and oils, glue and gelatin, and the following vegetable oils: corn, cottonseed, flaxseed, cocoa butter, coconut, nut, olive, palm, palm kernel, rape seed, soya bean and lemon.

**The Northern Hardwood Forest: Its Composition, Growth, and Management.** E. H. FROTHINGHAM. *Department Bulletin* 285. Contribution from the Forest Service. 80 pp. Paper, 20 cents.

**A Bacteriological Study of Retail Ice Cream.** S. HENRY AYERS AND WILLIAM T. JOHNSON, JR. *Department Bulletin* 303. Contribution from the Bureau of Animal Industry. 24 pp. Paper, 5 cents. This bulletin is a technical discussion of results obtained from the bacteriological examination of samples of ice cream purchased in various stores in Washington, D. C.

**Some Effects of Selection on the Production of Alkaloids in Belladonna.** A. F. SIEVERS. *Department Bulletin* 306. Contribution from the Bureau of Plant Industry. 20 pp. Paper, 5 cents.

**The Cultivation of Peppermint and Spearmint.** WALTER VAN FLEET. *Farmers' Bulletin* 694. Contribution of the Bureau of Plant Industry. 13 pp.

**Digestibility of Some Animal Fats.** C. F. LANGWORTHY AND A. D. HOLMES. *Department Bulletin* 310. 23 pp. Paper, 5 cents.

**Phosphate Rock and Methods Proposed for Its Utilization as a Fertilizer.** W. H. WAGGAMAN AND W. H. FAY. *Department Bulletin* 312. Paper, 5 cents. This bulletin discusses the various processes for treating phosphate rock and the manufacture of phosphoric acid and phosphoric fertilizers.

**Psychrometric Tables.** C. F. MARVIN. *Weather Bureau Document* 235. 87 pp. Paper, 10 cents. This is a reprint (with supplement) of the tables for obtaining the vapor pressure, relative humidity and the temperature of the dew point from readings of the wet and dry bulb thermometers, as prescribed for use in the Weather Bureau Offices.

## SMITHSONIAN INSTITUTION

**Magnetron Theory of Structure of Atom.** A. L. PARSON. Publication 2371. Reprinted from Vol. 65, No. 11, of the *Smithsonian Miscellaneous Collection*. 80 pp. Paper, 30 cents.

## NATIONAL ACADEMY OF SCIENCE

**Catalogue of Meteorites of North America, to January 1, 1909.** OLIVER C. FERRINGTON. *Memoirs of the National Academy of Sciences*. Vol. 13. 513 pp. and 36 map pp. Cloth, 85 cents.

**Turquois.** JOSEPH E. POGUE. *Memoirs of the National Academy of Sciences*. Vol. 12, Part II, Third Memoir. This gives a study of the history, mineralogy, geology, ethnology, archaeology, mythology, folklore, and technology of the turquois.

## GENERAL LAND OFFICE

**United States Mining Laws and Regulations Thereunder as to Mineral Lands.** Circular 430. 104 pp. Paper, 10 cents.

## BUREAU OF LABOR STATISTICS

**Industrial Poisons Used in Rubber Industry.** ALICE HAMILTON. *Bulletin* 179. 64 pp. and 12 plates. Paper, 20 cents.

## BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**Bureau of Foreign and Domestic Commerce Potash Pro-**



duction in California, and Potash from Kelp. THOMAS H. NORTON. Reprint from Commerce Reports of June 12 and June 19, 1915. 13 pp.

#### HYGIENIC LABORATORY

Excretion of Thymol in Urine. ATHERTON SEIDELL. Part 3 of Bulletin 101.

Modification of Rose's Method for Estimation of Pepsin. MAURICE H. GIVENS. Part 5 of Bulletin 101.

#### PUBLIC HEALTH SERVICE

State Laws and Regulations Pertaining to Public Health Adopted during 1914. ANONYMOUS. Reprint 279. This is a collection of 190 pages of regulations reprinted from the Public Health Reports of 1914-1915. Paper, 20 cents.

Standards for Determining the Purity of Milk. H. W. CONN. Public Health Reports, 30 (Aug. 13), 2349-94. This reports on an investigation to determine the accuracy of milk analyses. The most important generalization in the summary is as follows: "The standard methods of Milk Analysis, published by the American Public Health Association, are in emphatic need of revision. These standard methods lay great emphasis on some of the least important points, while they neglect to lay any emphasis on some of the most important ones. The revision of these methods is now in the hands of at least three committees, one appointed by the American Public Health Association, one by the Society of American Bacteriologists, and one by the Association of Instructors."

Public Health Administration in Chicago, Illinois. J. C. PERRY. Public Health Reports, 30 (Aug. 20), 2442-87; (Aug. 27), 2536-61; (Sept. 10), 2699-740; and (Sept. 24), 2850-77. This is a report of an investigation of the organization and efficiency of the city health department of Chicago, which was conducted from December, 1914 to April, 1915, by the Civil Service Commission of that city, assisted by the author of the papers as representing the United States Public Health Service. The report is of more than local interest since it indicates in many details methods or principles of organization which should be of general interest to chemists, physicians, and others having to do with state and municipal inspection and administration work of this general nature.

The Pharmacy of Useful Drugs. MARTIN I. WILBERT. Public Health Reports, 30 (Aug. 27), 2533-5; also as Reprint No. 297. This is a report upon the proposed list of useful drugs as arranged by the Committee of the American Medical Association and others. The list of drugs is not included at this time but the basis upon which it is being prepared is described.

An Efficient Liquid Disinfectant. A Formula by which One Can be Readily Prepared. ALBERT S. STEVENSON. Public Health Reports, 30 (Oct. 8), 3004-8; also as Reprint 304. This is a description of a preparation made from pine oil, "emulsified by saponified resin" by a definite procedure which is described. The estimates of costs are given and uses of the finished disinfectant stated.

#### SANITARY LEGISLATION

Recently adopted laws and regulations and recent court decisions on matters of chemical and sanitary interest are reported in the Public Health Reports for the current year (Volume 30) as follows (numbers in parenthesis are pages in P. H. R.):

Standards for Milk. Kansas Supreme Court Decision on Regulations of State Board of Health. *State vs. Meyer*, 146 Pac. Rep. 1007. (P. 2323.) The State statute which authorizes the State Board of Health to make rules and regulations governing the sales of foodstuffs and the regulations which have been made under this statute, are held to be valid.

Regulations of Offensive Trades. Regulations of the Department of Health, New York City, issued March 30. (P. 2346.) In these regulations are included specifications as to glue making, varnish or oil boiling, fat rendering and melting, distillation of alcoholic spirits, manufacture of lampblack,

turpentine or tar treating, and refining ores, metals, and alloys, etc.

Collection of Samples and Analyses of Drinking Water. Kansas Board of Health Regulations, issued June 8. (Pp. 2518-21.) These regulations include rules governing collection of samples and analyses of water from city supplies, both ground water and surface water, water supplied by common carriers, and water sold in bottles or other containers.

Sale of Preparations Containing Wood Alcohol Prohibited—Labeling Required. New Hampshire Statute Chapter 3, Act of February 17. (Pp. 2594-5.) Limits of the use of wood alcohol and labels required are prescribed.

Production, Care, and Sale of Milk and Milk Products. New York City Department of Health Regulations, issued March 30. (Pp. 2598-2611.) These regulations include definitions of milk, cream, pasteurized milk and cream, of grades A, B, and C, and skimmed milk including specifications as to bacterial count, etc.

Misbranding of Foods and Drugs. Connecticut Statute, Chapter 204, Act of May 7. (Pp. 2677-8.) This is an amendment of Chapter 255 in which misbranding is defined.

Adulterated Milk. New York Act Construed. *People vs. Martin*, 151 N. Y. Suppl. 69. (Pp. 2771-2.) This is a report on the N. Y. Supreme Court decision as interpreting the definition of adulterated milk and applying this definition not only to milk sold for butter making, cheese making, etc., but to all milk sold in the State. The standards which are fixed by the law are quoted in full.

Methods for Estimation of the Solids and the Acid Content of Vinegar. Massachusetts Board of Health Regulations, issued July 6. (P. 2912.) "According to the provisions of Chapter 239<sup>1</sup> of the General Acts of 1915, the following are hereby declared, until further notice, to be the methods for the estimation of the solids and the acid content of vinegar for determining the composition or value of said vinegar as a basis for payment in buying or in selling, or for the purpose of inspection:

"Solids—Measure 10 cc. of filtered vinegar into a tared flat-bottom platinum dish of 50 mm. diameter, evaporate on the water bath to a thick sirup and dry for exactly 2½ hrs. in the drying oven at the temperature of boiling water; cool and weigh. It is essential to use a flat-bottom dish.

"Total Acids—Titrate a suitable amount of the sample, which has been diluted until it appears very slightly colored, with standard alkali, using phenolphthalein as indicator. One cc. of N/10 alkali is equivalent to 0.0060 g. of acetic acid.

"All weights and measures, if used by a chemist of recognized standing, must have been standardized by himself, and if used by other than a chemist of recognized standing, must have been standardized by the Bureau of Standards at Washington, D. C. All alkali used in the estimation of the acid content of vinegar must have been standardized by a chemist of recognized standing."

Production, Care, and Sale of Milk and Milk Products. Durham, County and City, N. C. Board of Health Regulations, issued July 5. (Pp. 2973-86.) This includes definitions of the standard quality of milk of various grades. A similar regulation by the same body is given, Pp. 2986-87, covering the manufacture, care, and sale of ice cream.

Production, Care, and Sale of Milk and Milk Products. Brunswick, Georgia. Ordinance 142 as amended May 24. (Pp. 3054-5.) This ordinance as amended includes a definition of the quality of milk required for sale to the public.

Poisonous Substances in Food Stuff—Manufacturer Held Liable to Consumer. Decision of Tennessee Supreme Court. 177 S. W. Rep. 80. (Pp. 3095-7.) It is held that a manufacturer of foodstuffs that are placed on sale in sealed packages must exercise care to see that nothing unwholesome or in-

<sup>1</sup> Public Health Reports, July 23, 1915, p. 2199.

jurious is contained in the packages and that he is liable to the consumers for injuries resulting from negligence in filling the packages even when consumers purchase them from a dealer and not directly from the manufacturer.

**Production, Care, and Sale of Milk and Cream.** Bloomfield, New Jersey Board of Health Regulations, issued May 26. (P. 3106.) This defines the limiting bacterial count for pasteurized milk and cream and prescribes for the labeling of the pasteurized product.

**Securing of Samples of Food Stuffs and Drugs.** Connecticut Statute, Chapter 165, Act of April 28. (P. 3263.) This regulation amends the procedure for the taking of food and drug samples for analyses.

#### COMMERCE REPORTS—NOVEMBER, 1915

Large quantities of mangrove bark useful for **tanning**, are on hand in Madagascar, but inaccessible because of lack of ships for transportation. (P. 485.)

The Japanese **sulfur** industry, which has declined for years, is now being revived, owing to increased markets in the Orient, America and Europe. (P. 493.)

The **Aluminum Company** of America has purchased an unfinished aluminum works in North Carolina, the construction of which, by French interests, had been interrupted by the war.

**Lead mines** near Kingston, Ontario, abandoned two years ago, have been purchased by Americans, and will soon be reopened. (P. 499.)

The United States, formerly third, is now the largest purchaser of **rubber** from Java. (P. 500.) The United States continues to be the largest purchaser from the Amazon valley. (P. 501.)

The **beet sugar** industry of Canada is increasing. (P. 503.)

In an electric smelter at Belleville, Canada, steel is being produced directly from ore containing 7.5 per cent of titanium. The charge is preheated by the waste gases produced in the smelting of the ore. (P. 521.)

**Antimony** mining in Japan has been neglected in the past, but owing to the present high prices, is being revived. (P. 521.)

The principal **iron ore** deposits of Brazil, almost undeveloped, consist of bedded hematite, a conglomerate consisting of hematite cemented with limonite and hematite "float" and sand. Smaller deposits of magnetite (some titaniferous) exist. (P. 538.)

The production of **steel** in Germany is increasing. (P. 549.)

The **dye works** under English government control (British Dyes, Ltd.) to be established at Huddersfield, England, will occupy a 450 acre tract, and employ 10,000 adults. (P. 565.)

**Aluminum foil** is being produced in the United States as a substitute for tin foil for wrapping, etc. (P. 581.)

The principal **salt beds** of Canada, in the province of Ontario, are at a depth of about 1000 ft. The salt is obtained by evaporation of brine formed by leaching of the beds. (P. 603.)

The production of **aluminum** in the United States in 1915 is expected to be 100,000,000 lbs., about half the world's production. (P. 606.)

The use of natural **dyestuffs**, such as logwood, involves an increase of time and labor in the operations, thus materially cutting down the capacity of a plant. (P. 611.)

The Society of Chemical Industry, Basel, the largest Swiss dye makers, will pay a dividend of 16 per cent.

A company has been formed for the manufacture of **soda ash** and **caustic soda** in Switzerland. (P. 611.)

Attempts to promote the **monazite** industry of India have been hindered by an embargo on monazite except to the United Kingdom. (P. 614.)

Additions to the **steel industry** in South Africa, which is at present small, are being planned. (P. 638.)

The **rubber** production of the Malay peninsula shows an increase. (P. 642.)

While **tungsten ores** are known to exist in Brazil, their extent or commercial availability has not been determined. (P. 654.)

Experiments conducted by the Bureau of Standards have shown that **American glass-pot clays** are superior to German clays or mixtures of German and American clays. (P. 657.)

Shipments of **crude oil** from Mexico are about normal. (P. 691.)

The Italian government operates laboratories for the production of **quinine** for medicinal purposes. (P. 695.)

In a new **peat-distillation** process recently patented in England, the peat is compressed into briquets, which are partially dried, and then introduced into a retort consisting of several chambers at successively higher temperatures. The resultant coke has 92 per cent carbon and 5.7 per cent ash, and is especially suited for steel manufacture. The oil produced is nearly free from sulfur. About 20 lbs. of ammonia and 20 lbs. of paraffin wax are produced per ton of dry peat, as well as some toluene and acetone. The yield of oil varies with different peats, being with English peat about 26.5 gals. per ton of peat. (P. 716.)

Steps have been taken in Venezuela to encourage the cultivation of **fiber** producing plants, especially sisal. (P. 734.)

A large number of **drug materials** used in the United States, may be obtained in China. (P. 742.)

Among methods used in Germany for revivifying **bone black** is treatment with gaseous sulfurous acid. (P. 746.)

**Gold deposits** in Mysore, India, have yielded over \$200,000,000 and are not nearly exhausted. (P. 751.)

The efforts of Japan to further the **dyestuff** and **explosive** industries include subsidies sufficient to guarantee dividends of 8 per cent, restricted to one company for each of the above purposes. Serious objection has been raised to this discrimination against unprotected companies. (P. 772.)

The Bureau of Standards will be glad to furnish information and assistance to any American firms attempting to make **filter paper**. (P. 773.)

A large modern plant for drying **copra** has been erected in Laguna Province, P. I. (P. 777.)

Pebbles for **cement mills**, etc., formerly imported, are now obtained from Nevada. (P. 780.)

The seaweed found in the so-called "Sargasso Sea" in the Central Atlantic, and thrown upon the Bahama coasts, contains 9 per cent K<sub>2</sub>O, and is therefore suggested as a source of **potash**, even though it contains less than the Pacific kelps. (P. 781.)

The mineral products of Quebec province include **asbestos**, **chromite**, **copper**, **gold**, **silver**, **zinc**, **lead**, and **iron ores**; **feldspar**, **graphite**, **kaolin**, **mica**, **ocher**, and **phosphate rock**. (Sup. 23g.)

#### SPECIAL SUPPLEMENTS ISSUED DURING NOVEMBER

Ireland—19n	British India	50b	Siam	58a
Canada—23g	China—52j		German Southwest	
Guatemala—29a	Dutch East Indies		Africa—72a	
Salvador—36a	—53a		Portuguese	West
Brazil—40d	Japan—55l		Africa—77a	

#### EXPORTS TO THE UNITED STATES.

QUEBEC	PROVINCE	SUP	23c	(Pp.)
Calcium acetate	Creosote oil			DUTCH EAST INDIES—
Nitric acid	Glycerine			Sup. 53a
Aluminum	Gums			Benzine
Antimony	Sodium nitrate			Cubebs
Asbestos	Enameled brick			Damar
Bones	Mercury fulminate			Gambier
Are light carbons	Wool grease			Peanuts
Carbolic acid	Hides			Gum leucopannin
Citric acid	Iron ore			Gum copal
Oxalic acid	Sienna			Gutta percha
Tartaric acid	Paper stock			Hides
Wood alcohol	Pyrite			Jelutong
Ammonium sulfate	Zinc ore			Kapok
Aniline arsenate				Citronella oil
Balsam	SALVADOR	Sup.	36a	Quinine
Barium chloride	Balsam			Rubber
Bone-black	Gold			Sugar
Calcium carbide	Hides			Vanilla
				Paraffin
GREENLAND—477	IRELAND—Sup.	19n		
Cryolite	Hides	Magnesia		
BURMA, BRITISH				SIAM
INDIA—Sup.	50b			Sup. 58c
Cutch	Benzine			Camboge
Hides	Mineral wax			Hides
Lac	Copper matte			Palm-seed
				Tungsten ore



# BOOK REVIEWS

**The Chemistry of Agriculture for Students and Farmers.** By CHARLES W. STODDART, Ph.D., Professor of Agricultural Chemistry in the Pennsylvania State College. Illustrated with \$3 engravings and 1 plate. Lea and Lebiger, Philadelphia and New York. 364 pp. Price, \$2.00.

The author's purpose in writing the present volume has been to supply the "need for a text on general agricultural chemistry, which will cover the field briefly, in a logical manner, giving only the facts and not consisting of a disconnected series of quotations and tables from the very extended literature of the subject. The need for such a text has been particularly marked in teaching large classes of students at the Pennsylvania State College."

The purpose which Professor Stoddart has thus outlined in his preface has been very creditably performed. In a volume of 364 pages he has presented most interestingly the main facts of plant and animal chemistry. Beginning with the germination of the seed, the growth of the plant and formation of plant compounds are taken up in natural logical sequence; the rôle of the air, soil, fertilizers, and other factors in plant-growth are duly considered while the three concluding chapters of the book are devoted to a brief treatment of animal physiology and the chemistry of dairy products.

In the minds of those who have studied "The Elements of Agricultural Chemistry," by Davy, "Die Chemie in ihre Anwendung auf Agrikultur," by Liebig, or those two classics "How Crops Grow" and "How Crops Feed," by our own Prof. Johnson, there will arise, in reading Professor Stoddart's book, a serious doubt as to whether an Agricultural Chemistry for the use of students should not give something more than "only the facts." The older authorities, whom we have named, were imbued with the firm idea that the one lesson which the student should learn, before all others, is to verify his facts for himself. Prof. Johnson, for example, in discussing the relation of atmospheric nitrogen to vegetable nutrition, describes the experiments of Priestley, De Saussure, Boussingault, Ville, and Lawes, Gilbert and Pugh. In reviewing these experiments the student is not only initiated into the methods of agricultural-chemical research, but he is also taught to grapple with ideas and to weigh independently each opposing argument. Professor Stoddart in his preface makes the candid admission that in certain matters where "a difference of opinion exists among authorities" he has deemed it "better to present them as facts rather than to give the various arguments." For a popular treatise such a method of presentation is permissible, but it is open to question in a scientific textbook, where the main purpose should be to train the minds of students in habits of original and independent thought.

The historical side of agricultural chemistry, which was perhaps somewhat overemphasized by the older writers, is not touched upon in Professor Stoddart's new book. This restriction may have been due to the necessary limitations of space. A student's knowledge of agricultural chemistry, however, is not firmly grounded unless he have some knowledge of the parts played by Priestley, Liebig, Boussingault, Lawes and Gilbert and other investigators in laying the foundation-stones of the science. Every student of Penn. State should know something of the agricultural-chemical researches of Dr. Pugh.

An author, however, should not be blamed altogether for omissions which lie beyond his demarcations. The subject of agricultural chemistry has undergone so wide an expansion within the past quarter-century that the advantages of any one writer's method of treatment, whether it be descriptive, experimental, or technical, must be attended with certain limitations. The student will find the smooth level road, which Prof. Stoddart has laid out, to be enjoyable and time-saving, even though he miss the outlook and strengthening climb of steeper pathways.

The typography and illustrations of this new work are excellent in every way. While there are isolated statements to which specialists might object, the volume as a whole appears to be free from serious errors. For a brief descriptive presentation of the main facts of Agricultural Chemistry, Professor Stoddart's book is one of the best which has come to our attention and as such it is cordially recommended.

C. A. BROWNE

**Transactions of the American Electrochemical Society, Vol. XXVII, 1915.** 481 pages. Cloth bound, \$3.00; paper bound, \$2.75.

The meeting with which this volume is concerned was held in Philadelphia during April. An address by the retiring President, F. A. Ladbury, deals with the external relations of the Society. Much has been accomplished in this direction during the past few years and it is obviously of advantage to have electrochemical problems brought to the attention of others who are not directly concerned in the subject. It was pointed out, however, that much remains to be done, particularly with patent litigation and the conservation of power for electrochemical industries. The electrochemists may well cooperate with others who have common aims in these directions.

Twenty-one papers were presented of exceedingly varied interest, some of great value dealing with recent developments in electrochemistry and generally accompanied with the most interesting discussions. Indeed the discussions are fully worth the price of the volume if nothing more were to be found in it. The titles of the papers are as follows:

The American Electrochemical Society in its External Relations—*Presidential Address* by F. A. Ladbury.

The Development of Electro-Analysis in America—E. F. Smith. Some Problems in Copper Leaching—A general discussion.

Electroplating with Cobalt—H. T. Kalmus, C. H. Harper and W. L. Savell.

Electro-Deposition of Smooth, Solid Lead from Lead Nitrate Solutions—F. C. Mathers and Asa McKinney.

Cleaning and Plating in the Same Solution—O. P. Watts.

Depolarization in LeClanché Cells—M. deK. Thompson and E. C. Crocker.

Neutralization of Adsorbed Ions—W. D. Bancroft.

The Coagulation of Albumin by Electrolytes—W. D. Bancroft.

Formation of Magnesium Sub Oxide in the Electrolytic Preparation of Magnesium—F. C. Frary and N. C. Berman.

The Temperature of Reaction between Acheson Graphite and Magnesia—O. L. Kowalke and D. S. Grenfell.

Thermo-Electromotive Force of Certain Iron Alloys—T. S. Fuller.

Calorizing Metals—W. E. Ruder.

"Fibrox"—E. Weintraub.

The Thermal Conductivity of Refractories—Boyd Dudley, Jr.

Fixation of Atmospheric Nitrogen—Leland L. Summers.

The Cyanamid Process—Frank S. Washburn.

Commercial Nitrogen Fixation: A Polemical Note—S. Peacock.

An Illuminating Engineer's Conception of an Ideal Light—Herbert E. Ives.

Chemistry in the Development and Operation of Flaming Arc Carbons—William C. Moore.

Lighting of Electrolytic Tank Rooms—R. E. Harrington.

Those of the papers dealing with fixation of nitrogen are timely, and show with what importance the Society regards this subject. Some valuable data in regard to the economic conditions are presented.

Copper leaching is well discussed and much valuable information is to be found in connection with this complicated problem. Several papers dealing with light are of particular interest and the importance of artificial illumination and the problems connected with it are given much attention.

The excellent work of Kalmus and his associates on electroplating with cobalt is presented before this Society and a most valuable discussion adds much to this able paper.

S. A. TUCKER

## NEW PUBLICATIONS

By IRENE DEMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

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**Chemistry: Handbook of Chemistry and Physics.** CHEMICAL RUBBER COMPANY. 12mo. 375 pp. Price, \$2.00. Chemical Rubber Co., Cleveland.

**Chemistry: Jahrbuch der Chemie.** Vol. 24. Ed. by R. MEYER. 8vo. 478 pp. Price, \$4.50. F. Vieweg & Sohn, Braunschweig.

**Chemistry: La Chimie.** ANDRÉ JOB. 8vo. 40 pp. Larousse, Paris.

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**Aluminum Bronze Alloys.** W. M. CORSE. *Iron Trade Review*, Vol. 57 (1915), No. 24, pp. 1137-1138.

**Antimony: Electrolytic Antimony Refining.** ANSON G. BETTS. *Metallurgical and Chemical Engineering*, Vol. 13 (1915), No. 14, pp. 848-851.

**Beating Test for Papermaking Fibers.** E. SUTERMEISTER. *Paper*, Vol. 17 (1915), No. 9, pp. 11-18.

**Butter: Beschleunigtes Verfahren zur Wasser- und Fett-Bestimmung in Butter und Margarine.** A. A. BESSON. *Chemiker-Zeitung*, Vol. 39 (1915), No. 123, pp. 770-772.

**Camphene: Konstitutionsbestimmung in der Camphengruppe.** OSSIAN ASCHAN. *Annalen der Chemie*, Vol. 410 (1915), No. 2, pp. 222-256.

**Carbolic Oil: Verfahren zur Herstellung von Carboleol.** F. RASCHIG. *Zeitschrift fuer angewandte Chemie*, Vol. 28 (1915), No. 84, pp. 409-412.

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**Food Chemistry: Die Nahrungsmittelchemie im Jahre 1914.** J. RUEHLE. *Zeitschrift fuer angewandte Chemie*, Vol. 28 (1915), No. 82, pp. 405-408.

**Glass Factories: Gewinnung von Ammonsulfat und Teer aus den Generatorenrauen der Glasfabriken.** ROBERT DRALLE. *Sprechsaal*, Vol. 48 (1915), No. 45, pp. 399-400.

**Minium: Ueber Mennige.** JAROSLAV MILBAUER. *Chemiker Zeitung*, Vol. 39 (1915), No. 135, pp. 858-859.

**Petroleum: Die Petroleumvorkommen an der Kueste des mexikanischen Meerbassens in der Staaten Texas und Louisiana.** BRUNO SIMMERBACH. *Petroleum*, Vol. 11 (1915), No. 2, pp. 58-62.

**Petroleum: Gasoline Process Boosts Heavy Oil Yield.** A. M. MCAFEE. *National Petroleum News*, Vol. 7 (1915), No. 9, pp. 34-38.

**Potash from Wood and Plant Ashes.** H. BRADLEY. *Metallurgical and Chemical Engineering*, Vol. 13 (1915), No. 14, pp. 841-846.

**Rosin: Ueber die Autoxydation des Kolophoniums.** W. FAHRION. *Chemische Revue ueber die Fett- und Harz-Industrie*, Vol. 22 (1915), No. 11, pp. 97-98.

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**Steels: Heat Treatment of Modern Steels.** R. R. ARBUTT. *Iron Trade Review*, Vol. 57 (1915), No. 21, pp. 981-987.

**Trinitrotoluene.** MAURICE COPESAROW. *The Chemical News*, Vol. 11 (1915), No. 2921, pp. 247-248.



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Acetate of Lime, gray.....	100 Lbs	5.00	@	5 10
Alum, lump.....	100 Lbs	5.00	@	5 25
Aluminum Sulfate, high grade.....	100 Lbs	5.00	@	5 25
Ammonium Carbonate, domestic.....	Lb	8 1/2	@	9 1
Ammonium Chloride, gray.....	Lb	8 1/2	@	9
Ammonium Phosphate, commercial, 98-100%.....	Lb	11	@	11 1/4
Aqua Ammonium, 16% drums.....	Lb	2 1/4	@	2 1/2
Arsenic, white.....	Lb	3 7/8	@	4 1/4
Barium Chloride.....	Ton	105.00	@	115.00
Barium Nitrate.....	Lb	15	@	16
Barites, prime white, foreign.....	Ton	30.00	@	24.00
Bleaching Powder, 35 per cent.....	100 Lbs	10.00	@	11.00
Blue Vitriol.....	Lb	10 1/4	@	11
Borax, crystals, in bags.....	Lb	5 3/4	@	6
Boric Acid, powdered crystals.....	Lb	10	@	10 1/2
Brimstone, crude, domestic.....	Long Ton	22.00	@	22.50
Bromine, technical, bulk.....	Lb	5 00	@	6.50
Calcium Chloride, lump.....	Ton	—	@	11.78
Calcium Chloride, granulated.....	Ton	—	@	14.78
Caustic Soda, 74 per cent.....	Lb	5 3/8	@	5 1/2
Caustic Soda, 76 per cent.....	Lb	5 3/4	@	6
Chalk, light precipitated.....	Lb	4 3/4	@	5 1/2
China Clay, imported.....	Ton	11.00	@	16.00
Feldspar.....	Ton	8.00	@	12.00
Fuller's Earth, foreign, powdered.....	100 Lbs	80	@	1.05
Glauber's Salt, in bbls.....	100 Lbs	60	@	75
Green Vitriol, bulk.....	100 Lbs	80	@	1.00
Hydrochloric Acid, commercial, 18°.....	100 Lbs	2.25	@	3.00
Hydrochloric Acid, C. P., conc., 22°.....	100 Lbs	2.50	@	3.25
Iodine, resublimed.....	Lb	4.25	@	4.30
Lead Acetate, white crystals.....	Lb	12 1/8	@	12 1/2
Lead Nitrate.....	Lb	13 1/2	@	14
Litharge, American.....	Lb	6 1/2	@	—
Lithium Carbonate.....	Lb	90	@	1.00
Magnesium Carbonate.....	Lb	5 1/2	@	6 1/2
Magnesia, "Calced".....	Ton	30.00	@	35.00
Mercuric Chloride, commercial.....	Lb	1.75	@	2.00
Nitric Acid, 36°.....	Lb	7 1/2	@	8
Nitric Acid 42°.....	Lb	9	@	9 1/2
Phosphoric Acid, sp. gr. 1.750.....	Lb	30	@	32
Phosphorus.....	Lb	40	@	1.00
Plaster of Paris.....	Bbl	1.50	@	1 70
Potassium Bichromate, casks.....	Lb	40	@	—
Potassium Bromide.....	Lb	5.00	@	—
Potassium Carbonate, calcined, 80 @ 85%.....	100 Lbs	26	@	28
Potassium Chlorate, crystals, spot.....	Lb	48	@	50
Potassium Cyanide, bulk, 98-99 per cent.....	Lb	29	@	33
Potassium Hydroxide.....	Lb	49	@	54
Potassium Iodide, bulk.....	Lb	3.75	@	4.00
Potassium Nitrate.....	Lb	—	@	—
Potassium Permanganate, bulk.....	Lb	1.50	@	1.75
Quicksilver, flask, 75 lbs.....	Lb	130.00	@	140.00
Red Lead, American, dry.....	Lb	7 1/4	@	—
Salt Cake, glass makers'.....	100 Lbs	55	@	65
Silver Nitrate.....	Oz	34 1/8	@	36 1/8
Soapstone in bags.....	Ton	10.00	@	12.00
Soda Ash, 48 per cent.....	100 Lbs	2.00	@	2.25
Sodium Acetate.....	Lb	8 1/4	@	9
Sodium Bicarbonate, domestic.....	100 Lbs	1.20	@	1.30
Sodium Bicarbonate, English.....	Lb	3 1/2	@	3 3/4
Sodium Bichromate.....	Lb	25	@	—
Sodium Carbonate, dry.....	100 Lbs	1.25	@	—
Sodium Chlorate.....	Lb	25	@	50
Sodium Fluoride, commercial.....	Lb	15	@	—
Sodium Hydroxide, 60 per cent.....	100 Lbs	3.50	@	4.00
Sodium Hyposulfite.....	100 Lbs	2.75	@	3.00
Sodium Nitrate, 95 per cent, spot.....	100 Lbs	3.00	@	—
Sodium Silicate, liquid.....	100 Lbs	85	@	1.10
Sodium Sulfide, 30%, crystals, in bbls.....	Lb	2	@	2 1/2
Sodium Sulfite, crystals.....	Lb	2 1/2	@	2 3/8
Strontium Nitrate.....	Lb	22	@	—
Sulfur, flowers, sublimed.....	100 Lbs	2.20	@	2.60
Sulfur, roll.....	100 Lbs	1.80	@	2.15
Sulfuric Acid, chamber, 60°.....	100 Lbs	2.00	@	2.50
Sulfuric Acid, conc., sp. gr. 1.842.....	100 Lbs	3.00	@	3.25
Sulfuric Acid, oleum (fuming).....	100 Lbs	3.00	@	3.25
Talc, American.....	Ton	9.00	@	13.00
Terra Alba, American, No. 1.....	100 Lbs	75	@	80
Tin Bichloride, 50°.....	Lb	13 3/4	@	14
Tin Oxide.....	Lb	46	@	48
White Lead, American, dry.....	Lb	6	@	—
Zinc Carbonate.....	Lb	13	@	15
Zinc Chloride, commercial.....	Lb	8	@	8 1/2
Zinc Oxide, American process.....	Lb	8 1/8	@	8 7/8
Zinc Sulfate.....	Lb	6 1/2	@	—

## ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.....	Lb	1.30	@	1.35
Acetic Acid, 28 per cent, in bbls.....	100 Lbs	3.75	@	5.00

Acetic Acid, glacial, 99 1/2% in carboys.....	Lb	30	@	35
Acetone, drums.....	Lb	35	@	40
Alcohol, denatured, 180 proof.....	Gal	50	@	52
Alcohol, grain, 188 proof.....	Gal	2.68	@	2 70
Alcohol, wood, 95 per cent, refined.....	Gal	55	@	57
Amyl Acetate.....	Gal	5.50	@	4.00
Aniline Oil.....	Lb	95	@	1.10
Benzoic Acid, ex-toluol.....	Lb	4.00	@	1.50
Benzol, 90 per cent.....	Gal	80	@	90
Camphor, refined in bulk, bbls.....	Lb	42	@	—
Carbolic Acid, U. S. P., crystals, drums.....	Lb	1 60	@	1 70
Carbon Bisulfide.....	Lb	6 1/2	@	7 1/2
Carbon Tetrachloride, drums, 100 gals.....	Lb	16	@	20
Chloroform, domestic, crystals.....	Lb	60	@	65
Citric Acid, domestic, crystals.....	Lb	55 1/2	@	60
Cresol, U. S. P.....	Gal	1.15	@	1.25
Dextrine, corn (carloads, bags).....	100 Lbs	3.05	@	3.16
Dextrine, imported potato.....	Lb	10	@	12
Ether, U. S. P., 1900.....	Lb	15	@	20
Formaldehyde, 40 per cent.....	Lb	9 1/2	@	10
Glycerine, dynamite, drums included.....	Lb	45	@	55
Oxalic Acid, in casks.....	Lb	40	@	41
Pyrogallol Acid, resublimed bulk.....	Lb	1.25	@	1.45
Salicylic Acid.....	Lb	4.00	@	4.15
Starch, cassava.....	Lb	3 1/2	@	4 1/4
Starch, corn (carloads, bags).....	100 Lbs	2 05	@	2 16
Starch, potato.....	Lb	6 1/4	@	7
Starch, rice.....	Lb	7	@	8
Starch, sago.....	Lb	3	@	3 1/4
Starch, wheat.....	Lb	5	@	5 1/4
Tannic Acid, commercial.....	Lb	75	@	76
Tartaric Acid, crystals.....	Lb	52	@	52 1/2

## OILS, WAXES, ETC.

Beeswax, pure, white.....	Lb	47	@	55
Black Mineral Oil, 29 gravity.....	Gal	12 1/2	@	13
Castor Oil, No. 3.....	Lb	14 1/4	@	15 1/2
Ceresin, yellow.....	Lb	10	@	14
Corn Oil, crude.....	100 Lbs	7.85	@	7.90
Cottonseed Oil, crude, f. o. b. mill.....	Gal	54 1/2	@	55
Cottonseed Oil p. s. y.....	Lb	8 1/8	@	8 1/2
Croston, beechwood.....	Lb	6.00	@	6.50
Cylinder Oil, light, filtered.....	Gal	20	@	25
Fusel Oil, crude.....	Lb	3.20	@	3.30
Japan Wax.....	Lb	12 1/2	@	12 1/4
Lard Oil, prime winter.....	Gal	92	@	96
Linseed Oil, raw (car lots).....	Gal	61	@	—
Menhaden Oil, crude (southern).....	Gal	46	@	47
Naphtha, 68 @ 72°.....	Gal	23	@	24
Neat's-foot Oil, 20°.....	Gal	95	@	97
Paraffine, crude, 117 & 119 m p.....	Lb	3 1/2	@	4
Paraffine Oil, high viscosity.....	Gal	24 1/2	@	25
Rosin, "F" Grade, 280 lbs.....	Bbl	5.80	@	—
Rosin Oil first run.....	Gal	—	@	32
Shellac, T. N.....	Lb	21	@	22
Spermaceti, cake.....	Lb	25	@	26
Sperm Oil, bleached winter, 38°.....	Gal	72	@	73
Spindle Oil, No. 200.....	Gal	19 1/2	@	20
Stearic Acid double-pressed.....	Lb	13 1/2	@	14
Tallow, acidless.....	Gal	78	@	80
Tar Oil, distilled.....	Gal	30	@	31
Turpentine, spirits of.....	Gal	54 1/2	@	55

## METALS

Aluminum, No. 1, ingots.....	Lb	56	@	58
Antimony, ordinary.....	Lb	38	@	39
Bismuth, New York.....	Lb	3.25	@	—
Copper, electrolytic.....	Lb	20	@	—
Copper, lake.....	Lb	26	@	—
Lead, N. Y.....	100 Lbs	5.40	@	—
Nickel, electrolytic.....	Lb	50	@	—
Nickel, shot and ingots.....	Lb	45	@	—
Platinum, refined.....	Oz	47.50	@	52.50
Silver.....	Oz	54 3/8	@	—
Tin.....	100 Lbs	40.00	@	—
Zinc, N. Y.....	Lb	17 1/4	@	—

## FERTILIZER MATERIALS

Ammonium Sulfate.....	100 Lbs	4.00	@	—
Blood, dried.....	Unit	3.40	@	—
Bone, 4 1/2 and 50, ground, raw.....	Ton	35.00	@	—
Calcium Cyanamid.....	Unit of Ammonia	2.45	@	—
Calcium Nitrate, Norwegian.....	100 Lbs	—	@	—
Castor Meal.....	Unit	—	@	—
Fish Scrap, domestic, dried, f. o. b. works.....	Unit	3.75	@	10
Phosphate, acid.....	Unit	75	@	80
Phosphate rock; f. o. b. mine.....	—	—	@	—
Florida land pebble, 68 per cent.....	Ton	2.75	@	3.00
Tennessee, 70-80 per cent.....	Ton	5.00	@	5.50
Potassium "muriate," basis 80 per cent.....	Ton	480.00	@	500.00
Pyrites, furnace size, imported.....	Unit	13 1/4	@	—
Tankage, high-grade; f. o. b. Chicago.....	Unit	3.10	@	10

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## EDITORIALS

### MOBILIZATION OF AMERICAN INDUSTRIES

The coöperation of the American Chemical Society in the plan to mobilize American industries for public service has been announced by the President of the United States.

THE WHITE HOUSE, WASHINGTON  
January 13, 1916

My dear Sir:

The work which the *American Chemical Society* has done through its members on the NAVAL CONSULTING BOARD is a patriotic service which is deeply appreciated. It has been so valuable that I am tempted to ask that you will request your society to enlarge its usefulness to the Government still further by nominating for the approval of the Secretary of the Navy a representative from its membership for each state in the Union to act in conjunction with representatives from the *American Society of Mechanical Engineers*, the *American Society of Civil Engineers*, the *American Institute of Electrical Engineers*, and the *American Institute of Mining Engineers*, for the purpose of assisting the NAVAL CONSULTING BOARD in the work of collecting data for use in organizing the manufacturing resources of the country for the public service in case of emergency. I am sure that I may count upon your cordial coöperation.

With sincere regard,

Cordially yours,

(Signed) WOODROW WILSON

DR. CHARLES H. HERTY

President of the *American Chemical Society*,  
Chapel Hill, North Carolina

.....  
CHAPEL HILL, NORTH CAROLINA  
January 18, 1916

PRESIDENT WOODROW WILSON  
WASHINGTON, D. C.

My dear Sir:

I have the honor to acknowledge receipt of your letter of January 13, 1916, requesting the coöperation of the *American Chemical Society* with other national societies "in the work of collecting data for use in organizing the manufacturing resources of the country for the public service in case of emergency."

In behalf of the members of the *American Chemical Society*, it gives me pleasure to assure you of our hearty coöperation in this most important national undertaking.

I shall begin at once the work of securing the nomination of a member from each state, and shall forward such nominations promptly to the Secretary of the Navy for his approval.

Very respectfully yours,

(Signed) CHARLES H. HERTY

President, *American Chemical Society*

### THE UTILIZATION OF WOOD WASTE<sup>1</sup>

Mark Twain says, "We all talk about the weather, but nothing is done." So it is with wood waste utilization. The lumbermen are interested, of course, but their interest is tempered by weariness and restrained by skepticism. They are open to conviction but would like to see anyone who can convince them. Much the same situation may be found where any of our great industrial wastes are concerned. Those who are responsible for the wastes are so close to them and so long familiar with them that they have come

to regard them as the unavoidable accompaniment of the industry. Moreover, plans for waste utilization commonly involve the extension of a business into regions which, however familiar they may be to those doing business in them, are new and strange to the makers of the waste. Conversely, those whose specialized experience might enable them to utilize the waste to advantage, hesitate to incur the large capital expenditure required for establishing an industry dependent upon a raw material over which they have no control and the supply of which may cease at any time, as, for example, when a lumber mill burns down.

These are real and serious obstacles in the way of the utilization of wastes, but the things which anyone can do easily bring no great rewards. The world belongs to those who overcome difficulties and nowhere does it offer richer promise of potential wealth made actual than in the colossal wastes of lumbering.

The figures involved are of astronomical proportions and consequently make little more impression on the mind than the distances of the fixed stars. Let us, however, try once more really to comprehend them. On a total annual cut of 50 billion feet board measure of merchantable lumber, at least 75 billion feet, or about 112,000,000 tons, of wood waste are produced. For every man, woman and child in the country there is therefore annually wasted more than a ton of wood.

The proportion of waste to merchantable lumber varies within wide limits with the kind of wood. In the lumbering of hardwoods, according to Goodman, only 15 per cent of the weight of the standing timber appears as finished lumber. Sixty-five to seventy per cent of the original tree is left on the ground and the mill waste amounts to over a cord per 1,000 feet of lumber. Frankforter, who had exceptional opportunities for studying the lumber industry in the middle, northern and western states, reports that in these sections of the country the best equipped and most skilfully operated mills utilize a little less than 40 per cent of the total weight of wood in lumber, lath and shingles. Our own large scale studies on long-leaf yellow pine have proved that under the best operating conditions only 33.42 per cent of the average tree becomes available as lumber, box shooks, lath and shingles; two-thirds is wasted. In the estimate of total annual waste given above an average of 60 per cent of the entire tree was reckoned as waste but in view of the loss on yellow pine, which is our most important timber tree, and the far greater proportionate loss on hardwoods, it is evident that the total annual waste is substantially more than 75 billion feet and may even reach 90 billion feet. Frankforter's estimate of 100 billion feet on a smaller annual cut is undoubtedly too high and not in accordance with his other figures.

Of all our timber trees none lends itself more readily to waste utilization than long-leaf yellow pine. It is cut more largely than any other species and the indi-

<sup>1</sup> Address before the 8th Annual Meeting of the American Institute of Chemical Engineers, Baltimore, January 12 to 15, 1916.

vidual operations are commonly on a great scale which ensures the local concentration of waste in vast amounts. For these reasons and because my associates and I have studied the waste utilization problems presented by this wood more carefully than those of any other species, I shall ignore hardwood distillation, the use of extracted chestnut chips for pulp and paper making, and the occasional use of mill waste from northern conifers in sulfite pulp mills, and ask you to direct your attention solely to the utilization of wood waste from long-leaf yellow pine.

The present annual cut of this species is about 15 billion feet, board measure. The waste is equivalent to 30 billion feet. It may be said at once, without fear of successful contradiction, that the potential profits in this waste are far greater than any actual profits which this branch of the lumber industry can be made to yield from lumber. When this waste is intelligently considered, not as waste but as raw material, it will be seen to afford a basis for building up the greatest group of co-related by-product industries the world has ever seen. The products of these industries will comprise wood pulp, pulp boards, paper, paper bags, paper twine, turpentine, rosin, pine oil, charcoal, tar, ethyl alcohol, cattle feed, varnishes, ether, and not improbably acetic acid, wood alcohol, acetone and producer gas.

The wood of long-leaf pine is heavy, exceedingly hard, very strong, tough, coarse-grained, compact, durable and very resinous. Its density varies with the height from the ground, the age of the tree and its content of pitch or oleoresin. Sargent gives the average specific gravity as about 0.7, which would seem to be too high: determinations in the Forest Products Laboratory ranged from 0.426 to 0.583. Determinations in our own laboratory gave 0.626 as the specific gravity of round wood averaging 7 inches in diameter. The weight per cubic foot for logging waste we found to be 39.1 lbs. bone-dry. The weight per cord depends greatly upon the shape and size of the pieces. On the dry basis we have found the sawdust to weigh about 1,400 lbs., mill waste with little or no bark 2,340 lbs., with much bark 1,708 lbs.; logging waste in the form of fairly smooth, round logs weighs about 3,260 lbs., and if rough and irregular will average 1,860 lbs., while mature long-leaf pine consisting largely of heartwood will run about 4,300 lbs. to the cord, bone-dry.

We find the ultimate composition of long-leaf pine to be:

Carbon	Hydrogen	Oxygen	Nitrogen	Sulfur	Ash	Total
53.96	7.13	38.65	0.03	0.04	0.16	100 per cent

Our determination of fuel value of average sawmill dust gave 9,240 B. t. u., dry basis. Moisture in green wood averages 34.15 per cent, fresh green stumps average 28.69 per cent, lightwood 13.35 per cent. Stumps about 6 years old carry around 20 per cent of water and kiln-dried lumber contains an average of about 10 per cent. The proportion of bark varies to some extent with the age of the tree and is relatively high. Small, round, Mississippi wood had about 9 per cent, Florida pulp wood over 11 per cent, and Florida

trees over 18 inches diameter bore 8.6 per cent of bark by weight. Determinations in our laboratory of the fiber length of long-leaf pine gave a maximum of 7.40 mm., minimum 3.00 mm. with an average of 4.60 mm. as compared with 3 to 3.5 mm. for spruce.

In determining the amount of field waste under careful operation, members of our organization selected five plots of one acre each as truly representative as possible of the average quality of yellow pine timber. As soon as the timber had been felled the waste between 3 inches and 9 inches was collected, classified and weighed. Much of it was also corded and scaled to determine relations between weight, cord measure and volume. Each stump was measured and its volume and weight computed. Needles from four trees were weighed.

The main points of accumulation of mill waste are the main refuse conveyor and the main dust conveyor. Actual determinations by weight of the amounts of waste carried by these conveyors in very large scale operations were made by members of our staff. The results of these determinations in the field and at the mill enable us to state with a very close approximation to the truth the relative proportions of the initial products of the average yellow pine tree. They have perhaps never been ascertained before within such limits of accuracy or upon so large a scale. The proportions of the several products are as follows:

YIELD FROM ENTIRE TREE		YIELD FROM LOGS	
	Per cent	PERCENTAGE OF WHOLE TREE	
Needles and twigs.....	2.25	Red and rotten.....	1.45
Limbs under 3 in.....	2.54	Slabs, edgings and trimmings..	18.07
Cordwood.....	6.42	Sawdust and shavings.....	17.62
Pulpwood.....	4.54	Shingles.....	0.06
Red and rotten.....	6.60	Lath.....	1.39
		Lumber and box shooks.....	31.97
TOPS AND CULLS.....	22.35		
LOGS, as indicated.....	70.56		70.56
STUMPS.....	6.48		
LIGHTWOOD.....	0.61		
	100.00		

Comprehensive studies were conducted on these wastes for a period of eight months. The different classes of wastes were carefully and repeatedly analyzed and their content of rosin and turpentine determined. Papers in great variety were made in our experimental paper mill under direction of Mr. V. E. Nunez, and extractions and distillations on the small commercial scale carried out in our Forest Products Department by Dr. L. F. Hawley. The results obtained, together with data from actual commercial practice, point incontestably to the following stupendous totals:

Upon an annual cut of 15 billion feet of yellow pine the lumber industry in our southern states now wastes raw materials sufficient for the concurrent daily production of 40,000 tons of paper, 3,000 tons of rosin, 300,000 gallons of turpentine, and 600,000 gallons of ethyl alcohol, together with fuel sufficient to meet the requirements of all these industries.

Despite the prevailing opinion to the contrary among lumbermen, and even among papermakers, long-leaf yellow pine lends itself admirably to the manufacture of paper. It is too pitchy for the sulfite



process but is readily reduced to pulp by the soda process. Much the best results are, however, obtained by the sulfate process, which, when carried out under proper conditions, yields an excellent kraft pulp and paper. The pulp bleaches with some difficulty but may with care be brought to good color without serious impairment of strength. The bleached pulp makes good wood writings and when mixed with pulp from gumwood can be run off into good book papers. A cord and half of round waste makes a ton of paper as against about two cords of spruce costing northern mills from \$9 to \$13 a cord.

The production of ethyl alcohol from yellow pine waste by the Ewen and Tomlinson process has been fully demonstrated as a technical proposition, about 90,000 gallons of high-grade 95 per cent alcohol having been made in the plant of the Standard Alcohol Company at Fullerton, La. The commercial merit of the proposition remains to be demonstrated since this company is now in the hands of the receiver for reasons altogether apart from the technical merit of the process. It may, however, be said that every technical man familiar with the process believes that it is capable of producing 95 per cent alcohol at a cost, including cooperage and all fixed and manufacturing charges, of not more than 20 cents a gallon. Such alcohol is worth to-day about 56 cents a gallon. The yield per cord of sawdust or hogged wood waste containing 50 per cent water is 10 gallons in large scale operation, but yields much higher have been obtained in the laboratory.

The process is based, of course, on the observation of Braconnot in 1819 that cellulose, by treatment with mineral acid, is converted into reducing and fermentable sugars. For nearly 100 years experimenters have endeavored to develop this observation into a commercial process. With the exception of Ewen and Tomlinson all have failed to produce alcohol in commercial quantities. Simonsen in Sweden, in 1889, began a series of brilliant researches which cleared up many points of difficulty and ultimately enabled him to secure very satisfactory results on the large laboratory scale. Attempts at commercial operation, however, developed fresh obstacles and led to the abandonment of the process. The well known German chemist, Alexander Classen, patented during the year 1900, 1902 and 1903 various modifications of the general process of producing sugars and alcohol by treatment of comminuted wood with strong acids under heat. Subsequently several plants were built in this country for carrying out one or another of these modifications. In none of them were any substantial amounts of alcohol produced, and the Classen process must be regarded as commercially inoperative. It remained for Ewen and Tomlinson to overcome the fundamental technical difficulties underlying all these attempts and to put forward the first process capable of large scale production of ethyl alcohol from wood.

The Ewen and Tomlinson process is essentially one for producing fermentable sugars. The fermentation of these sugars, once produced, may be carried out and the alcohol recovered in any distillery by the

usual methods. It is my belief that the process affords the cheapest known method for producing these sugars and that it therefore is ultimately destined to become an important if not the most important source of industrial alcohol.

In carrying out the process, hogged wood waste, usually containing about 50 per cent of water, is loaded into a rotary digester holding about 7 cords and having a protective and heat-insulating lining. Sulfuric acid in relatively small amount is sprayed upon the wood and then steam is admitted to the digester. The critical temperature is reached as quickly as possible and the reaction is then extremely rapid if not indeed nearly instantaneous. Pains are therefore taken to reduce the pressure immediately and to empty the digester of its contents as promptly as may be. About 25 per cent of the weight of the wood is converted to reducing sugars, not all of which are fermentable.

The cooked material, which is not unlike coarse coffee grounds in appearance, is transferred by conveyors to a diffusion battery or other extraction apparatus in which the sugars are dissolved out. The spent chips go to a continuous press for removal of excess water and are then available as fuel. The extracted juice is neutralized with lime and is then ready for fermentation. The concentrated slop from the stills finds use as cattle feed and is about equivalent to molasses for that purpose.

In a modification patented by me the process may be diverted as a whole to the production of carbohydrate cattle feed. In this modification hydrochloric acid is substituted for sulfuric and subsequently removed so far as is readily possible by heating or blowing air through the mass. The remaining acid is then converted to common salt by the addition of an equivalent amount of sodium carbonate. The juice is extracted and concentrated to the consistency of molasses.

A major economic problem in the South which is bound up with the utilization of wood waste is that of the agricultural development of the cut over lands. It has been demonstrated that by a steam puller yellow pine stumps may be pulled for about 33 cents each. In the trials made the stumps averaged 563 lbs. each, which makes the cost of pulling \$1.16 per ton. Where logging tram roads are still in place, the stumps can be brought to a central plant for treatment at a total cost well within \$2.50 per cord. Treated by solvent extraction they should yield per cord about 6 gallons of turpentine, 2½ gallons of pine oil and 380 lbs. of rosin. The extracted chips, as pointed out by Veitch and Merrill, and amply demonstrated in our experimental paper mill, are available for the manufacture of an excellent grade of kraft paper. Strangely enough, and contrary to our first impression, the charred portions common in such stumps are easily removed in the process and leave the paper clean. The chips are of course also available for alcohol production.

Stumps and the highly resinous wood residues termed lightwood, together with the box slabs from

turpentine trees, are directly available for treatment by several processes of distillation. The average green wood with 35 per cent moisture contains about 50 per cent rosin but in selected samples of wood the rosin may run higher than 50 per cent. No large quantities are usually to be had, however, containing more than 30 per cent. The composition of the rosin is variable but in green wood it runs about 80 per cent rosin and 20 per cent volatile oils; about 80 per cent of the latter are turpentine and the balance pine oil.

Destructive distillation is carried on in retorts operated commonly without temperature control. Average yields under these conditions are:

Light oils 6 gallons	Turpentine 6 gallons	Heavy oil 16 gallons	Tar 48 gallons	Charcoal 35 bushels
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Various processes in which the retort temperature is controlled, as in the bath process and the processes of Gautier, Pritchard, and others, have been proposed and several put in operation for a time on either the commercial or large experimental scale. They offer advantages in the way of better yields and quality of turpentine, but these gains are so nearly offset by higher fuel costs and higher maintenance charges that the commercial superiority of these more complicated processes has yet to be demonstrated.

Ten years ago recovery of turpentine from comminuted waste by steam distillation was practiced in many plants, the steam being blown through the mass of chips either upward or downward and carrying the volatile oils with it to the condenser. The decline in the price of turpentine in 1907 and 1908 proved so severe a blow to the industry that it is to-day practically wiped out.

The well known Yaryan process added to the steam distillation method the subsequent step of extracting the chips with a volatile solvent from which the dissolved rosin could later be recovered. Several plants of large capacity were operated successfully until in

1913 the failure of the American Naval Stores Co. caused a heavy drop in the price of rosin which was followed by the failure of the company operating the Yaryan process. A contributory cause may well have been the large losses of solvent incident to the process.

Several methods have been proposed for the recovery of turpentine, pine oil and rosin from yellow pine wastes by the action of water solutions of alkali but none are thought to be operating commercially. They depend upon the fact that the wood is only slightly attacked by the dilute alkali in which the rosin is readily soluble. Nevertheless, some wood is dissolved and the difficulty of separating this so-called "humus" from the rosin has prevented the introduction of processes of this type. The difficulty has been overcome in a simple and ingenious way by Whitaker and Bates, who salt out the rosin soap by increasing, after the initial treatment of the wood, the concentration of the alkaline solution to 3.5 per cent free alkali. The treated chips are then available as a raw material for papermaking.

When the real work of wood waste utilization has once begun and the attention of chemical engineers and financial men has been drawn more generally to the huge potential values now ignorantly thrown away we may expect the rapid development of these by-product industries and the initiation of many new ones to the great enrichment of the South and in somewhat less degree, that of the Northwest. It would doubtless be too sanguine to expect the directive impulse for this new development to come from the lumbermen themselves. They are too close to the wastes. They are blinded by the sawdust. But if they fail much longer to grasp the opportunity which has been so long beside them they must be content to see others reap the benefits and profits which will come through control of processes, special apparatus, and, above all, of technique.

ARTHUR D. LITTLE

## ORIGINAL PAPERS

### POTASH FROM FIR WOOD MILL-WASTE

By HARPER F. ZOLLER

Received December 27, 1915

Several exploitative articles on potash supplies in the recent engineering journals have revealed many possible sources but only a few which are likely to become economically practicable, and capable of bridging the loss caused by the non-approachable taffsurt deposits.

Lately an effort is being made to rejuvenate interest in the historic "first source" of potash, *viz.*, from wood-ash, or, more correctly, from vegetable ash. These efforts, which are chiefly journalistic as yet, have caused the writer to publish the following experiments conducted by himself over a year ago within the vicinity of the "great wood-waste district"—the Pacific Northwest.

While the articles which directly bear upon "potash

from wood-ashes" are of extremely recent issue, it is none the less certain that the possible problem set forth in them was, in a certain measure, seriously considered for some time in advance of their publication, and was experimentally dealt with where its solution was most inevitable. Indeed there are but few problems about the lumber industry which the expert lumbermen have not considered, but in order that a problem may appeal interestingly to a lumberman it must not only be technologically possible but it must also be economically and readily possible of application.

The articles concerning potassium from wood-ash which have appeared since the potash shortage occurred, and with which the writer is familiar, are two in number. The first appeared in the *Journal of the Board of Agriculture*, 22 (1915), 146-8 on "Sawmill Waste as a Source of Potash," by C. T. Gimingham.



And the later and more general article on "Potash from Wood and Plant Ashes," by Harlow Bradley in the *Metallurgical and Chemical Engineering Journal* for Nov. 15, 1915. This latter article contains many analyses and statements having a more direct bearing upon the specific matter to be considered by the writer.

While it is not my intention to make this consideration exhaustive or a complete solution of the stated problem, it is my desire to report the results of experiments which were carefully performed and to offer certain information concerning the conditions to be confronted in attacking the question. This information being derived from immediate contact with the lumber region may be of value to those who were not so fortunately located.

#### EXPERIMENTAL

My interest in the recovery of potash from wood ashes was aroused by an employee of the St. Paul and Tacoma Lumber Co.<sup>1</sup> This man obtained samples of ashes from the large mill-waste incinerators or burners used to dispose of the excess butts, slabs and sawdust collecting daily in voluminous amounts. The log "off-fall" consisted chiefly of Douglas Fir. The samples were a heterogeneous mixture of white ash, charcoal and inorganic matter from occluded soils. The charcoal existed in fine division as well as large lumps, and made up a large bulk of the sample. A rough quantitative analysis was run upon these samples as to their potassium and sodium content, the potassium and sodium content being considered as those sodium and potassium salts which were soluble in water during a period of 24 hours' leaching. One-pound portions of the above samples were employed in the leachings and the total potassium and sodium content of the leachings was determined.

Potassium was determined by the perchlorate method as outlined by Cumming and Kay on pages 203-4 of their "Quantitative Chemical Analysis." Sodium was determined by the difference of their mixed chlorides.

It was our next endeavor to determine whether or not more potassium salts were extractable with hot water from the above samples during the same leaching period. These experiments were preliminary to the final and more detailed analysis. Partly because of this fact and mainly because I wished to obtain the samples for myself, to be certain of their representative character, I do not quote the results of these preliminary analyses. The results are not contradictory, however, to those published herewith. It was during the preliminary analysis that the extraordinary amount of sodium chloride was discovered to be present in the ashes.

One-pound portions of each new sample were placed in large one and one-half liter beakers. One liter of water heated to 90° C. was poured over the ashes in each beaker and the whole was set for 24 hours in a hot-water bath regulated between 80° and 90°.

<sup>1</sup> A large and representative lumber mill located in Tacoma, Wash., and visited by the members of the American Chemical Society during its recent meeting in Seattle.

At the end of the period the insoluble portion was filtered from the extract and the residue was washed with hot water until the filtrate again measured one liter. The total extractable portion from one pound of ashes was divided into two portions of exactly 500 cc. each and the potassium content was determined with the procedure before mentioned. This division of the total extract was made in order to have check analyses on the same sample. The averages of the check results are reported. Analysis was conducted on three distinct samples of the incinerator ash.

Table I gives the results of analyses conducted upon samples of Douglas Fir waste ashes obtained from the incinerator of the aforementioned mill and which seem representative of the general character of the ashes therefrom.

TABLE I—POTASSIUM EXTRACTED FROM 1 LB. SAMPLES OF WASTE ASHES

SAMPLE	No.	Grams			Lbs.	
		KClO <sub>4</sub>	per lb. ash		per ton ash	
		Grams	K <sub>2</sub> O	KCl	K <sub>2</sub> O	KCl
Douglas Fir.....	1	5.22	3.557	2.813	15.65	12.38
	2	4.624	3.152	2.491	13.87	10.96
	3	7.105	4.842	3.828	21.30	16.85
Cedar.....	1	2.005	1.362	1.077	5.992	4.739

Sample 3 was secured three weeks after Samples 1 and 2, but from the same incinerator.

At a slightly later date a sample of ash was obtained from an incinerator, from a different mill, in which was burned slabs, butts, etc., from cedar logs. Analyses were performed upon this ash employing the same procedure as in the foregoing analysis, with the results given.

#### INTERPRETATION OF RESULTS

In glancing over the results it is evident that little more than approximate knowledge of the potash content can be gained. I found that it was absolutely impossible to get samples from different parts of the incinerator that would be representative of the whole. This was due to two very significant reasons:

1—A large quantity of charcoal (unburned wood) was always found heterogeneously mixed with the ash. This not only contained large amounts of unextractable potash, but also mechanically held portions of the already ashed wood which were particularly resistant to leaching.

2—Various portions of wood possessing different ash content were burned at varying intervals. Hence in certain parts of the burner appeared ashes possessing different potassium content. Charges appear in the incinerator sometimes as follows: a charge of sawdust, then log slabs consisting mostly of bark and cambium layer, then perhaps butts embracing more or less of the heart of the tree.

From these remarks one sees a possible explanation of the discrepancies appearing in the analyses. While Samples 1, 2 and 3 were composed of ashes almost entirely from Douglas Fir the non-water extractable portion of them runs high. The charcoal present amounted to at least one-half the weight of the samples. No exact measurement of the carbon content was undertaken as it would be a fluctuating factor. This content varies, of course, with the physico-chemical conditions within the incinerator at the time

"burning." The incinerators are not constructed with the idea of ideal draft conditions and efficiency in incineration, but for the purpose of expeditiously disposing of the mill-waste at the lowest possible cost.

The analysis of the ash from the cedar wood incinerator indicated that cedar wood ash does not yield as large a potassium value as the fir wood ash. This is in keeping with results obtained by investigations of the inorganic content of certain woods. The same of cedar wood ash did not appear to contain as much charcoal as did the ash from the fir wood. This is undoubtedly due to the conditions within the incinerator, as this is a controllable factor.

The large excess of sodium, as NaCl, found in the preliminary tests was a surprising factor and was quite unexplainable without a knowledge of the logging conditions of the wood in question. Many of the large lumber concerns in the Pacific Northwest are built either directly on the shore-line or tributaries of Puget Sound or upon river banks, islands or inlets on the Pacific Slope. Many of these mills utilize the water facilities either for log transportation or storage. Hence the log "off-fall" becomes impregnated with salt sea-water, which accounts for the presence of the excess NaCl in the mill-waste ash samples. Of course many mill-waste incinerators in this part of the Northwest are not bothered with the presence of the NaCl excess. Nevertheless, this is an important factor to be considered in the production of potash from mill-waste ash.

We can safely say that it is possible to obtain potash, calculated as  $K_2O$ , from Douglas Fir mill-waste incinerators in the amounts of from 10 to 20 lbs. per ton of "ash" employed. Furthermore, that this potash may be obtained, along with other extractable matter, by merely leaching the ash in suitable vats with hot water for a 24-hour period and in all probability a 12-hour period would be as efficient.

#### DISCUSSION

From Bradley's article in the *Met. and Chem. Eng. Jour.* (already mentioned) we deduce the following concerning the inorganic analysis of fir wood: Fir-wood bark, next to the needles, yields the largest quantity of ash and here only 1.78 per cent. From Musurre's analyses of 'firs from different localities (localities not mentioned)' the ashes yield from 3.6 to 7.36 per cent of  $K_2CO_3$ . And in Table 12 ('The Analysis of Fir Wood Ashes,' by Berthier), of the same article, we find the potash content to be 15.32 per cent. In this last analysis it was not mentioned whether or not it was the whole wood analyzed or certain portions."

Now if one is to advocate the construction of special incinerators for fir wood scrap in general in order that an abundance of ash may be secured from which to extract potash, more reliable information must be secured in the way of analysis of the various portions of fir wood scrap and statistics as to the amounts of the various portions obtainable. Perhaps the "off-fall" in the forest, *i. e.*, stumps, branches, tops and needles, would yield a larger quantity of potash

per given weight of its ash. This would be deduced from the summary of Prof. E. Emmon's analyses quoted in the above article. Perhaps the Douglas Firs of a particular locality are richer in potassium salts than Douglas Firs from another locality. Again, data as to the potassium content of the "off-fall" from Sitka Spruce, Western Hemlock, Western Cedar and, above all, Larch from the Idaho and Montana districts, must be secured, as all these woods are interspersed throughout the lumber tracts of the Northwest in larger or smaller quantities.

Plainly the mill-waste fir from the hundreds of lumber mills presents a different problem than that just mentioned. And it is with this problem that this article is designed to directly deal. Many questions must be thoroughly considered which both militate against and favor the incineration of sawmill waste for the production of potassium salts. A few of these will be considered briefly.

1—Expense of erecting efficient incinerators for properly burning the fir mill-waste, so as to prevent the local fusions of the ash at the high temperature often developed within the burners. Also to prevent the occlusion of some ash in the charcoal clumps always found in the ash of the burners of the ordinary type.

2—Increased cost to the mill for the establishment of suitable leaching vats, where the extraction of the ash is to be accomplished within the same mill producing them. Also, in this respect, suitable processes for effecting the separation of the excess NaCl in case the incinerators are found in localities where sea-water mill-waste is common. The presence of large quantities of salt (often over 16 per cent of the entire ash) would present no small difficulty to the leaching process.

3—Would the average daily run from a moderately sized fir sawmill yield a quantity of ash suitable for the production of extractable potash in amount sufficient to compensate for the investment involved? From good authority it is possible for the average fir wood sawmill to yield daily, within its incinerators, from three to eight tons of ash, depending upon conditions within the incinerator and the kind of mill-waste burned. I am confident that an ash free from charcoal will yield a value for extractable  $K_2O$  considerably larger than those published from my analyses—perhaps twice as large.

4—Will the value of the extracted potash be equivalent to the loss of charcoal, wood alcohol, wood oils, rosin, tannin, etc., in which products the mill-waste abounds and which would be lost in the gases from the incinerators?

5—Would this wholesale incineration of mill-waste for potash production be more economically justifiable than the use of the mill-waste for the production of softwood cellulose from which it is possible to obtain a good grade of paper-pulp, wood-flour and ethyl alcohol?

6—Would it be more advantageous for each mill to extract its own incinerator ashes, or for a centralized concern to contract for the ashes from the great



number of fir wood sawmills for given periods, and estimate the value of the ashes on the amount of pure ash they contain?

While these questions arise from the consideration of the Douglas Fir mill-waste alone it is probable that many of them would apply to the potash problem from nearly any kind of wood mill-waste within the Northwest country.

Observing casually the enormity of the lumber industry in the Pacific Northwest, one is apt to be misled by the possibilities of the potash problem from that territory and from this source. Inasmuch as the majority of the standing timber bordering Puget Sound is of Douglas Fir, and since fir wood yields a large amount of potassium salts as compared with other woods in this region, this outwardly appears to be a likely possibility. The Report of Commerce and Labor for 1913 on "The Lumber Industry," Vol. I, in coöperation with the *Forest Service*, pages 278, Table I gives the following statistics for the State of Washington: "In the State of Washington we find a total of 714 sawmills at the expiration of the year 1909. Arranging these according to output, we find only 13 with an output of less than 50 M. board feet, while there are 110 with an output of from 1,000 to 2,500 M. board feet and 8 with an output of over 50,000 M. board feet. The total output for the State for that year was 3,862,916 M. board feet, leading all of the States in the Union in production of Lumber." When we consider that Washington is second in total amount of standing timber with Oregon ranking foremost, it is little wonder that we consider the Pacific Northwest as a possible but a highly improbable factor in the production of potash from waste wood ash. Although the lumber industry in the State of Washington is growing rather than waning, still the values of the figures in the above Report for 1913 are probably much changed during the intervening time—since the number of lumber mills and total board feet cut are markedly fluctuating factors.

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## NOTES ON A NEW PROCESS OF BLEACHING<sup>1</sup>

By S. F. PECKHAM

Some years ago a man brought to me some flax fiber and asked me to bleach it by a quick process without injury to the fiber. He said that a certain party that he named claimed to have done it. I said to him, "You will have nothing left but paper pulp," and after some talk he owned up that that was the case.

I knew that about 30 years ago one Charles Toppan had taken out a patent for a bleaching compound of which petroleum and the fixed oil of mustard were the essential ingredients. Great claims were set forth for this mixture, but nothing came of it as there was too little fixed oil of mustard produced in the world to supply the demands of one large bleachery. At that time the only petroleum on the market was Pennsylvania petroleum and it was a well known fact

that the crude petroleum and its distillates would dissolve in a solution of soap. A study of this process from all available sources led me to conclude that Toppan's compound, which was originally a lubricating compound, consisted of a fixed mustard-oil soap dissolved in petroleum, and that by varying the proportions his bleaching compound consisted of petroleum or its distillates dissolved in a solution of fixed mustard-oil soap.

A complete study of the chemistry of the fixed oil of mustard led me to conclude that any other pure vegetable oil soap might act in a similar manner. The cheapest oil soap of that description on the market is what is known as cotton-oil soap stock. Having procured some of this, I proceeded to make a solution of Pennsylvania petroleum distillate in a solution of the soap. This oil readily dissolved and on boiling the flax in the solution it came out in a condition to be readily bleached in bleaching solution, but I concluded that the result was not wholly satisfactory as the bleaching solution had to be so strong or the immersion had to be so long that the fiber was tendered.

I then concluded that I would try all the hydrocarbons on the market that came within range of practicability as to price and sufficiency of supply. I first made up a solution of a distillate of California petroleum and on boiling and bleaching the flax it came out very much better in every respect. Reflecting on the fact that California petroleum consists of benzol and its derivatives, while Pennsylvania petroleum consists of paraffins, the idea occurred to me that perhaps still better results could be obtained by using pure or nearly pure benzols.

I found that the different benzols dissolved in soap solution much more readily than the petroleum distillates and that the cleansing effect on the flax fiber was marvelous. Immersion in a very dilute bleaching solution produced a perfect dead-white bleach and left the fiber unimpaired in strength. In fact I had accomplished precisely what the gentleman had asked me to do.

This method can be successfully applied to all vegetable fiber, as linen is the most difficult to bleach of all of them without injury to the fiber.

I have never seen any mention made in chemical literature that benzol and its derivatives are soluble in a solution of soap, nor did I ever hear any statement to that effect. No fixed formula can be designated, as soap is soluble in water in all proportions and the stronger the solution of soap the more benzol the solution will dissolve. The formula used for 100 lbs. of flax was:

WATER, 50 gals.	SOAP, 10 lbs.	BENZOL, 3 gals.
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This was used for a heavy woven line damask, where for ordinary light cottons, such as "gray cloth," very much less material is necessary. Pure benzol need not be used; any of the light distillates of coal tar, coke oven tar or blast furnace tar, freed from impurities by washing and proper treatment, answers the purpose equally well.

<sup>1</sup> Presented at the 8th Annual Meeting of the American Institute of Chemical Engineers, Jan. 12-15, Baltimore.

My invention consists of a process of bleaching by substituting for the usual lime and soda boils a single boil in a solution of soap, preferably a pure vegetable oil soap, in which is dissolved a sufficient quantity of benzol ( $C_6H_6$ ) or its homologues or derivatives, as found in the light distillates of coal tar and similar liquids and in light distillates of some varieties of petroleum, especially that of California, as distinguished from the light distillates of paraffin petroleum. The strength of the solution in both soap and benzol would depend upon the kind and character of the material to be bleached, light cotton fabrics requiring less than heavier cottons, and any cotton less than flax, jute or hemp.

After thorough squeezing and washing to remove the soap solution, the goods or fiber may be bleached in any known chemic. I prefer one of my own preparation consisting of a solution of sodium hypochlorite, prepared by pouring together, cold, a solution of 58 per cent soda ash and a solution of calcium hypochlorite stirring the mixture and allowing it to settle. Both solutions should be prepared cold, and after mixing the solutions they should be allowed to stand at least 4 days or until all the available chlorine in the calcium hypochlorite shall be found in combination with the sodium and in solution. No formula can be assigned for this mixture as calcium hypochlorite varies indefinitely in strength. The quantities taken should be such that there will be a slight excess of the sodium carbonate. After a great many experiments upon this chemic I have found this method of preparation, which is very unlike any which is laid down in the books, to be the only one that will bring all the available chlorine in the calcium hypochlorite into solution as sodium hypochlorite. It is better to prepare this solution of a strength 3-5° Twaddell, and dilute it to such a strength that an immersion of the goods from 3 to 5 hours will effect a bleach. After washing the bleached goods in water they are soured, washed and calendered as usual.

By this method a complete bleach of either cotton or linen can be had in from one to two working days.

I have described a process of bleaching by which the goods or fiber are prepared for the chemic by boiling in a solution of soap in which has been dissolved a sufficient quantity of benzol or its homologs or its methylated derivatives, either separately or mixed together, as found in coal-tar naphthas and similar liquids and the distillations from some petroleum as above set forth.

The soap which I have used is the cheapest that I know of on the market, as it is a by-product of the refining of cottonseed oil and is used in its crude state without further treatment.

The apparatus used is a Kier with a steam jacket to which is attached an inverted condenser which returns the evaporated hydrocarbons to the Kier. The process was applied on a small scale and thoroughly tested out with the most gratifying results. Of course the goods are singed and sheared as is customary. Goods in small pieces were digested for various periods of time and the resulting goods subjected to a great

variety of tests excepting the effects of time upon finished goods. It was found that if the goods were thoroughly dried after thorough washing to free them from soap the effect of the chemic was very much more satisfactory than when they were introduced into the chemic damp, directly from the squeezers. This is not surprising when very dilute solutions of chemic are used as the water remaining in the goods from the squeezers not only dilutes the chemic still further but filled the pores of the goods, thus getting in the way of the chemic and preventing it from doing its work.

An application was made for a patent on the above process with the confident expectation that a valuable invention had been perfected, but the officials at the Patent Office in Washington quoted Toppan's and other patents against me and I found that no amount of argument would convince them that there was the slightest difference between the substances designated "Benzine" and "Benzene"—in fact they declared they were identical. Comment is unnecessary in this place upon such an highly unscientific administration of the Patent Laws.

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#### THE MICROSTRUCTURAL CHANGES ACCOMPANYING THE ANNEALING OF BRONZE (Cu 0.88, Sn 0.10, Zn 0.2)<sup>1</sup>

By HENRY S. RAWDON

Received September 25, 1915

Most of the questions which this study attempts to answer arose in connection with the work on the standard specimens of zinc-bronze (Cu 0.88, Sn 0.10, Zn 0.2) carried on at the Bureau of Standards. The samples used here were chosen from the series prepared in that investigation.

The physical properties of cast bronze are very materially altered by heat treatment, this modification of properties being accompanied by decided changes in the microstructure of the metal. These structural differences are especially marked if the sample has been subjected to mechanical work of any kind previous to the heat treatment; Figs. 1 and 2 illustrate this change. The structural changes here noted, as accompanying the annealing after distortion, may be taken as typical of the copper-rich brasses and bronzes and, in general, of alloys in which copper is the predominating constituent.

#### AIM AND SCOPE OF THE WORK

The general purpose of the work is to show the stages through which the alloy passes in going from the condition shown in Fig. 1 to that shown in Fig. 2, and the conditions necessary for this change of structure to occur. While it is quite generally understood that the condition shown in Fig. 2 is the result of annealing, following distortion of the original structure, the opinion is by no means general that this is always true. Inasmuch as the common commercial use of annealing in the application to brass or bronze is to relieve the internal stresses of material, which has been mechanically "cold-worked" in some way,

<sup>1</sup> The complete report of the results of this study will appear as a Technologic Paper of the Bureau of Standards.



the resulting change of structure is often, though erroneously, regarded as an effect of annealing, pure and simple. By some this change of microstructure

eye; the size of such crystals will depend upon the rate at which the alloy cooled during the solidification, the freedom from mechanical disturbances, etc.

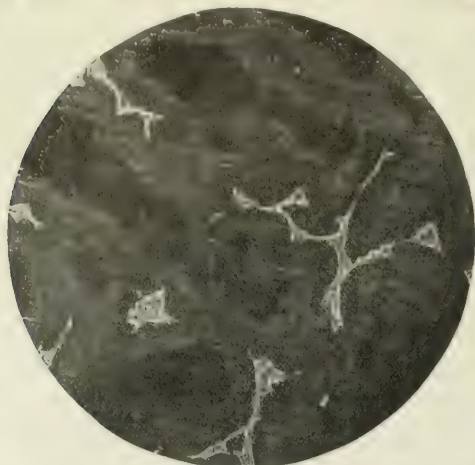


FIG. 1—BRONZE (Cu 88, Sn 10, Zn 0.2) DIRECTLY AFTER CASTING; MAGNIFICATION, 100 $\times$ ; ETCHING, AMMONIUM HYDROXIDE AND HYDROGEN PEROXIDE

ture is regarded in the same light as the grain refining of steel.

Instances are found in the literature on this subject of the recrystallized state resulting directly from the cast condition upon annealing without the intermediary of the preliminary distortion of structure.<sup>1</sup> One of the main objects of this work is to see if such be true for this bronze, *i. e.*, whether a condition resembling, in the effect produced on heating, a "cold-working" of the alloy can be brought about by very unusual methods of cooling, etc.

The temperatures at which the different structural changes are completed together with the period of heating required at these temperatures are carefully noted. No attempt was made to test out any of the various theories as to the exact nature of this process of recrystallization, although the results obtained appear to materially substantiate one of the two main theories on this subject.

#### STRUCTURE OF THE ALLOY

**CAST CONDITION**—The microstructure of the metal upon solidifying after casting is shown in Fig. 1. The metal is composed essentially of a matrix consisting of a solid solution,  $\alpha$ , of tin in copper (disregarding the zinc, which does not cause any pronounced structural change) in which are embedded inclusions of a eutectoid consisting of this same  $\alpha$  solution and another one,  $\delta$ , which is hard and brittle in its nature. The formation of the cored structure which is characteristic of solid solutions in general, will be made clear by reference to Fig. 3, which shows a portion of the equilibrium diagram of copper and tin.

The bronze, directly after casting, consists of "grains" or crystals relatively large in size, *i. e.*, large enough to render them plainly visible to the unaided

<sup>1</sup> Portevin, *Rev. de Mét.*, 6 (1913), 713. Several instances of such observations are summarized here.



FIG. 2—SAME MATERIAL AS FIG. 1; ANNEALED AFTER MECHANICAL DISTORTION; THE LIGHT AND DARK PARALLEL BANDS INDICATE THE "TWINNED CRYSTALS;" 100 $\times$

Each "grain" has a complex structure and consists of a tree-like framework of a solid solution of copper and tin, the branches of which are not uniform in

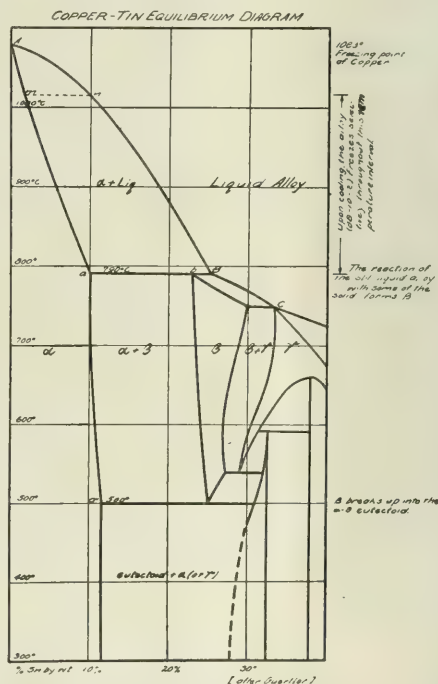


FIG. 3—Cu-Sn Equilibrium Diagram, Taken from GUERTLER.

composition but have a core rich in copper. The branches intersect during the growth and form a tangled mass with tiny crevices in the angles between

the branches filled with a second metallographic constituent—a eutectoid of two different solutions of copper and tin, comparable to the constituent, pearlite, in steel.

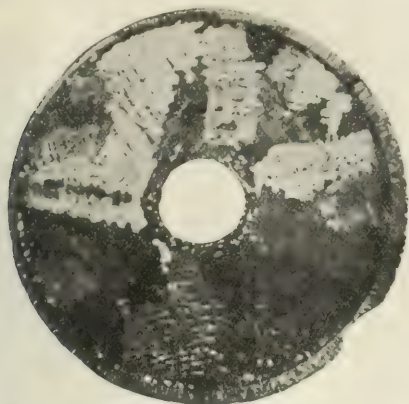


FIG. 4—BRONZE AFTER ANNEALING 1 HOUR AT 800° C. THE THIN LAYER OF RECRYSTALLIZED METAL SHOWS JUST BENEATH THE PROTECTIVE COATING OF COPPER COVERING THE SURFACE AND LINING THE CENTRAL HOLE; MAGNIFICATION, 5 X; ETCHING, FERRIC CHLORIDE

**ANNEALED STATE**—In its annealed state, represented by Fig. 2, the alloy consists of crystals generally much smaller than before. The large macroscopic “grains” have disappeared, as has also their interior dendritic structure with the accompanying eutectoid inclusions. The crystals are not only smaller but are polyhedral forms quite characteristic of this condition. Twinned

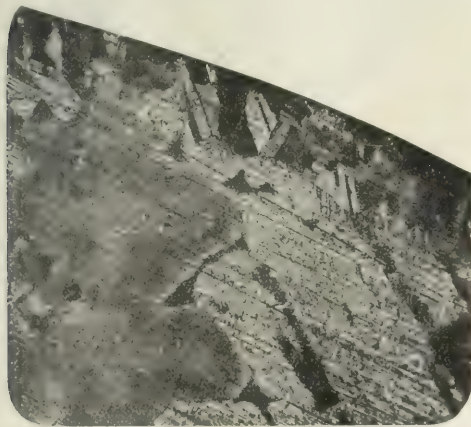


FIG. 6—SIMILAR TO FIG. 4; ANNEALED 2 HOURS AT 600°. MAGNIFICATION, 100 X

crystals are also common (Fig. 2). The grains, or crystals, are now very homogeneous in structure throughout and consist of the  $\alpha$ , or solid solution of copper and tin richest in copper. It may be noted, also, in passing, that inclusions, such as stannic oxide, are unchanged in amount or distribution by the annealing process.

**TRANSITION OF ONE FORM TO THE OTHER**—Guillet<sup>1</sup>

<sup>1</sup> Guillet, *Rev. de Mét.*, 3 (1906), 243, or C. H. Desch, “Metallography,” p. 191.

has suggested a method for converting a ternary alloy into a pseudo-binary one, for purposes of discussion and comparison. In the case of the alloy under discussion (Cu 0.88, Sn 0.10, Zn 0.2), the application of Guil-

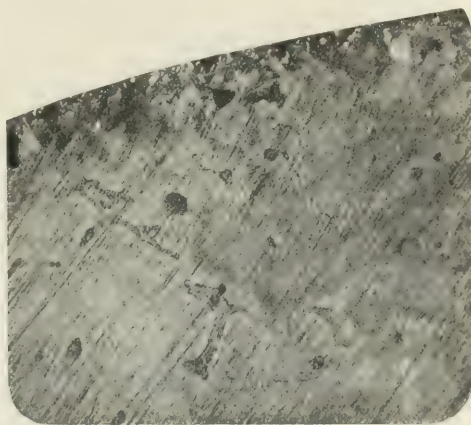


FIG. 5—SIMILAR TO FIG. 4; ANNEALED 8 HOURS AT 400°; MAGNIFICATION 100 X

let's formula shows that the alloy may be considered for all practical purposes as one with a tin content of approximately 11 per cent. As Portevin<sup>1</sup> has pointed out, the first step in the annealing process is to bring the alloy into the condition of “physico-chemical equilibrium” as shown by the equilibrium diagram. The second, or tin-rich phase, will disappear by being

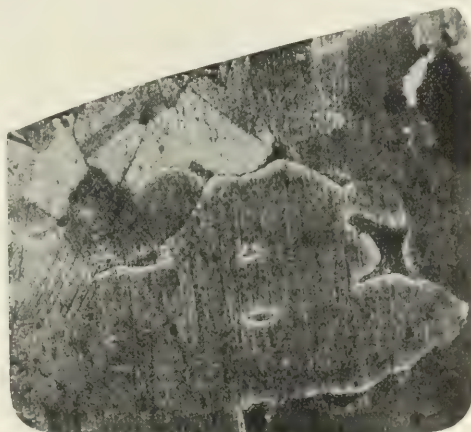


FIG. 7—SIMILAR TO FIG. 4; ANNEALED 8 HOURS AT 800° C.; MAGNIFICATION, 100 X

absorbed by the  $\alpha$ -solution; the heterogeneity of the  $\alpha$ -solution will disappear by diffusion. To produce the condition of “crystalline equilibrium”<sup>2</sup> shown in Fig. 2, the large crystals must be subdivided, re-oriented and rearranged. The main point of this study is to show the conditions under which this “crystalline equilibrium” results.

<sup>1</sup> Portevin, *Rev. de Mét.*, 6 (1913), 677

<sup>2</sup> Portevin, *Loc. cit.*



## SAMPLES USED: PREPARATION AND TREATMENT

1. CHEMICAL COMPOSITION—The material used was chosen at random from broken test bars used in the investigation of the properties of the standard zinc-bronze. The chemical analysis of a casting made

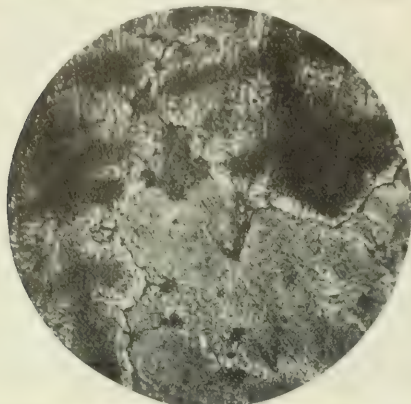


FIG. 8—PERSISTENCE OF THE DENDRITIC STRUCTURE. THE SAMPLE WAS HEATED 8 HOURS AT 600° C. MAGNIFICATION, 100 X. THE APPARENT EARLIER DISAPPEARANCE FROM SOME OF THE CRYSTALS IS DUE TO DIRECTION IN WHICH THE CRYSTAL IS CUT. ETCHING, AMMONIUM HYDROXIDE AND HYDROGEN PEROXIDE

by melting about 25 broken test bars gave the following results:

Copper.....	88.2% Per cent
Tin.....	9.5% Per cent
Zinc (by difference).....	2.3% Per cent
Iron.....	Trace
Lead.....	Not detected

2. PREPARATION—In order to answer the questions set forth, the thermal treatment during the prepara-

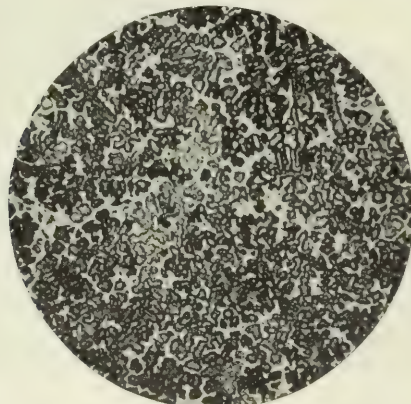


FIG. 9—BRONZE QUENCHED WHILE IN THE MOLTEN STATE; MAGNIFICATION, 100 X; ETCHING, AMMONIUM HYDROXIDE AND HYDROGEN PEROXIDE

tion of the samples was made such as to include all possible cases arising in practice.

The samples after casting received a certain amount of surface "cold-working" by being turned down in the lathe to the required diameter. In this way only the surface layer is distorted and the greater portion of the interior may be used for comparison with the distorted surface metal after annealing. The preparation may be summarized as follows:

Series 1—1-inch hexagonal bars cast in green sand, turned down to a  $\frac{3}{4}$  inch cylinder. This method of casting gives a structure such as is commonly found in the bronze as prepared in commercial foundry practice.

Series 2—Cylinders  $\frac{15}{16}$  inch in diameter (25 grams) were prepared as individual crucible melts and cooled at different rates: *viz.*, quenched after solidifying (approx. 700° C.), air-cooled, and furnace-cooled. These were turned down to  $\frac{3}{8}$  inch diameter.

Series 3—Melts (25 grams) quenched directly from the molten state, no work being done upon them.

Series 4—Cylinders  $\frac{15}{16}$  inch diameter, prepared as in Series 2 and furnace-cooled, were turned down to a diameter of  $\frac{3}{8}$  inch. The amount of metal removed at each cut was carefully noted and the depth of lathe cut was very nearly the same for all the cylinders, thus all received the same amount of "cold-working."



FIG. 10—SIMILAR TO FIG. 9; ANNEALED 8 HOURS AT 800°; MAGNIFICATION, 100 X. THE "RECRYSTALLIZATION" UPON ANNEALING ILLUSTRATES THE FACT THAT VERY SUDDEN COOLING IS EQUIVALENT IN ITS EFFECTS UPON THE CRYSTALLINE STRUCTURE TO A MECHANICAL DISTORTION. ETCHING, FERRIC CHLORIDE

Samples which were to be annealed at the same temperature for different periods were cut from the same cylinder to insure identical structural conditions in each. All samples were copper-plated to prevent surface oxidation during annealing.<sup>1</sup>

3. THERMAL TREATMENT—The annealing temperatures decided upon were 400°, 600°, and 800° C., as the temperatures used ordinarily in a commercial way fall well within this range: 800° C. was chosen as the upper limit as this temperature is very close to the beginning of the melting range for this alloy and it was desired not to complicate the annealing process by the introduction of incipient fusion of the metal. The samples were held at each of these temperatures for periods of 1, 2, 4, and 8 hours. If the process of recrystallization is a progressive one from the

<sup>1</sup> This electro-plating of samples with some metal such as copper renders it easy to heat small metallographic samples, *e. g.*, steel, without fear of oxidation or decarburization, without the use of a vacuum furnace. This is valuable in case the sample is to be examined up to the extreme edge. It also permits the use of very small specimens.

exterior in, the thickness of the recrystallized layer should be proportional to the time of annealing and thus easily measured.

The following tabulated results for the first and the last series indicate the general nature of the observations made and the results obtained.

The samples of Series 1 were not protected against oxidation so that the measured thickness of the re-

These observations are in accordance with and in support of Tammann's theory of recrystallization of "cold-worked" metals.<sup>1</sup> Briefly this theory may be thus summarized: After distortion the metal is in a state of unstable equilibrium. A force analogous to surface tension in the gliding planes of the lamellae into which the crystals have been distorted, is resisted by the "strength of the crystals," *i. e.*, their

TABLE I—(SERIES 1 ABOVE)

This series may be considered typical of this bronze as prepared in commercial foundry practice. Due to surface oxidation, the measured thicknesses do not represent the true depth to which the metal was worked. Average weight of sample, 20 grams.

Specimen	Mechanical treatment	Thermal treatment	Thickness of "recrystallized" layer(a)	Amount of eutectoid(b)	DENDRITIC STRUCTURE	REMARKS
B 1	Two hexagonal bars 1 in. on a face were cast, ground and turned down to $\frac{3}{4}$ in. diameter and cut into sections $\frac{1}{4}$ in. long.	1 hr. 400° C.	0.056 mm.	85.0	} Very evident	Eutectoid was found shattered to a depth of } 0.10 mm. 0.113 0.15
B 2		2 hr. 400° C.	0.076 mm.	82.0		
B 3		4 hr. 400° C.	0.088 mm.	85.5		
B 4		None	None	83.0		
B 6		8 hr. 400° C.	0.07 mm.	76.5		
			Av., 0.072		} The outlines of the cores are indistinct, diffusion has begun	Av., 0.135
B 7		1 hr. 600° C.	0.161 mm.	41.5		
B 8		2 hr. 600° C.	0.181 mm.	19.0		
B 9		4 hr. 600° C.	0.163 mm.	12.0		
B 10		8 hr. 600° C.	0.183 mm.	6.5		
			Av., 0.172		} Dendrites are found in some grains, and are quite plainly seen in oblique illumination(c)	Very faint trace of cores under oblique illumination
B 11(d)		$\frac{1}{4}$ hr. 800° C.	0.34 mm.	4.0		
B 12(d)		1 hr. 800° C.	0.33 mm.	0.4		
B 13(d)		2 hr. 800° C.	0.34 mm.	0.0		
B 14(d)		4 hr. 800° C.	0.37 mm.	0.0		
			Av., 0.345		All dendritic structure is erased	

(a) The thickness of the recrystallized layer in all cases was directly measured by means of a micrometer ocular.

(b) To obtain an approximately quantitative expression of the rate of absorption of the eutectoid, the number of inclusions in the successive microscope fields taken contiguously along a diameter of the sample (magnification 100 X) was counted. On account of the difference in size of the particles, this method is a rough approximation only.

(c) When the dendritic structure appears to have disappeared entirely, upon examination under vertical illumination with oblique illumination it is still to be seen.

(d) Samples 11, 12, 13 and 14 were slowly heated for 2 hours until 800° was reached, then held at that temperature for the time indicated above.

crystallized layer does not represent the true thickness of this layer—as it does in Series 2. No effort was made to ensure the amount of "cold working" being the same in the different series. This accounts for the differences in the thickness of this layer as measured in the two series after similar treatment.

#### PROGRESS OF RECRYSTALLIZATION UPON HEATING

The uniformity of thickness of the recrystallized layer of samples heated to the same temperature is

resistance to change of form. Upon heating, a state of equilibrium results; the "surface tension," if it predominates, causes the crystal fragments to agglomerate and thus the crystals grow in size until the two forces are balanced. Thus for any given temperature the final grain or crystal size is a determined one. All of the observations and measurements made upon the thickness of the recrystallized layers are in support of this hypothesis.

TABLE II—(SERIES 4 ABOVE)

Specimen No.	Mechanical treatment	Thermal treatment	Thickness of outer layer of recrystallization (a)	REMARKS
B 35-1	Samples 35, 36, and 37 were turned down from $\frac{3}{4}$ inch to $\frac{1}{2}$ inch diameter with a fine finishing cut taken in each case. No. 34 was unworked.	2 hr. 400° C.	0.067 mm.	Shattered eutectoid was detected to a depth of } 0.087 mm. 0.104 mm. 0.08 mm.
B 35-2		4 hr. 400° C.	0.075 mm.	
B 35-3		8 $\frac{1}{2}$ hr. 400° C.	0.068 mm.	
			Av., 0.07 mm.	
B 36-1		2 hr. 600° C.	0.131 mm.	Av., 0.09 mm.
B 36-2		4 hr. 600° C.	0.131 mm.	
B 36-3		6 hr. 600° C.	0.164 mm.	
B 36-4		8 $\frac{1}{2}$ hr. 600° C.	0.144 mm.	
			Av., 0.142 mm.	
B 34-1		8 $\frac{1}{2}$ hr. 600° C.	None observed	None observed
B 37-1		1 hr. 800° C.	0.187 mm.	
B 37-2		2 hr. 800° C.	0.231 mm.	
B 37-3		4 hr. 800° C.	0.279 mm.	
B 37-4		8 hr. 800° C. (b)	0.260 mm.	
			Av., 0.24 mm.	None observed
B 34-2		8 hr. 800° C.		

(a) The measured thickness of the recrystallized layer is very probably the true thickness as there was no surface oxidation as in Series 1 and 3.

(b) Because of variation in the heating current, the temperature rose to 840°, during this interval.

very striking. So far as the measurements taken indicate, there is but little, if any, increase in thickness with prolonged annealing. The process is not a progressive one from the exterior inward, but starts simultaneously throughout the layer which is capable of being affected at that temperature. As the time of holding at a given temperature is increased, the crystals grow in size but the thickness of the layer, so far as can be seen, remains unchanged.

The influence of temperature is also illustrated by this series of measurements. Up to 400°, only the most severely worked metal is able to rearrange itself and thus "recrystallize." When the distortion is very great the brittle  $\delta$ -constituent of the eutectoid is shattered. The observations on specimens annealed at 400°, given in Tables I and II, show that the thickness of the outer recrystallized layer is well within

<sup>1</sup> Tammann, "Lehrbuch der Metallographie," pp. 74-84.



the limit to which the eutectoid is broken up and therefore within the limit of high distortion. The inner boundary of the layer of recrystallized metal, for 400° and 600°, is sharp and definite. At 800° this is not so marked; in this case, in making the measurements, the maximum depth was chosen.

Figs. 4, 5, 6 and 7 show the appearance of this outer layer of recrystallization.

#### SUMMARY OF RESULTS

I—The metal, upon annealing, is first brought into "physico-chemical equilibrium." The dendritic structure persists until heated for approximately two hours at 800°. The absorption of the eutectoid depends much upon how the cast sample was cooled while solidifying; four hours' heating at 800° is required for its disappearance in those samples which solidify very slowly.

II—No evidence was found suggesting a change of crystal size of cast samples which had not been distorted in any way.

III—Recrystallization, including "twinning," was found, only, to follow distortion; samples which were highly strained as a result of very sudden cooling from the molten state behave upon annealing the same as those mechanically distorted. Chill castings may be expected to behave in a similar manner.

IV—The progress of recrystallization upon annealing for different periods of time at the same temperature is in agreement with Tammann's theory of recrystallization.

V—Aside from the crystal size and the modification introduced by "twinning," the end condition of material annealed directly after casting and that annealed after a preliminary distortion of the crystalline structure is the same in the two cases (Figs. 2 and 7).

BUREAU OF STANDARDS, WASHINGTON, D. C.

### EXPERIMENTS ON THE PRODUCTION OF GASOLINE FROM HYDROCARBON OILS OF HIGH BOILING POINTS<sup>1</sup>

By EARLE L. DAVIES

Received October 15, 1915

Gasoline is one of the materials used by the rubber industry in fairly large quantities, and, since it is used chiefly in cements, etc., which must be dried entirely free from any tarry matter, or similar oily or greasy matter, such ingredients, even in very small amounts, render it unsuitable for use. About the first of the year 1913, when these experiments were made, the price of straight run gasoline was extremely high and, to us, the prospects for any reduction in price did not seem bright. The object of our work was, therefore, to find a feasible and profitable process for the production of a satisfactory supply of gasoline from some heavy fuel oil or similar cheap hydrocarbon oil.

In all of the samples of gasoline which we had examined, made by so-called "cracking" processes, a considerable amount of unsaturated hydrocarbons, tarry matter, etc., was present. It was, therefore,

evident that our process must include some cheap and efficient hydrogenation feature, from which it followed that nascent hydrogen would be desirable. The well known method of producing hydrogen by passing steam over red-hot chips of iron or steel suggested itself as being feasible. Some modification of this method has been the subject of various patents which it is not the purpose of the author to review in this paper.

Our problem, therefore, resolved itself into two parts:

I—A study of the best conditions for cracking the oil.

II—The determination of the most favorable conditions for saturating with hydrogen, those portions which were converted into unsaturated compounds.

In all of our work, except as otherwise noted, we used an oil obtained under the name of "Distillates" from the Factory Oil Co., of Akron (a marketing concern). Yields were determined by fractionating 200 cc. of the product condensed in the apparatus, through a three-bulb Le Bel-Henninger distilling tube and collecting that portion which came over below 175° C.; this temperature, which was arbitrary, represented a product averaging 60° Bé.

Our apparatus for studying the problem of cracking consisted of an iron retort holding 1½ liters, made by capping a piece of 4-in. standard wrought-iron pipe. From this retort a piece of 1-in. (S. W. I.) pipe 40 in. long was passed through a 30-in. combustion furnace to a condenser, made by coiling one 20-ft. length of 1-in. (S. W. I.) pipe, at the outlet of which was placed a pressure gauge and finally a valve for regulating back pressure on the apparatus. The retort was heated with an ordinary laboratory gas blast lamp.

We first studied the effect of distilling the oil and condensing under pressure, substantially as described by Burton's patent.<sup>1</sup> Experiments were made distilling under 10, 25, 50, 75 and 90 lbs. gauge pressure; the furnace under the 40-in. length of pipe was not lighted. Our highest yields gave only about 3 per cent naphtha, determined as above described; we attributed the low yields obtained as due to the fact that a relatively large portion of the oil had distilled over and condensed before the desired back pressure was obtained.

The next step was a study of the effect of superheating the vapors as they passed through the 40-in. length of pipe. Unfortunately, in this series of experiments, we had no means of measuring the temperature of the vapors, but the tube was kept red-hot and was probably heated to about 600° to 650° C. Rates of distillation, superheat, etc., were kept as nearly constant as possible. The results of the series were as follows:

Back Pressure of System—Lbs.....	0	20	30	45	60	90
Yield of Naphtha—Per cent.....	2	7	9	13	18	23

These experiments were repeated after filling the 40-in. tube with broken pieces of tile and brick. At 90 lbs. pressure we obtained a yield of 26.2 per cent, which was repeated twice.

The naphtha obtained in these experiments was

<sup>1</sup> U. S. Pat. No. 1,049,667.

<sup>1</sup> Application has been made by the author for patents on this process.

lightly straw-colored; it possessed a distinct odor and was attacked more or less vigorously by cold, concentrated sulfuric acid, proving the presence of unsaturated hydrocarbons.

Thus far we had succeeded in showing:

- 1—That pressure is essential.
- 2—That a combination of pressure and superheat is desirable.
- 3—That a refractory material in the superheated portion is desirable.
- 4—That carbonization, to a certain extent, takes place in the retort.
- 5—That the naphtha did contain unsaturated hydrocarbons.

This gave us sufficient data to start on the second main problem of our work, that of hydrogenating the unsaturated products. Mention has already been made of our intention to obtain nascent hydrogen by means of the action of steam on iron chips. This, it seemed, might easily be done in the chamber in which the oil vapors were superheated and so much of the cracking took place. The iron chips would have the advantage of acting as a refractory material to

ture measured at  $D_2$  were mixed with the superheated steam in the Tee  $H$ , the mixture then passing on through the cracking and hydrogenating chamber  $K$  and out at a temperature indicated at  $D_3$ , into the condenser  $L$ ; the temperature of the condensate was indicated at  $D_4$  and back pressure, indicated at  $G_4$ , on the apparatus, was regulated by valve  $M$ . The condensate was collected in  $N$  where the condensed excess steam separated from the oily condensate, and was drawn off at the bottom, while the gases after bubbling through the condensate, escaped at the top through the trap  $O$  and meter  $P$  at a pressure of 10 in. of water, maintained by bubbling through that depth of water.

The details of the process were as follows:

Steam was obtained from the Power Plant, about one-quarter mile away; its quality probably was not much above 90 per cent dry steam. A Type T-B-2 General Electric Co. steam flow meter was used. Fig. II shows a cross section of the superheater  $C$ , which consisted of 55 to 60 ft. of  $\frac{5}{32}$  in. wall by  $1\frac{1}{4}$

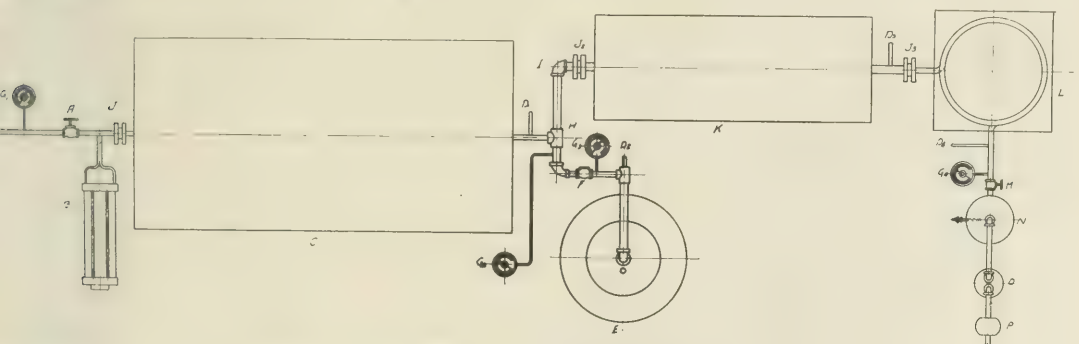
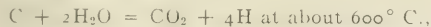


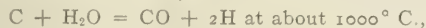
FIG. I—PLAN OF APPARATUS

- |                  |  |   |
|------------------|--|---|
| Valve            | $G_1$ $G_2$ $G_3$ $G_4$ —Pressure Gauge              | $K$ —Cracking Chamber   |
| Steam Flow Meter | $H$ —2 in. $\times$ 2 in. $\times$ 1 in. Hydraulic T | $L$ —Condenser  |
| Superheater      | $I$ —3 in. Hydraulic L                               | $M$ —Valve for Regulating Back Pressure                                 |
| Retort           | $H$ to $I$ —2 in. Hydraulic Tube                     | $N$ —Apparatus for Collecting Condensate and Separating Condensed Steam |
| Check Valve      | $J_1$ $J_2$ —Hydraulic Malleable Flange Unions       | $O$ —Trap for Separating Liquid from Gases Formed                       |
|                  | $J_3$ to $J_5$ —2 in. I. D. Seamless Steel Tube      | $P$ —Meter for Measuring Gases Formed                                   |

retard the flow of the oil vapors and the nascent hydrogen would be present to act upon the unsaturated products at the moment of their formation. In connection with the action of steam on iron it is well to bear in mind the analogous reaction in the manufacture of water gas,<sup>1</sup> viz.:



while the reaction becomes



from which we may venture that best results are probably obtained at temperatures which are not too high.

For the succeeding work, we built the experimental plant shown diagrammatically in Fig. I. Steam at the pressure indicated by  $G_1$  was admitted through the valve  $A$  at a rate indicated by steam flow meter  $B$  and passed through the superheater  $C$  into the Tee  $H$  at a temperature measured at  $D_1$  and pressure indicated by  $G_2$ . Oil was distilled from the retort  $E$  at a pressure indicated by  $G_3$ . The vapors at a tempera-

in. O. D. "Shelby" cold-drawn-seamless steel mechanical tubing bent into a trough-shaped coil of  $5\frac{1}{2}$  turns, the top coil of which was about 20 in.  $\times$  60 in., all joints being electrically welded. The tubing steel, containing from 0.17 to 0.20 per cent carbon, seemed to withstand excellently the severe conditions imposed; a scale of oxide appeared to form both outside and inside the tube, which, if undisturbed, prevented further rapid corrosion. Crane's malleable iron pipe fittings for 1500 lbs. pressure were used throughout. Temperatures were measured by Hoskins' base metal thermocouples connected to one meter by means of one of their four-point selective switches. The retort was made by drilling a 10-in. hole in a piece of 12-in. shafting and welding on a collar for bolting and sealing the top. The cracking chamber consisted of one piece of "Shelby" seamless steel mechanical tubing  $2\frac{3}{8}$ -in. O. D.,  $\frac{1}{16}$ -in. wall by 7 ft. long enclosed in a furnace with 4-in. wall built of fire brick, and heated by natural gas; this tube was filled with iron and steel shavings. The gas burners used for superheater and "Cracker" are shown in detail in Figs. III and IV: this

<sup>1</sup> Thorpe's Dict. App. Chem., Vol. II, p. 706.



construction gave equal distribution of the flame throughout the entire length of the burner.

In conducting the experimental work, the following factors were to be studied:

- 1—Confirmation of our previous opinions as to the desirability of pressure.
- 2—Rate of flow of steam as compared to the amount of oil.
- 3—Temperature of the steam entering the Tee H.
- 4—Final temperature of the mixed vapors at  $D_3$ .
- 5—The rate of distillation of the oil.
- 6—The construction of the cracking chamber.
- 7—The nature of the catalyzer used.

The first series of experiments made with this apparatus was to study the influence of pressure. The type of burner shown in Fig. III, having an ordinary air mixer, was used, but with it we could not get anything like the desired temperatures (we had no pyrometer at this time); the pressure at  $G_2$  and  $G_3$  was maintained at a point which gave an average flow of steam of about 100 lbs. per hour; all other factors were kept as nearly constant as possible. The results were as follows:

Back Pressure at $G_1$ —Lbs. per sq. in.	60	75	90	100
Yield of Naphtha—Per cent.	9.0	10.0	11.0	11.5

Although these results are low as compared with our previous experiments without steam, the same

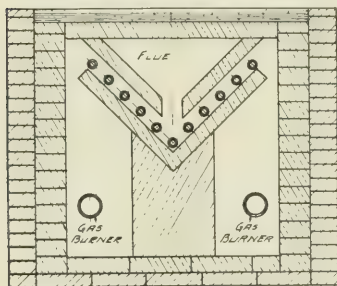


FIG. II—STEAM SUPERHEATER

tendency to increase with pressure is evident, the low yields being caused by low temperatures. We think, therefore, that it has been conclusively demonstrated that pressure is essential. It would have been interesting to have studied the effect of pressures higher than 100 lbs., but for our work we were limited to 105 lbs. pressure on the steam line; we did not think it worth while to make provisions for higher pressures inasmuch as difficulties would be encountered in the safe operation of a commercial plant under greater pressure at the high temperatures in use.

After the just mentioned series of experiments, the burners were all fitted with compressed air mixers as shown in Fig. VI; these burners gave excellent results.

We now performed a few experiments to determine the best rate of flow for the steam. The best results, judging from the appearance of the product, were obtained with pressure at  $G_2$  about 100–105 lbs. and the pressure at  $G_1$  about 90 lbs., which gave us about 10 lbs. of steam per gallon of oil. In all subsequent work, the steam was regulated accordingly.

Our work had been carried on without a pyrometer up to this point, but during this series of experi-

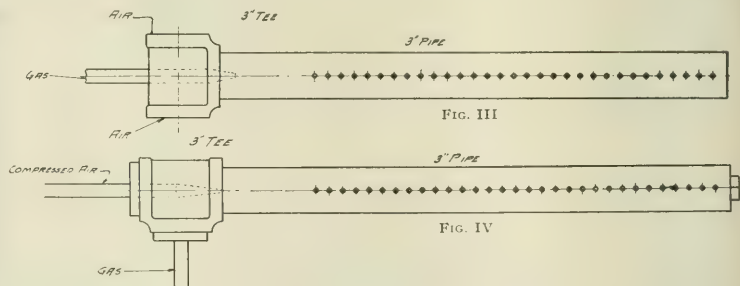
ments such an instrument was installed. The results obtained are given in Table I.

TABLE I

Rate of distillation for 1 gal.	Av. temp. steam at $D_1$	Av. temp. mixed vapors at $D_2$	Sp. gr. of condensate	YIELD OF NAPHTHA		GAS FORMED Cu ft.
				Per cent	Per cent	
	Without pyrometer	Bright red	...	15	34.0	...
		Dull red	...	12	29.5	...
		Red	...	14	34.0	21
		Red	...	13	34.5	20
20 min.	585° C.	645° C.	41° Bé.	15	34.2	21
30 min.	560	635	38	18	30.5	30
15 min.	605	635	38	12	25.0	26.1
18 min.	480	635	37	12	22.0	15.0
25 min.	490	640	38	12	22.0	17.5
15 min.	525	600	36	4	18.0	12.2

These results indicate that the steam should be heated to about 600° C. before mixing with the oil vapors, which must in turn be distilled so as to pass through the cracking chamber at the proper rate, which would in all probability depend upon the length of the cracking period.

We next wished to determine the effect of increasing the length of the cracking chamber upon the rate at which the oil could be fed into the apparatus, thereby obtaining data which would enable us to design a commercial plant; moreover, with the flames hitting the tube only once, then going up the chimney, we were losing a vast amount of heat which was being measured in terms of gas supplied to the furnace as



FIGS. III AND IV—SPECIAL GAS BURNERS

fuel. The "cracking" chamber was therefore changed to the construction shown in Figs. V and VI:  $2\frac{3}{8}$ -in. O. D. by  $\frac{1}{16}$ -in. wall, 3–4 per cent nickel steel seamless mechanical tubing was used; unions were provided after each passage through the furnace in order to permit the introduction of the refractory catalyzer and the frequent renewal of the same.

The series of experiments recorded in Table II was intended as a check upon the indications of Table I, under the just mentioned changed conditions, but does not present a clearly defined series of experiments with only one factor varied at a time, and for various reasons was not carried to a conclusion.

Chips and shavings of iron and steel were used as a catalyzer in the tubes of the cracking chamber. For the best results they should be renewed rather frequently, since a scale of oxide forms on the outside which renders them less active. We performed a few experiments with about 5 lbs. of nickel chips and nickel wire gauze mixed with the iron shavings. After about a week, most of the nickel had disappeared nor could we see any marked improvement in the product while using the nickel.

That we were able to produce hydrogen was shown by running steam alone (no oil) through the apparatus, thereby obtaining a gas at the rate of about 5 feet per hour, which analysis showed to be nearly pure hydrogen.

Several experiments were made, using, in place of the new oil, residues from which the naphtha formed in previous runs had been distilled with similar conditions; the net yield was about the same. We also tried placing the condensate recovered in *N* back in the retort before distilling off the naphtha, and found that gas was not formed faster than could be attrib-

small amounts as 2 gallons in so large an apparatus, it would be easy to lose quite a considerable percentage. We see no reason why the loss could not be kept under 10 per cent in operating a plant on a commercial scale.

The naphtha obtained by our process differs very little in appearance from commercial naphtha; it is very nearly water-white and has very little unnatural odor; it is decidedly superior to the samples of commercial "cracked" naphtha which we have examined. Upon treating our product with sulfuric acid, it was acted upon less than any commercial "cracked" naphtha

TABLE II

Exp. No.	Rate of distillation Per gal. of oil	Av. Temp. (°C.)		Sp. gr. of condensate	Loss Per cent	YIELD OF NAPHTHA Per cent	GAS FORMED Cu. ft.	APPEARANCE OF CONDENSATE
		Steam	Mixture					
1.	17 min.	625	650	34.0° Bé.	20	38.0	63.2	A little carbon
2.	25 min.	645	725	38.0	50	38.5	115.4	Very much free carbon
3.	12	No superheat		610	35.5	5	18.0	Very clear
4.	10	400	660	36.0	10	26.0	36.4	Very clear
5.	10	560	640	35.5	8	25.5	25.0	Very clear
6.	7	590	720	39.0	35	33.0	74.0	Very much free carbon
7.	7	540	700	34.0	18	26.5	55.0	Some carbon
8.	15	550	615	37.0	15	26.0	23.6	Very clear
9.	10	580	650	36.0	20	30.0	39.3	Some carbon
10.	7	605	660	34.5	10	24.0	59.2	Fair
11.	7	575	675	36.0	15	30.0	56.2	Fair

uted to the action of the steam on the iron until the temperature at *D*<sub>2</sub> of the oil vapors was over 300° C., showing that the lighter portions were broken down further only with great difficulty.

A few experiments were made upon a very viscous and dirty Ohio crude oil, having a specific gravity 36° B.; it yielded 27 per cent by fractionation and collecting that portion which came over below 175° C., it contained about 2 per cent moisture. We ran this oil through the process without previously distilling off the naphtha which it contained. Assuming that

which we have seen, in spite of the fact that it had not been subjected to any of the usual washing treatments, our purification having been limited entirely to distillation. Several gallons were tried in motorcycle and automobile motors; in these tests there was no apparent difference between our naphtha and commercial 72° naphtha; we looked especially for such troubles as carbonization, but could find no evidence of them.

#### COST OF NAPHTHA PRODUCED

The cost of naphtha produced by this process may be estimated as follows: Our experiments show that the entire apparatus could be maintained at the proper temperature, and the oil distilled, by the use of 30 cu. ft. of natural gas as fuel, per gallon of raw oil; natural gas if computed at its equivalent in coal is not worth more than 7 cents per 1000 cu. ft. It must be remembered that our furnaces were designed with the view to easy manipulation rather than economy of fuel; in a commercial plant, the whole thing could be enclosed in one furnace and waste heat from the superheater used to heat the cracking chamber and to vaporize the oil. The product could be separated by fractional condensation in a dephlegmator without the use of additional heat. Thirty pounds of steam, and very probably much less, would be amply sufficient. Steam may be produced for 6 cents per 1,000 lbs.

One gallon of naphtha could be produced from 3 1/3 gallons of raw oil, leaving the residue, minus about 10 per cent loss, worth as much as before. The cost would therefore be:

One gallon raw oil (converted).....	= x cents
10 per cent of 3 1/3 gals. oil lost at xc per gal....	= x/3 cents
100 feet of gas at 7c per 1000.....	= 0.007 cent
30 lbs. of steam at 6c per 1000.....	= 0.002 cent

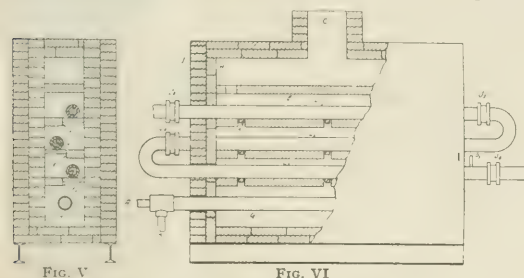
Which may be expressed in the form of the equation

$$C = 1.33X + 0.9$$

where

*C* = cost of naphtha obtained in cents per gal.

*X* = cost of raw oil in cents per gallon.



FIGS. V AND VI—CRACKING CHAMBER  
A—Compressed Air Inlet H—Fire Brick  
B—Gas Inlet I—Red Brick  
C—Flue J, J<sub>1</sub>, J<sub>2</sub>, J<sub>3</sub>—Hydraulic Malleable Flange Union  
D<sub>2</sub>—Well for Pyrometer K—1 × 1 1/4 in. Iron Bar Support  
E—Partition L—2 in. I. D. Seamless Steel Tube  
F, F<sub>1</sub>, F<sub>2</sub>—Baffle Plate M—Steel Shavings  
G—Burner

none of this naphtha was broken up into gas and that the remaining 73 per cent produced 34 per cent of naphtha in the process, we would expect a total yield of 51.8 per cent; as a matter of fact, the total yield of naphtha obtained was 54.5 per cent. The loss due to the formation of gas was high. The residues, after the naphtha had been distilled, was as good, for future use, as the fresh "Distillates" (Paragraph 4).

The greatest item of expense in the process seems to be in the amount of oil lost through carbonization, gas formation, etc. When we obtained the best net results, this loss, in our experimental plant, averaged from 10 to 12 per cent. When starting with such



## SUMMARY

These experiments have established the following facts:

1—That a satisfactory naphtha may be obtained by means of this process wherein the oil is cracked in the presence of nascent hydrogen.

2—That superheating the oil vapors is desirable for "cracking."

3—That pressure is necessary for "cracking."

4—That a combination of pressure and superheat is essential.

5—That the presence of a refractory material in the "cracking chamber" acts as a catalyzer, aids the "cracking," and increases the yield of naphtha obtained.

6—That hydrogen is formed in the manner described, and that it evidently does unite with a greater portion of the unsaturated decomposition products formed, producing saturated compounds.

7—That iron or steel shavings in the cracking chamber constitute a satisfactory catalyzer.

8—That the catalyzer should be frequently renewed.

9—That the yields of naphtha obtained increase as the pressure is increased up to 100 lbs.; above that pressure we have no data.

10—The best results were obtained when using about 10 lbs. of steam per gallon of oil.

11—That the steam should be superheated to at least 600° C. before mixing with the oil vapors.

12—That the mixture of superheated steam and oil vapors should be heated to 650° to 675° in the "cracking chamber."

13—That the residue, obtained by distilling off the naphtha formed, is worth just as much as the original "raw" oil.

14—That carbonization takes place in the retort and more or less gas is formed in the process.

15—Oils having higher boiling points are "cracked" easier than those having lower boiling points, but the quantity of gas formed is greater.

16—That the cost of naphtha produced by this process may be approximately expressed by the equation

$$C = 1.33x + 0.9,$$

where

C = the cost of the naphtha in cents per gallon,

X = the cost of the starting oil in cents per gallon.

As to future work on the problem, we have considered the following:

I—More careful study of the temperature to which the steam should be superheated before mixing with the oil. This might lead, in the construction of a commercial plant, to placing the steam superheater next to the fire and utilizing the heat for cracking, after it leaves this superheater.

II—A study of spraying the cold oil into the superheated steam in a mixing and vaporizing chamber, which later might or might not have to be heated.

III—A more careful study of the construction of the cracking chamber, and the method of passing the vapors through the same, with the idea of determining whether it is not better to heat the vapors to the desired temperature as quickly as possible.

In conclusion, the writer desires to express his thanks to Mr. W. W. Sanders and to Mr. L. M. Bourne, under whose supervision these experiments were performed, for their interest and suggestions.

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REFINING VEGETABLE OILS<sup>1</sup>

By CHARLES BASKERVILLE

Crude vegetable and animal oils contain a variety of impurities traceable to a great variety of causes. The character of the crude oil depends not only upon the kind and part of the vegetable (wood, nut, seed, etc.) or animal (fish, whale, etc.) used, but the quality of the raw material at the time of expressage or extraction (rusting, rotting, fermentation, sprouting, heating, etc.), the method followed, the care exercised in the process, and the conditions to which the oil is subjected prior to its refining. It is not proposed to discuss these matters in detail, as this communication deals more specifically with certain of the vegetable oils.

A distinguished oil chemist in a recent interesting summary of the "Contributions of the Chemist to the Cottonseed Oil Industry,"<sup>2</sup> has said, "the chemist \* \* \* found that the quality of the oil closely followed the free fatty acid present"<sup>3</sup> and "The chemist's greatest service to the industry has been in the refining of the oil, \* \* \* and finally bringing into use the tintometer for measuring the color against standard glasses \* \* \*."<sup>4</sup>

The present customary practice for refining vegetable oils referred to depends upon neutralizing the free fatty acids in the crude oil, usually by agitating the oil with an aqueous solution of an alkali, the strength and the amount having been previously determined by laboratory tests, agreed upon as a standard, and then heating the mixture during agitation to a suitable temperature until the oil "breaks." The mass is then allowed to stand until the "foots" settle to the bottom of the kettle, when the supernatant oil is drawn off by means of a swivel siphon. Invariably some "dreg" floats on top of the oil. If this be very great, its settling is sometimes facilitated by throwing salt on top of the oil in the kettle. In any event, the oil drawn off is clouded, perhaps on account of the presence of some dissolved soap, globulated moisture and suspended matter, doubtless colloidal in nature. This oil is then "brightened" after drawing off, by throwing in small amounts of fuller's earth, heating again, and passing through a filter press.

The time-factor in settling (6 to 12 hours) of the "foots" materially affects the completeness of the separation referred to above, but in any event the "foots" is wet with oil. The "foots" also entrains oil. Consequently, during the rush season, the effi-

<sup>1</sup> Read before the New York Section, American Chemical Society, April 9, 1915, and the Inter-State Cottonseed Crushers' Association, Birmingham, Ala., May 18, 1915. Since brought up-to-date, Jan., 1916.

<sup>2</sup> Wesson, THIS JOURNAL, 7 (1915), 277.

<sup>3</sup> I have determined that this is true only in a general way, as was no doubt meant by the writer quoted.

<sup>4</sup> One familiar with the color changes in glass may question the real accuracy attainable in the use of such standards. However, it is the best now available.

ciency of yield of refined oil must be sacrificed for speed and quantity refined; in other words, more speed in refining, more loss of refined oil, whatever the analysis upon which purchase and sale are based, may indicate. Coconut oil sometimes requires forty-eight hours to settle.

A process which would reduce the amount of oil entrained in the "foots" to a minimum, thus increasing the yield of a refining, and one which would not be dependent upon the slow subsidence of the "foots,"

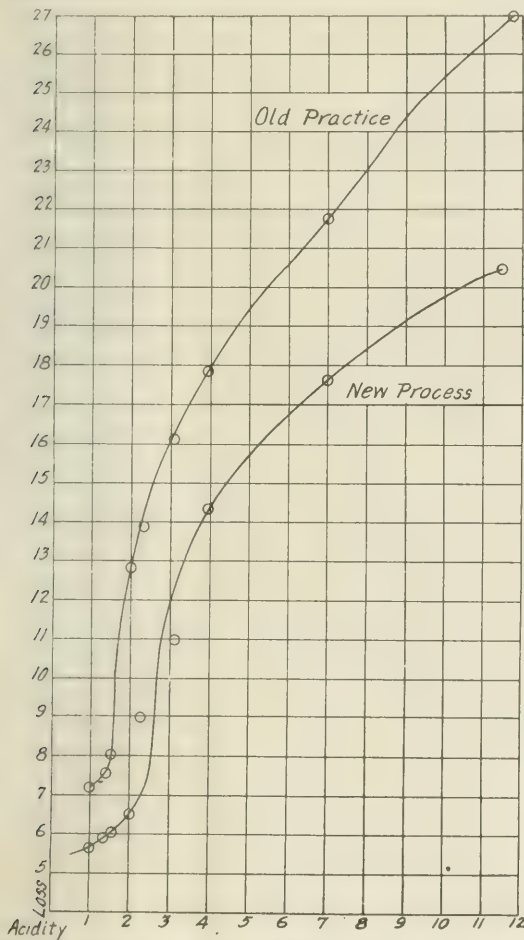


FIG. 1.—COMPARATIVE LOSSES IN REFINING COTTONSEED OIL BY OLD PRACTICE AND NEW PROCESS

i. e., admit of rapid separation with consequent increase in capacity of a refinery, therefore, seemed not only to be desirable, but, if secured, would approximate the highest efficiency one might hope for in such an industrial operation.

I have succeeded in working out such a process, and shall now proceed to describe the principles involved. The technical laboratory tests with batches of 12 to 20 lbs. have been verified in the factory on the commercial scale.

The aims to be accomplished are:

1—To reduce the amount of oil entrained in the "foots," thus increasing the yield of "whole oil."

2—To reduce the time of contact of the excess alkali (necessary for the "break" and to secure the best "color") to the minimum.

3—A technological corollary calls for the utilization of any by-products.

It is assumed that all oils, good, bad and indifferent, are to be treated. However, this may not be necessary, as in some cases only the good, and perhaps the indifferent oils are refined at some places.

In my investigations, lasting through several years, I have taken various kinds of crude vegetable oils from various sources with various (extreme) conditions and refined them. In many cases I have been told that no attempt would ordinarily be made to refine a particular oil, as it should be sent to the soap kettle, the corresponding price only being expected. Such oils would have presented much better values if they could have been refined by the present practice. These oils have yielded to my process and have been refined.

If we can get the "foots" into such a condition that it may be filtered and then squeezed, we may reduce the amount of whole oil entrained. If we can do this immediately after the "break" and while the oil is still hot, we shall be able to reduce the time the "whole oil" is exposed to the saponifying action of the excess alkali necessary.

There are present in oils groups of bodies which in general terms are called colloids. These colloids may or may not be colored; may or may not make the oil turbid, for colloids are of such a state of subdivision that they remain suspended in the liquid, where they may be, for a long period of time. Some colloids may be and are coagulated by heat, some by acids, some by alkalies, some by salts, or electrolytes, and in time will settle out. For example, linseed oil may be and is refined by adding lime and allowing the mixture to stand for several months, during which time the colloids settle out. Colloids that have been coagulated, or lumped, may be filtered out. Some coagulated colloids in their formation absorb coloring matter.

Suitably prepared cellulose fiber will absorb some coloring matter. It will bring out an agglomeration of the material precipitated from oils by treating the oil with alkalies and heating, and it will bind the particles together so that they lose their somewhat slimy character and may be filtered away from the oil in which they were produced. I have also found short-fibered "linters" is a suitable form of cellulose for some oils.

Therefore, I add cellulose suitably prepared along with the caustic to the oil to be refined. The "break" takes place normally on heating as in the ordinary process, but the precipitated mass is in such a physical condition that it may be separated from the oil immediately by filtration.

As mentioned above, some colloids, perhaps colored, are thrown down by salts, so in certain cases some salt (1 per cent of sodium chloride) may be added



If there be a slight excess of water present, the sodium chloride serves also to "salt out" any soap in that water. The addition of salt, however, is not necessary in all cases.

I have also discovered that the tendency of the soaps formed by the caustic alkali treatment to emulsify with the oil, or so to distribute themselves through the oil as to render their separation difficult, may be overcome by subjecting the oil, at a suitable stage of the treatment, to the action of an anhydrous salt which is capable of taking up water of crystallization, the preferred salt being dry sodium carbonate (soda

which it is filtered. At first some soap may pass through the filter cloths. In that event, the first filtered oil may be run directly back into the refining kettle, and pumped through the press until the oil is "bright." This usually occurs within a few minutes. In fact the speed of filtration is directly dependent upon the speed of the pumps. This re-filtration also improves the color. This oil is neutral and can be bleached and deodorized, or both at once, or it may be stored safely. If "linters" is used,  $\frac{1}{4}$  to  $\frac{1}{2}$  per cent of the dry cellulose is added.

The danger of making a whole kettle into soap-stock through failure of the refiner to be "on the job" is reduced to a minimum, as in several thousand trials this has not occurred, the trials having been made by different people with various grades of oils of different character. In other words, the process is nearly "fool-proof." Any man of fair intelligence can operate the process and the air of mystery surrounding the professional refiner is dissipated. The superintendent has a double check on the refinery by weighing the finished oil and cake. The daily reports when summed up should coincide with the annual inventory. I have known of cases where as much as 100,000 lbs. of oil have failed to appear in the inventory, but were reported daily and had to be charged to profit and loss when the operation was under the usual process.

The curves in Fig. I have been made from a series of cottonseed oils very variable in character, to show the comparative losses by the normal, present practice and my process. Fig. II shows the comparative saving with several other oils.

I have also been able to secure a farther 1-3 per cent. saving by subjecting the "cake" to hydraulic pressure. This extra saving is not shown in the charts.

The process is very rapid, the controlling factor being filter-press capacity. A study of plate filter-presses has indicated a preference for a center feed press making  $1\frac{1}{2}$ - to 2-in. cakes. The filter press problem in connection with the process is not one of filtering area but cake capacity. Presses, as the Kelly or Sweetland, which are dumped mechanically, meet the conditions better than plate presses. A new Sweetland press recently devised for this process promises the best results. It is provided with bottom exits and the under bivalve swings through an arc of  $165^\circ$ . Monel metal filter cloth makes the machine practically permanent. By a slight increase in filter press capacity the output of a refinery may be doubled or even tripled.

#### UTILIZATION OF BY-PRODUCT

The cake may be converted directly into soap, the cellulose becoming very finely comminuted. It forms an unobjectionable filler for some grades of soap, especially soap powders. The cake may be "cut" with acid directly. The cellulose settles quickly in the aqueous layer from the black oils, which latter may be drawn off ready for market or use. When the cake is to be converted into black grease, I use anhydrous sodium sulfate "salt cake" in place of soda ash as the "agglomerator." Printed instructions for the use of

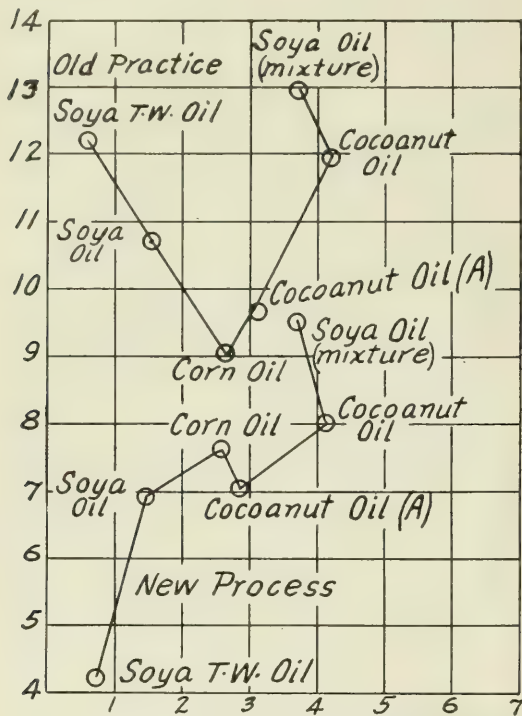


FIG. II—COMPARATIVE LOSSES WITH VARIOUS OILS

ash) which, as is well known, is capable of taking up one, seven, or ten molecules of water of crystallization, according to temperature conditions. By such treatment, the soaps which have already been formed by the treatment with caustic alkali, and which have become so incorporated with the oil as to be incapable of complete separation by ordinary filtration, are hardened, presumably by dehydration, and are so modified that they are readily separated by simple filtration. Sodium sulfate, which acts in the same way, may be used instead of the soda ash.<sup>1</sup>

The process is carried out by adding ordinarily 2 per cent of prepared cellulose (less than 1 per cent real cellulose), a suitable amount of caustic soda (usually much stronger than commonly used), and a determined amount of soda ash. The whole is thoroughly agitated by mechanical means while it is being heated ( $45^\circ$ – $65^\circ$  C.) to produce the "break," after

<sup>1</sup> These ideas are covered by U. S. Patents Nos. 1,105,744; 1,105,743; 1,130,698; 1,114,095.

the method as an analytical procedure or working the process on a commercial scale may be had on application to the author.

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THE THERMAL VALUES OF THE FATS AND OILS  
I—THE HEAT OF BROMINATION

By J. W. MARDEN

Received September 10, 1915

INTRODUCTORY AND HISTORICAL

According to Hehner and Mitchell,<sup>1</sup> "the action of bromine upon unsaturated bodies is instantaneous and is attended with a considerable evolution of heat. It is complete and quantitative. \* \* \* It is not complicated to any extent by secondary reactions. The amount of hydrogen bromide formed measures the substitution, and is very small in most cases." Hehner<sup>2</sup> found this value, when a number of fats and oils were mixed with bromine, to be as follows:

FAT OR OIL	Olive	Castor	Butter	Boiled Linseed
Per cent free HBr.....	1.5 to 2.7	2.7	0.9	8.8

It has been found more recently by McIlhiney's method,<sup>3</sup> however, that there are a few fats and oils where the substitution is very large.

Hehner and Mitchell also showed that each oil, when treated with an excess of bromine, gave a characteristic temperature rise and that the quantitative data obtained by this temperature change, when the fats and oils were mixed with bromine in a suitable tube, furnished more reliable data on their purity than the Maumené sulfuric acid test. They expressed the opinion that a method worked out on this basis could well replace the longer method for the iodine number as a test for the purity of a fat or oil. In their method 1 gram of oil, dissolved in 10 cc. of chloroform, is placed in a Dewar vacuum test tube and exactly 1 cc. of bromine, previously brought to the same temperature as the oil solution, is added. The rise in temperature is measured by an accurate thermometer graduated to one-fifth of one degree. A test tube packed in cotton was first used but later replaced by a Dewar tube. As one would expect, the test tube packed in cotton gives lower results. The whole operation takes only a few minutes.

Table I gives the results obtained by Hehner and

OIL OR FAT	Rise in temperature	IODINE NUMBER			
		Experimental	Calculated	DEVIATION	
				Absolute	Per cent
Lard.....	10.63 C.	57.15	58.3	1.15	2.0
Butter.....	6.6	37.07	36.3	-0.77	-2.1
Almond.....	17.6	96.64	96.68	0.04	0.04
Olive.....	15.0	80.76	82.50	1.74	2.1
Maize.....	21.5	122.0	118.2	-3.80	-3.2
Cottonseed.....	19.4	107.13	106.7	-0.43	-0.4
Castor.....	15.0	83.77	82.5	-1.27	-1.5
Linseed.....	30.4	160.7	167.2	6.5	3.9
Rape 1.....	18.4	88.33	101.2	12.87	12.7
Rape 2.....	17.6	77.2	96.8	19.6	20.0
Cod Liver.....	28.0	144.03	140.0	-4.03	-3.8

(a) Abbreviated from Lewkowitsch's "Chemical Technology and Analysis of the Oils, Fats and Waxes," Vol. I, Macmillan & Co. (1909).

Mitchell. The rise in temperature due to the bromination of each oil multiplied by the factor 5.5 very nearly gives the same value for the iodine number as Hehner and Mitchell obtained experimentally. The factor

<sup>1</sup> Hehner and Mitchell, *Analyst*, **1895**, p. 148.  
<sup>2</sup> Hehner, *Analyst*, **1895**, pp. 20, 49.  
<sup>3</sup> McIlhiney, *J. Am. Chem. Soc.*, **21** (1899), 1084.

must be determined, of course, with each individual apparatus, because of its heat capacity.

Wiley<sup>1</sup> has proposed a more convenient method of

TABLE II—RESULTS BY WILSON (HEHNER-MITCHELL METHOD)

OIL OR FAT	Rise in temperature	IODINE NUMBER			
		Experimental	Calculated	DEVIATION	
				Absolute	Per cent
Cocoanut.....	1.4° C.	8.4	8.2	-0.2	-2.4
S. A. Tallow.....	7.3	44.0	43.2	-0.8	-1.8
Olive, pure.....	14.0	82.0	82.5	0.5	0.6
Rape.....	18.0	103.4	104.5	-1.1	-1.06

handling the oil and bromine which he uses in somewhat the same way as Hehner and Mitchell.

Table II gives a few of the results obtained by Wilson,<sup>2</sup> using the original Hehner and Mitchell method, which show very good agreement between the calculated value and the iodine number found by analysis.

The work of Jenkins<sup>3</sup> does not show such good concordance when an attempt is made to obtain the iodine number from the temperature rise by multiplication with a factor.

TABLE III—RESULTS BY JENKINS

OIL	IODINE NUMBER		DEVIATION	
	Experimental	Calculated	Absolute	Per cent
Blown Rape.....	55.3	74.1	18.8	34.0
Blown Cottonseed.....	62.2	78.1	15.9	25.6
Neat's Foot.....	71.6	72.4	0.8	1.1
Olive.....	80.1	81.5	1.4	1.7
Castor.....	84.1	83.8	-0.3	-0.36
Japanese Wood.....	165.7	133.4	-32.3	-19.5
Raw Linseed.....	174.3	173.9	-0.04	-0.02

Since there are many discrepancies between the two iodine values, it is suggested<sup>4</sup> that each individual oil be given a constant to suit the apparatus in which the work is done. This would, of course, make this method too cumbersome for practical use in replacing the method for the determination of the Hübl iodine number.

Gill and Hatch<sup>5</sup> have tried the method with about the same degree of success. More recently Steipel<sup>6</sup> has published several contributions on the determination of the iodine number of the fats and oils by means of the bromine thermal test. He has repeated practically all of the previous work and his results agree well with former determinations. He finds that he is unable to calculate the iodine number from the bromine thermal value with accuracy but that he must have a constant for each individual oil and each apparatus.

An attempt has been made also to throw some light on the structure of certain unsaturated compounds when they combine with bromine. Louguinene and Koblukoff<sup>7</sup> have measured the heat produced when various compounds dissolved in carbon tetrachloride react with bromine, also dissolved in carbon tetrachloride. They found that the heat of solution of most fats and oils in carbon tetrachloride is very small and that the heat produced per gram molecule of bromine, when accurately determined, varies considerably with each individual compound. In spite of these tests, however, there has been no technical attempt to measure the heat of bromination of the fats and oils by a rapid calorimetric method and to put this de-

<sup>1</sup> *J. Am. Chem. Soc.*, **18** (1896), 378.  
<sup>2</sup> *Chem. News*, **1896**, p. 87.  
<sup>3</sup> *J. Soc. Chem. Ind.*, **16** (1897), 194.  
<sup>4</sup> Archbutt, *J. Soc. Chem. Ind.*, **1897**, p. 310.  
<sup>5</sup> *J. Am. Chem. Soc.*, **21** (1899), 27.  
<sup>6</sup> Steipel, *Seifenfabrikant*, **31** (1911), 349, 393, 421, 445, 473, 501, 525.  
<sup>7</sup> Louguinene and Koblukoff, *J. Chem. Phys.*, **4** (1906), 209 and 489; **5** (1907), 186; *Compt. rend.*, **150** (1910), 915.



termination on the same scientific basis as many of our other calorimetric tests.

#### OBJECT OF THIS PAPER

The object of this paper is to devise an apparatus for the rapid calorimetric determination of the thermal reactions of the fats and oils, and to determine the heat of bromination of some of them; also to show whether or not the iodine number calculated from the true heat of bromination compares favorably with experimentally determined iodine numbers.

#### APPARATUS

The apparatus for these experiments consists in an especially constructed mixing chamber placed in water contained either in the ordinary form of water calorimeter or, as it has been more recently used, in a large Dewar tube. A small calorimeter was also devised for the rapid although somewhat rough determination of the specific heats of the brominated oil mixtures. Figs. I, II and III show these pieces of apparatus set up ready for use.

In Fig. I, *A* represents the cross section of a Dewar tube, 7 x 30 cm., inside measure, and *B* represents a Beckmann thermometer. Fig. II shows a cross section of the mixing chamber, (Fig. I, *M*) of copper 3.2 x 6.8 cm. inside measure with a flange (Fig. II, *F*) around the inside 0.5 cm. wide and 3.5 cm. from the top of the chamber. The chamber is fitted with a cover of the same material. On the outside of this mixing chamber, there are four flanges 0.5 cm. wide and fastened at a slight angle so that when it is rotated these wings stir the surrounding water. The joint between the cover and the chamber is carefully ground and the cover is held in place and water-tight by three or four small screw clips made for the purpose. The mixing chamber is connected by thin-walled glass tubing to a shaft and pulley so that it can be rotated. A narrower glass tube passes down through the outside tube; at the lower end of the smaller tube is a small paddle stirrer and at the upper end a pulley. The mixing chamber was covered with a thin layer of paraffin to protect it from the action of the acid and bromine.

Fig. III shows a smaller Dewar tube 3 x 20 cm., inside measurement, containing copper wire stirrers *C* and *D*, a Beckmann thermometer and a thin-walled glass tube *T* 0.8 x 23 cm. sealed off at the bottom. The use of these instruments will be described with the sample experiments given below.

The Beckmann thermometer readings were corrected by a certificate (from the U. S. Bureau of Standards). The pipettes were all calibrated with water at 20° C.

#### THE OILS AND REAGENTS

The oils used for these experiments were mostly commercial samples, the origin as far as possible being stated in Table VI. The bromine used was Merck's best, free from chlorine and iodine. Archbutt<sup>1</sup> has found that commercial samples of bromine give about the same temperature rise as more carefully dried samples so that especial care was not taken to dry the bromine. A good grade of technical carbon tetrachloride was used. The mineral oil was Liquid Petrolatum, U. S. P. "snow-white" sold by J. S.

Merrell Drug Co., St. Louis. The solution of bromine in carbon tetrachloride was made in the proportion of 1 to 3, by weight, respectively, because a solution of this strength can be handled conveniently in a burette if the upper end of the burette is connected to a potassium hydroxide absorption apparatus. All other reagents used were carefully tested for their purity and the standard solutions were twice checked for their strength.

#### STANDARDIZATION OF THE CALORIMETERS

The calorimeters were standardized by using the heat liberated by the dilution of sulfuric acid of known concentration. Brönsted<sup>1</sup> has very accurately determined the heat of dilution of sulfuric acid by the method of mixtures, using an 8-liter calorimeter. Table IV gives the results obtained by Brönsted. When the data in this table are plotted (the moles of water per one mole of acid against the calories of heat developed), a curve is obtained from which the heat of dilution can be read for any number of moles of water per mole of sulfuric acid.

Moles H <sub>2</sub> O per 1 mole H <sub>2</sub> SO <sub>4</sub>	Calories of heat	Moles H <sub>2</sub> O per 1 mole H <sub>2</sub> SO <sub>4</sub>	Calories of heat
0.1	0.806	1.5	8.790
0.2	1.586	2.0	10.020
0.3	2.331	3.0	11.640
0.4	3.054	4.0	12.830
0.5	3.750	5.0	13.710
0.6	4.418	6.0	14.370
0.7	5.054	7.0	14.890
0.8	5.654	8.0	15.260
0.9	6.212	9.0	15.580
1.0	6.710		

In standardizing the large calorimeter (Fig. I) sulfuric acid (the strength of which had been checked

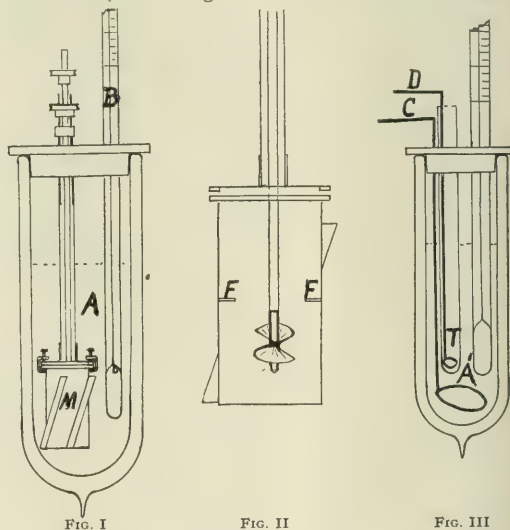


FIG. I

FIG. II

FIG. III

by specific gravity and by precipitating and weighing the barium sulfate) was weighed out into the lower compartment of the mixing chamber; a "medium thin" coverglass, such as is used for microscopical work, was then sealed on the ledge with paraffin and a weighed amount of water placed in the upper compartment. The mixing chamber was next clamped together as shown in Fig. II, the inside stirrer being

<sup>1</sup> Archbutt, *J. Soc. Chem. Ind.*, 1897, p. 310.

<sup>1</sup> *Z. phys. Chem.*, 68 (1909), 693.

held up by a small sized paper clip. The mixing chamber was then plunged into the water in the calorimeter, which had been previously weighed. When the apparatus was all in position (Fig. 1), the mixing chamber was rotated and the water in the Dewar tube stirred by the flanges. When the temperature had been read on a calibrated Beckmann thermometer four or five times at one minute intervals the small inside stirrer was loosened and forced down, breaking the coverglass and mixing the acid and water inside of the mixing chamber. The small stirrer was rotated in the opposite direction to that of the mixing chamber, to insure rapid and thorough mixing of the acid and water. The temperature rise was noted each minute and calculated in the same way that the temperature rise is found at present in the calorimetric determination of coal.<sup>1</sup> The time of half the total temperature change was about 1 minute. It took approximately 4 to 5 minutes to reach the maximum temperature, when the stirrers made about 300 revolutions per minute, so that the total rise in temperature was corrected for 1 minute at the rate of change before breaking the coverglass and for 3 to 4 minutes at the rate of change after.

The specific heat of the diluted sulfuric acid in the mixing chamber, needed in the subsequent calculations, was taken from the work of Biron,<sup>2</sup> his data being given in Table V.

TABLE V—SPECIFIC HEATS OF DILUTED SULFURIC ACID (BIRON)

Moles H <sub>2</sub> O per 1 mole H <sub>2</sub> SO <sub>4</sub>	Specific heat	Moles H <sub>2</sub> O per 1 mole H <sub>2</sub> SO <sub>4</sub>	Specific heat
0.0	0.3352	7	0.6475
0.4856	0.3786	8	0.6771
1.0	0.4408	9	0.7020
2	0.4628	10	0.7231
3	0.5012	11	0.7412
4	0.5420	12	0.7584
5	0.5805	13	0.7717
6	0.6152	14	0.7837

When these data are plotted, the specific heat against the moles of water per one mole of sulfuric acid, a curve is obtained from which can be read the specific heat of any concentration of sulfuric acid.

A statement of the data obtained in one of the determinations of the heat capacity of the large calorimeter and a subsequent calculation of this will best illustrate the use of the apparatus.

STATEMENT OF DATA

WEIGHTS	GRAMS	TEMPERATURE
Acid and Mixing Chamber.....	80.7455	11.31 1.795
Mixing Chamber.....	46.1024	11.32 1.803
Acid used.....	34.6431	11.33 1.813
Mixing Chamber, Acid, Paraffin and Glass..	81.4900	11.34 1.823(a)
Paraffin and Glass.....	0.7445	11.35 1.830
Water, Chamber, Paraffin, Etc.....	101.3214	11.36 3.450
Water.....	19.8314	11.37 4.460
Water used in Dewar Tube.....	700.00	11.38 4.470(b)
(a) Coverglass broken.		11.39 4.470
(b) Maximum temperature.		11.40 4.469
Temperature before breaking coverglass.....		11.41 4.470
Maximum temperature.....		11.42 4.470
Difference.....		11.43 4.470
Rate of change before breaking coverglass.....		1.823° C.
Rate of change after breaking coverglass.....		4.470
Correction.....		2.647
Corrected temperature rise.....		0.010
		0.000
		-0.010
		2.637

METHOD OF CALCULATION OF THE HEAT CAPACITY OF THE LARGE CALORIMETER

By repeated trials the sulfuric acid was found to

<sup>1</sup> Noyes, THIS JOURNAL, 5 (1913), 527.  
<sup>2</sup> Z. anorg. Chem., 43 (1905), 48.

have an average specific gravity of 1.77505 at 20° C. which corresponds to 84.61 per cent sulfuric acid by weight. One mole of acid, therefore, at this concentration was mixed with 0.99012 mole of water. According to Brönsted's curve the heat dilution at this concentration is 6,650 calories.

Each gram of the 84.61 per cent acid contains 0.008627 mole of sulfuric acid and 0.0085425 mole of water. The weight of acid used multiplied by 0.008627 gives the moles of acid used for a determination. Let this value equal X. The weight of the water placed in the upper part of the mixing chamber divided by 18.016 equals the moles of water weighed out. This value plus the product 0.0085425 multiplied by the weight of the acid weighed out in the lower part of the mixing chamber equals the total moles of water used, which value divided by X gives the moles of water per mole of H<sub>2</sub>SO<sub>4</sub>. The heat of dilution for this concentration is located on Brönsted's curve, 6,650 subtracted from it, and the result multiplied by X, which is the total heat added to the system. The result divided by the total corrected temperature rise gives the number of calories necessary to raise the temperature of the system 1° C., which value must be corrected for the heat capacity of the diluted acid (Biron's curve).

The heat capacity of the coverglass and the paraffin was found to be so small and always so nearly the same that it was unnecessary to take account of this factor.

A sample calculation of the water equivalent of the large calorimeter is given below, using the data given above.

Moles of Sulfuric Acid used.....	0.29885
Total Moles of Water used.....	1.3967
1 Mole Acid is equivalent to.....	4.6735 moles water
Heat of Dilution at this concentration.....	6.790 calories in this case
Heat added to system.....	2029.28 calories
Temperature Rise.....	2.637° C.
Calories per 1° C.....	769.5
Specific Heat of Diluted Acid.....	0.57
Heat Capacity of Diluted Acid.....	31.0 calories
Water Equivalent of Calorimeter.....	738.5

Four determinations of the heat capacity of the larger apparatus were made:

No.	1	2	3	4	AVERAGE
Value.....	739.0	739.8	736.1	738.5	738.3

The calculated value from the specific heats of the materials of the apparatus gave a value of 738.5 calories.

The above figures show a total variation of about 0.5 per cent. Undoubtedly, the average value is very close to the true one. Result No. 3 is much lower than the other values, but no reason could be found for discarding it. The value 738.3 calories was taken as the heat capacity of the apparatus.

THE HEAT CAPACITY AND USE OF THE SMALL CALORIMETER

The heat capacity of the small calorimeter (Fig. III), which was used for the specific heat determinations, was found in the same way as in the case of the larger calorimeter. Fifty grams of water were placed in the Dewar tube A' and 1 cc. of sulfuric acid run into T from a carefully standardized pipette. Another 1 cc. pipette, filled with water and stoppered at the top, was hung in T. The thermometer was placed in the water in A' and when the temperature conditions were constant the stopper at the top of the pipette



containing the water was opened and the acid and water in *T* allowed to mix. By carefully standardizing the pipette and always allowing the same time for draining, very closely checking results were obtained. The stirring was done by hand with the copper wires *C* and *D*.

In determining the specific heat of the oils and their mixture, they were placed in *A'* in place of the water, always using the same volumes. The calculations were similar to those for the other calorimeter and to the ordinary specific heat calculations.

#### THE HEAT OF BROMINATION

Many oils, like sandalwood and linseed oil, when added directly to bromine, combine with it with explosive violence, and much bromine is volatilized so that the test can not be carried on quantitatively unless the reaction is made to take place in a bomb calorimeter. In order to use the apparatus described it is necessary to dilute the bromine or the oil in order to have a quantitative reaction. Wiley suggested the dilution of bromine with chloroform and others later have used carbon tetrachloride in place of the chloroform because there is practically no thermal change when bromine dissolves in it.

It was found advisable in the present work to dilute

in the historical part of this paper that the temperature rise obtained in the determination of the bromine thermal number multiplied by a factor does not in some instances check the iodine number. The heat of bromination is therefore compared with the Hülb iodine number in Table VI.

#### DISCUSSION OF RESULTS

The results in this paper were always checked under 0.5 per cent total variation, but it is not claimed that they are closer than 1.0 per cent of the true value since in certain cases, errors might be additive. It is doubtful, however, if so much error could creep in with the experimental methods used.

It will be seen that about the same agreement is obtained when the heat of bromination is compared with the iodine number as when the temperature rise obtained by Hehner's method is compared with the iodine number. In all cases but two, the variation between the calculated and the observed iodine number is not great. In these two cases the variation is considerable.

A perfect agreement, however, should not be expected between these two values because when bromine reacts with the fats and oils not only direct additions take place such as happen in the determination of

TABLE VI—HEATS OF BROMINATION (AUTHOR'S RESULTS) COMPARED WITH IODINE NUMBERS

No.	OIL OR FAT	SOURCE OF OIL	HEAT OF BROMINATION Author's results	IODINE NUMBER Found experimental	Calculated factor 0.846	DEVIATION	
						Absolute	Per cent
1	Sandalwood	Unknown	274	270	232	—38	—14.1
2	Raw Linseed	Local Pharmacy	206	172.5	174.2	1.7	0.98
3	Boiled Linseed	Local Pharmacy	204.6	169.0	173	4.0	2.36
4	Chinese Wood	Standard Varnish Works, Chicago	150.0	156.0	127	—29	—18.6
5	Corn	E. H. Sargent Co., Chicago	146.2	123.1	123.8	0.7	0.57
6	Sesame	E. H. Sargent Co., Chicago	126.4	108.2	107	—1.2	—1.12
7	Rape Seed	E. H. Sargent Co., Chicago	120.8	105.8	102.2	—3.6	—3.4
8	Cottonseed	Local Grocery	117.9	101.7	99.0	—2.7	—2.6
9	Sperm	E. H. Sargent Co., Chicago	109.0	93.4	92.2	—1.2	—1.28
10	Castor (Highest Purity)	E. H. Sargent Co., Chicago	104.1	88.8	88.1	—0.7	—0.79
11	Castor (Commercial)	E. H. Sargent Co., Chicago	102.2	87.5	86.5	—1.0	—1.14
12	Peanut	E. H. Sargent Co., Chicago	102.2	83.2	86.5	3.3	3.96
13	Olive I	Merck	100.7	84.0	85.2	1.2	1.43
14	Olive II	Waldenburg & Scharr, Chicago	96.6	80.0	81.7	1.7	2.12
15	Olive III	(California) Local Grocery	95.4	80.3	80.7	0.4	0.5
16	Neat's Foot	E. H. Sargent Co., Chicago	83.0	68.7	70.2	1.5	2.2
17	Lard	Local Meat Market	79.3	68.6	67.2	—1.4	—2.04
18	Mineral	Local Pharmacy	Nil	...	...	...	...

the bromine with carbon tetrachloride and the oil to be tested with a mineral oil which gave no thermal reaction with bromine, and to mix the resulting solutions. In one or two cases where the oil was very viscous or a solid fat was tried, they were diluted with carbon tetrachloride.

In the determination, the oil and mineral oil were weighed out into the lower compartment of the mixing chamber and an excess of bromine dissolved in carbon tetrachloride (1:3 by weight), placed in the upper compartment. The apparatus was set up as described in the standardization and when the rate of temperature change was uniform the two solutions were mixed. The temperature rise was determined in the ordinary way.

The calculation of the heat of bromination in terms of calories per gram of oil is simple. The heat capacity of the apparatus, 738.3 calories, plus the heat capacity of the bromine-oil mixture, multiplied by the total temperature rise and this value divided by the grams of oils used, gives the calories per gram of oil.

The heats of bromination of a number of the common fats and oils are given in Table VI. It has been shown

the iodine number but also a varying amount of substitution occurs which in the case of many oils is small (1 to 4 per cent), but in the case of others is quite large. Also, without knowing the way in which bromine may add, whether it adds to doubly or triply-bonded carbon atoms, etc., one could hardly expect that the heat of bromine reactions would be comparable to the weight of bromine or iodine absorbed. Louguinine and Koblukoff have shown too that the molecular heat of addition of bromine to a molecule of oleic acid is 28,757 calories, to crotonic aldehyde 19,349 calories, and to pinene about 36,000 calories. Such variation can not be due to experimental error but the conclusion is that if the iodine number and the bromine thermal reaction are exactly comparable it happens that the bromine in many cases adds to the oils in about the same way. In certain instances, at least, it is evident that this is not the case.

#### CRITICISM OF THE METHODS

In a test such as has been proposed there are several factors to be considered. An analysis on paper shows at least seven of these, although perhaps Nos. 3 and 5 in the list should be considered together.

- 1—The heat capacity of the apparatus.
- 2—The heat of separation of the bromine from the carbon tetrachloride solution.
- 3—The heat of solution of the brominated oil in the carbon tetrachloride.
- 4—The heat capacity of the brominated oil-carbon tetrachloride mixture.
- 5—The heat of solution of the mineral oil in the carbon tetrachloride.
- 6—The heat of bromination of the mineral oil.
- 7—The heat of bromination of the oil tested.

If all of these values were large, determinations would be laborious but fortunately most of these factors are negligibly small. A discussion of these factors and an elaboration of some good and bad points in the method, which have been brought out in this work, are given below.

There is one case where the method in its present state can not be used. The heat of bromination of turpentine can not be determined with this apparatus because of the solubility of paraffin in this liquid. No great trouble was experienced due to the dissolving of the paraffin except in this instance. Paraffin is very slightly soluble in carbon tetrachloride or carbon tetrachloride solutions of the oils.

The use of a copper dish as a mixing chamber is not very objectionable unless the cover should leak, in which case, in the presence of a little water, bromine attacks the dish vigorously. The dish was cleaned after each experiment by dipping it into hot paraffin which melts off the brominated oils and when the dish cools leaves a thin layer of paraffin over it to protect it in the next trial. It is suggested here that a porcelain enameled dish would serve much better for this work and that instead of a ground joint such as was used here between the cover and the mixing chamber, a small washer of thin gasket rubber be used to make this joint tight.

The heat of breaking the coverglass and the subsequent dropping through of the carbon tetrachloride solution of bromine was found to be nil. In testing this, the bromine solution was put in above the coverglass in the mixing chamber and the lower compartment of the mixing chamber left empty. When the temperature conditions were constant the coverglass was broken in the usual way and the result noted.

The heat of reaction of the bromine when it goes out of carbon tetrachloride solution to combine with the oils was found to be very small. This heat has of course the same value with the opposite sign as the heat of solution of the same amount of bromine in the same amount of carbon tetrachloride. In this case the bromine was sealed below the coverglass of the mixing chamber and the carbon tetrachloride above it. It was found that every gram of bromine dissolving in three times its weight of carbon tetrachloride gave a lowering of temperature of about 0.002° C. (heat capacity of apparatus, 738 calories).

The heat of solution of the oils in carbon tetrachloride was also found to be very small. Ten grams of mineral oil dissolving in 15 cc. of carbon tetrachloride give a temperature lowering of —0.015° C. The heat of decomposition of the bromine solution being "plus,"

the conditions were so regulated that when 10 cc. of mineral oil were used as a diluent and about 15 cc. of bromine-carbon tetrachloride solution were used for the bromination, these errors were cancelled.

The heat of solution of most of the oils which were tried in carbon tetrachloride was very small. Castor oil gave a notable lowering —0.020° C. to —0.030° C. per 10 grams of oil in 15 cc. of carbon tetrachloride. If this oil is diluted with carbon tetrachloride, however, instead of mineral oil, this variation drops out.

The specific heat of the brominated oil mixture does not vary greatly when about the same proportion of the oil to be tested, mineral oil and the bromine solution, are used. The specific heats of some of the mixtures determined are given in Table VII.

TABLE VII—SPECIFIC HEATS OF MIXTURES

MIXTURE	SPECIFIC HEAT
China Wood Oil, Bromine, Carbon Tetrachloride, Mineral Oil...	0.251
Lined Oil, Bromine, Carbon Tetrachloride, Mineral Oil.....	0.251
Olive Oil, Bromine, Carbon Tetrachloride, Mineral Oil.....	0.256
Cottonseed Oil, Bromine, Carbon Tetrachloride, Mineral Oil.....	0.275
Peanut Oil, Bromine, Carbon Tetrachloride, Mineral Oil.....	0.250

These are cases, of course, where the ratios of oil, mineral oil, bromine and carbon tetrachloride are not much varied. This shows, however, that under ordinary working conditions the specific heat need not be determined for every mixture but an average value can be taken. An error of several per cent in this value is easily allowable. If there is, for instance, 50 grams of this mixture used in a determination and the specific heat is taken as 0.30 and the true heat capacity is 0.25, in an apparatus having a total heat capacity of 750 calories per ° C. this would make an error of 2.5 calories or less than 0.4 per cent error.

This specific heat value can also be closely calculated by taking the sum of the heat capacities of the substances present multiplied by the weights of the materials used. For example, Table VIII will show the calculated specific heat of the mixture containing China wood oil.

TABLE VIII—CALCULATED SPECIFIC HEAT OF CHINA WOOD OIL MIXTURE

MATERIAL	WT. USED Grams	SPECIFIC HEAT	CALCULATED HEAT CAPACITY
Bromine.....	9.07	0.107	0.97
Carbon Tetrachloride...	27.2	0.207	5.63
China Wood Oil.....	9.0	0.231	2.08
Mineral Oil.....	10.5	0.416	4.38
TOTAL WEIGHT.....	55.77	TOTAL HEAT CAPACITY...	13.06
		SPECIFIC HEAT OF MIXTURE =	$\frac{13.06}{55.77} = 0.234$

The specific heat figured this way is 0.234. It was found by direct determination to be 0.254. These values check so closely that the error is negligibly small. It is therefore unnecessary to determine the specific heat of every mixture and if the method were to be used much, a table could easily be prepared from which the specific heat of any proportioned combination could be read with sufficient accuracy.

The handling of 1:3 solution of bromine in carbon tetrachloride is easy in a burette, the upper end of which is connected to a small wash bottle containing sodium or potassium hydroxide. If this is kept under the hood no discomfort is experienced on account of bromine fumes.

Special attention should be called to the specific heat apparatus. If a very quick method is desired



for the true heat of bromination, the apparatus could be worked in the same way as it was standardized, using oil and bromine in place of sulfuric acid and water. This should give results which are accurate to perhaps 1 or 2 per cent. This should make also a convenient apparatus for certain student calorimetric work where it could well be used in place of larger and more expensive types of calorimeters.

It might be noted, too, that the stirring must be vigorous in the large calorimeter. Several types of stirrers were tried inside of the mixing chamber and a spiral form was finally adopted as being the most efficient for this purpose.

#### CONCLUSIONS

I—A special apparatus and a method for the determination of the true heat of bromination have been proposed and tried.

II—A new apparatus on the same principle has been proposed for the quick determination of specific heat but it could well be used for other purposes, such as the determination of heat of neutralization, the Maumené number in terms of calories per gram of oil, etc.

III—The heats of bromination in calories per gram of oil have been determined on a number of oils and these values compared with the iodine numbers.

IV—It has been shown that the heat of bromination is not directly comparable to the iodine number, and the reason why such an agreement could not be expected has been pointed out.

V—The heats of solution of bromine and most oils in carbon tetrachloride have been shown to be very small.

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### OPTICAL DISPERSION OF CHINESE WOOD OIL AS AN INDEX OF PURITY

By E. E. WARE

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The peculiar properties exhibited by Chinese wood oil have led to the development of some interesting methods of examination for the detection of adulteration. In practically all cases, although the property upon which the individual method is based is characteristic enough to warrant its use as the basis of a method of examination, difficulties have arisen in the control of the conditions of operation, in consequence of which different laboratories report widely varying results.

The two methods offered by Ware and Schumann,<sup>1</sup> one of which depends upon the insolubility of the sodium soap of elaeomargaric acid in absolute alcohol, and the other upon the insolubility of the light-converted elaeostearic acid glyceride in high gravity petroleum ether, produce accurate results when operated under properly controlled conditions of temperature and concentration; but they do not seem adapted to the use of the factory control laboratory.

The heat test as modified by Committee D-1, Subcommittee III, of the American Society for Testing Materials,<sup>2</sup> is a logical method of analysis, inasmuch as it depends for its accuracy upon the careful observation of the progress of a gelatination which is

characteristic of this oil, and upon which is dependent the development of such varnishes as contain it. The report of the committee, submitted as a result of a series of tests carried out by different operators upon accurately prepared samples, shows that the method must be carefully handled to produce closely agreeing results, and that under ordinary circumstances it should not be relied upon to detect adulteration under 5 per cent.

The iodine jelly test, as investigated by the same committee, seems but little better. However, as mentioned in an earlier paper,<sup>1</sup> the gelatination of wood oil by iodine in chloroform solution is subject to a marked retardation by the presence of small amounts of alcohol. This fact may explain some of the variations in results, as the different operators were not using chloroform from the same source, and no doubt some of the chloroform might have contained traces of alcohol.

The index of refraction of wood oil, as has been pointed out by various investigators, is considerably higher than that of other drying and semi-drying oils. All attempts to calibrate, for analytical use, the variations in refractive index, due to mixing other oils with wood oil, have been unsuccessful in establishing the use of the refractometer in the quantitative estimation of adulteration. In this method

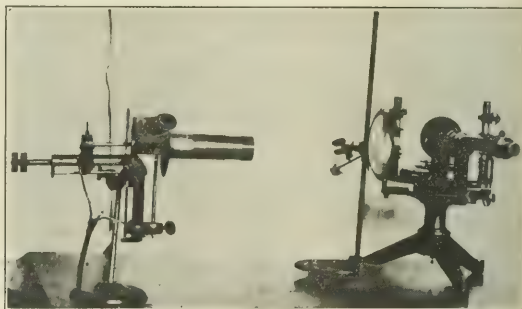


Fig. 1

the temperature correction factor is large enough to make possible an error of one per cent for every degree variation in temperature control. There exists also the difficulty of making an exact setting of the cross hairs of the reading telescope upon the dividing line between the illuminated and the dark fields. This difficulty is quite pronounced when using white light as a source of illumination, for the line of division between the fields is not sharp, even after a careful adjustment of the compensator, to correct for dispersion.

E. C. Holton<sup>3</sup> noticed, when working with the Abbé direct reading refractometer, that the rotation of the prism required for correct compensation for wood oil and for other oils is very different. He has gathered together considerable unpublished data in an attempt to calibrate this difference in compensator reading to a point where he can make use of it as an analytical method.

Brier<sup>4</sup> takes advantage of this property of abnor-

<sup>1</sup> This Journal, 7 (1915), 571.

<sup>2</sup> Private communication.

<sup>3</sup> This Journal, 7 (1915), 953.

<sup>4</sup> This Journal, 6 (1914), 806.

<sup>5</sup> Proc. Am. Soc. Test. Mat., 1915, p. 204.

mally wide dispersion exhibited by wood oil, in a method in which he demonstrates that when using a Pulfrich refractometer equipped with a prism whose relative dispersion is not large, the compensation offered by the secondary prism made up of oil is sufficient to produce an effect of anomalous dispersion. The compensation by other oils will narrow the spectrum but will not reverse it.

Inasmuch as this compensation offered by the secondary oil prism is due to the natural dispersion of the oil, it is possible to simplify the examination by



FIG. II

making a direct reading of this dispersion uninfluenced by the dispersion of any other medium. This may be accomplished by using as the refracting medium a hollow prism filled with the oil to be examined.

The most convenient instrument for the measurement of such relative dispersion is the ordinary spectrometer equipped with an autocollimating eyepiece. Fig. I shows such an instrument in use in this laboratory.

If light of a definite wave length be focused on the small totally reflecting prism in the eyepiece of the telescope, it is reflected through the slit and the objective lens, from which it enters the oil prism as parallel rays. After becoming refracted by the oil, it is reflected from the silvered rear face of the prism and refracted back along its original path to the slit from which it came. The angle through which the table of the spectrometer must be rotated to properly focus the slit image upon the slit itself, is the angle from which, knowing the angle of the prism, may be computed the refractive index for that particular wave length, according to the formula

$$\mu = \frac{\sin \frac{1}{2} (A + D)}{\sin \frac{1}{2} A},$$

where  $\frac{1}{2} D$  is the angle of rotation of the table minus the angle of the prism. If, instead of using a monochromatic source of light, we use a source emitting light of several wave lengths, we may, by making settings on the several bright lines characteristic of the source of light, measure the indices of refraction for the several wave lengths, and express the relative dispersion for any two of them according to the general formula

$$\begin{aligned} \mu_c &= \mu_F \\ \mu_c &= 1' \end{aligned}$$

in which  $\mu_c$  is the index of refraction for light of wave length 0.65629 and  $\mu_F$  for wave length 0.48614. In order to get a maximum value for the relative dispersion angle the author made use of a brass electrode arc lamp as a source of light. This light gives characteristic bright lines in both the red and the blue, with several other lines in the green and the yellow. Fig.

II gives some idea of the spectrum from the brass arc after dispersion by wood oil. The lines marked are the ones used for the measurements reported. They persist without adsorption by any of the oils used.

The angles  $D_1$ ,  $D_2$  and  $D_3$ , from which are computed the refractive indices for lines 1, 2 and 3, vary with the nature of the oil, with the temperature, and according to the angle of the prism; but for the same oil in a definite prism they are constant for a fixed temperature. The difference  $D_2 - D_1$  is just as accurately a measure of the relative dispersion for an individual prism as is the difference between the corresponding refractive indices. This fact simplifies the procedure of the method, for the fine adjustment of the spectrometer has sufficient range to permit the reading of the angular difference  $D_2 - D_1$  without resetting the spectrometer circle. The vernier of the instrument illustrated has a least reading of 6" with a possibility of interpolation to one second.

The dispersion or angular difference for wood oil as measured while confined in a hollow prism of angle  $20^\circ 1'$  is  $26' 54''$ , while for soya bean oil for the same temperature it is  $12' 54''$ , or expressed in vernier units of 6' each, it is 269 and 129, respectively.

As is shown in Table I and Fig. III, the dispersion of wood oil adulterated with varying percentages of

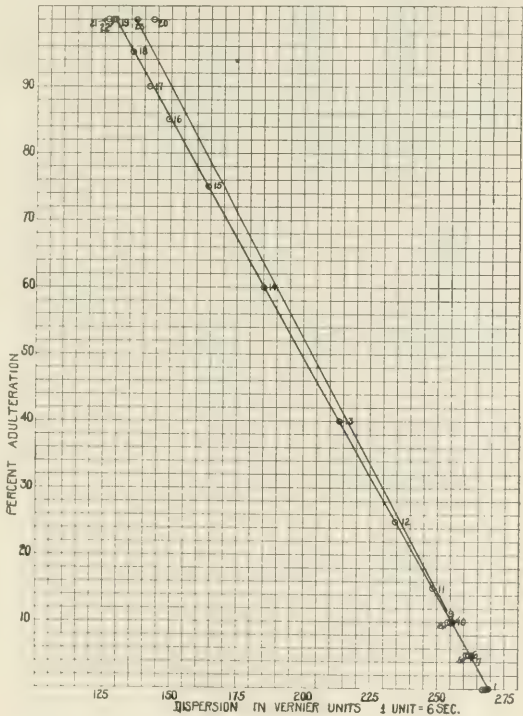


FIG. III

soya bean oil may be expressed quite accurately by a straight line, if we select, as coordinates, percentage adulteration and angular dispersion. This curve



will be reasonably accurate for other adulterants, for although there may be some variation between the dispersions of the various adulterating oils, when used with wood oil to 15 per cent or less, the differences in their effects upon the dispersion of the wood oil is relatively small. This fact may be better appreciated by comparing the two curves of Fig. III, which start from somewhat different points but lack little of being coincident at the lower ends, representing adulterations up to and including 15 per cent

The temperature correction for the angle of dispersion is quite small, about one second per degree Centigrade, which, figured in percentage adulteration, is 0.1 per cent. This is very considerably less than the correction on the index of refraction. The angle  $D_3$  reading of Table I shows something of the effect

Oil No.	Per cent wood oil	Adulterant oil	Angle $D_1 - D_1/2$	Angle $D_2$	Vernier units	Apparent adulteration Per cent	Error
1	100		26° 54"	22° 37' 48"	269		
2	100		26° 54"	22° 36' 12"	269		
3	100		26° 48"	22° 34' 24"	268		
4	100		26° 42"	22° 35' 24"	267	1.5	
5	95	Soya	26° 6"	22° 30' 36"	261	5.5	0.5
6	95	Soya	26° 12"	22° 30' 24"	262	5.0	
7	95	Linseed	26° 12"	22° 30' 48"	262	5.0	
8	90	Soya	25° 24"	22° 23' 12"	254	10.7	0.7
9	90	Linseed	25° 30"	22° 26' 24"	255	10.0	
10	90	Soya	25° 36"	22° 24' 48"	256	9.3	-0.7
11	85	Soya	24° 48"	22° 19' 48"	248	15.0	
12	75	Soya	23° 24"	22° 8' 48"	234	25.0	
13	60	Soya	21° 18"	21° 48' 40"	213	40.0	
14	40	Soya	18° 30"	21° 25'	185	60.0	
15	25	Soya	16° 24"	21° 6' 48"	164	75.0	
16	15	Soya	14° 54"	20° 56' 36"	149	85.7	0.7
17	10	Soya	14° 12"	20° 48' 24"	142	90.7	0.7
18	5	Soya	13° 36"	20° 43' 36"	136	95.0	
19	0	Soya	12° 54"	20° 36' 54"	129	100.0	
20	0	Tallow seed	14° 18"	21° 3' 48"	143		
21	0	Sesame	12° 42"	20° 29' 12"	127		
22	0	Rape	12° 48"	20° 29'	129		
23	0	Linseed	13° 42"	20° 55' 36"	137		

No. 1—Am. Soc. for Test. Mat. 1915: Pure Wood Oil

No. 2—Gillispie and Sons: Pure Wood Oil

No. 3—Acme White Lead and Color Works: Pure Wood Oil

No. 4—Acme White Lead and Color Works: Rejected shipment

Nos. 6, 7, 9 and 10—Am. Soc. for Test. Mat. 1915

of variation in temperature. Although precautions were taken to maintain the temperature constant throughout the work, slight variations were unavoidable, and each slight variation made a big change in angles  $D_1$ ,  $D_2$  and  $D_3$ , although the effect upon  $D_2 - D_1$  was relatively small. If it were possible to equip a spectrometer with a satisfactory constant temperature device, it is very probable that the variations in angle  $D$ , due to added impurity, would make a satisfactory means of detecting adulteration. The advantage gained by the measurement of this angle by the spectrometer rather than by the ordinary refractometer would be in the greater accuracy in reading.

The method of examination of wood oil by measuring its dispersion should appeal to the factory chemist. The individual readings may be made rapidly; there are no computations involved; the apparatus is not expensive nor difficult to keep in adjustment, and the accuracy of the method compares very favorably with that of any other in use at the present time.

The author wishes to acknowledge his indebtedness to Mr. W. W. Sleator, Instructor in Physics, for suggestions and assistance.

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## THE NEPHELOMETRIC DETERMINATION OF SMALL AMOUNTS OF ESSENTIAL OILS

By A. G. WOODMAN, R. T. GOOKIN AND L. J. HEATH

Received July 27, 1915

The two general methods most commonly employed for determining essential oils in such food products as extracts and cordials are: (1) extraction of the oil with a suitable solvent, and (2) precipitation of the oil and measurement of its volume after collection by centrifugal force. These methods give results much too low with very small amounts of oil, because both of the appreciable loss of oil during the evaporation of the solvent and of the proportion of oil which does not separate by centrifugal action.

The fact that an alcoholic solution of most essential oils will form a cloudy emulsion on the addition of water suggested the possibility of using the degree of turbidity as a measure of the quantity of oil present.

The emulsion formed consists of a large number of tiny oil globules which are capable of reflecting light. The number of globules and hence the amount of light reflected is evidently dependent on the amount of oil present. It remains, then, only to find some method of measuring the amount of light reflected, and by comparison with a standard containing a known weight of oil, a method is available for determining the amount of oil in an unknown sample.

### APPARATUS

The simplest instrument which suggested itself for this purpose was the well known candle turbidimeter. This, however, was not found suitable for use with translucent precipitates like oil emulsions because the light passes through the globules and makes the end point obscure and inaccurate.

It was therefore necessary to use a nephelometer, the form actually employed being that devised by Kober.<sup>1</sup> The basis of the instrument is the well-known Duboscq colorimeter, in which the length of column of liquid is varied by moving two glass plungers up or down by means of thumb screws on the back of the instrument. The length of each column is indicated on a scale by a pointer which moves up and down with the plunger.

To convert the colorimeter into a nephelometer, it is necessary:

1—To paint the sides of the plungers with black asphaltum paint, leaving the ends clean and with sharply defined edges. The black coating prevents any reflections entering the plunger except through the bottom. (This change may be permanent as it does not interfere with the use of the instrument as a colorimeter.)

2—To arrange a shield which will surround the tubes and by a central partition prevent any reflection from one to the other. Two apertures are made in the shield directly in front of the tubes and the only way in which light can reach the tubes is through these openings.

3—To enclose the eyepiece with a box into which the head may fit comfortably. This prevents reflections on the eyepiece.

<sup>1</sup> J. Biol. Chem., XIII, 4, 485; J. Am. Chem. Soc., 35 (1913), 1585.

The necessary apparatus for thus changing the colorimeter to a nephelometer can be obtained from Eimer & Amend, New York. Our experience, however, with the outfit supplied by the dealers showed that several of the parts were unnecessary and they were therefore discarded. The instrument as finally used consisted of the Duboscq colorimeter in its entirety with the following additions:

1—Black painted discs were placed on the bottom of the tubes to prevent light entering from beneath.

2—A black tin shield was placed around the tubes with a partition in the middle to prevent reflection from one tube to the other, and in this shield there was an opening opposite each tube to allow the light from the lamp to enter.

3—A black casing was used to surround the instrument on three sides, leaving the back open for manipulating the plungers, and this shield had a hole cut in the front for the passage of light from the lamp to the emulsion. The casing extended about a foot above the top of the instrument to shield the eyes of the observer from the lamp and from direct daylight. Just below the eyepiece there was placed a horizontal partition with a hole in it large enough for the eyepiece to go through. This prevented reflection into the eye from the lower part of the instrument. This casing or shield could be briefly described as two boxes, one on top of the other, the instrument being in one and the eyepiece protruding through a small opening into the other.

4—The sides of the plungers were painted black with asphaltum paint.

A 100-watt Mazda lamp was used as the source of light.

Anyone possessing a Duboscq colorimeter can get results of considerable accuracy by much simpler apparatus. Taking the colorimeter in its ordinary form, on the bottoms of the tubes (outside) should be placed two black discs (pennies of exactly the right size). The shield around the tubes may be made from cardboard painted with asphaltum paint.

Two squares of cardboard may be perforated with holes of the proper size and slipped over the plungers to prevent reflection from the tubes to the eyepiece except through the plungers.

The eyes should be protected from the light of the lamp by some simple shade, as a cardboard box or a piece of cloth.

#### STANDARDS

For quantitative determinations with the nephelometer it is of course necessary to have a standard of known value, and this can be done in several ways:

1—Standardize with permanent standards.

2—Standardize with one standard concentration and plot the readings of different known concentrations against the ratio of the known to the standard concentration.

3—Prepare a standard for each determination with the concentration of the unknown and standard approximately equal, treating both in exactly the same way.

The last plan, the one followed in this work, seems

much more accurate than the others since there can be no error introduced by different conditions of preparation of the known and unknown. These conditions are very important for accurate work, and unless they are the same the determination may be valueless. Richards and Wells<sup>1</sup> have pointed out that the amount of light reflected is not exactly proportional to the weight of precipitate, but is dependent to a considerable degree on the condition of the precipitate, the concentration of the solution and the length of column.

Hence, to get the best results, the condition of the precipitate should be exactly the same in the standard as in the unknown. This is insured by treating equal volumes of the unknown and standard with the same amount of reagent and by having the temperature and other factors the same. Besides this, the concentration of unknown and standard should be approximately equal and for this reason a preliminary precipitation of the unknown should be made and an approximately equal amount of standard used.

#### EXTRACTS

In general, 5 cc. of an extract were diluted with 25 cc. of water and compared with a standard in the nephelometer. Experience showed that the emulsions should be freshly prepared in order to give the best results, since on standing the globules of oil tend to coalesce and rise to the surface, thus offering less reflecting surface to the light and giving low results. It was found also in working with fairly high concentrations of some essential oils that the oil exerted an appreciable solvent action on the asphaltum with which the plungers were painted, making it advisable to keep the plungers out of contact with the emulsion except during the time of actual reading.

PEPPERMINT OIL—A typical series of readings is shown in the case of peppermint oil in the following table:

STANDARD.....	0.5 Per Cent Solution
Column Length (mm.).....	15.0
TEST SOLUTION:	
Concentration, %... 0.75 0.625 0.56 0.5 0.44 0.375 0.31 0.25	
Col. Length (mm.) (a) 7.4 10.7 13.0 15.0 17.1 20.9 25.0 36.5	

(a) These values are in each case the average of nine readings.

These values are expressed graphically in Fig. I, the ordinates representing the length of column of the test solution and the abscissae representing the ratio of the concentrations of the two solutions.

In the figure is also shown the theoretical curve, in which the lengths of column of two solutions are inversely proportional to their concentrations. A consideration of the figure will show that peppermint oil follows the theoretical curve fairly closely when the ratio of concentrations lies between the limits of 0.7 and 1.2. On both sides of these limits the actual plot deviates distinctly from the theoretical curve and corrections must be applied to get the true percentage.

There are thus two methods of procedure in determining the percentage of oil in an unknown sample which lies outside these limits of concentration ratios:

1—Compare the unknown with the standard in the usual way and read off the percentage on the plot.

<sup>1</sup> *Am. Chem. J.*, **31** (1909), 235.



2 Compare the unknown with the standard approximately and from the indicated result prepare a standard more nearly approaching the concentration of the unknown. Using this as a standard, the percentage of oil in the unknown can be computed.

The second method seems to be much safer and serves also as a check on the approximate determination,

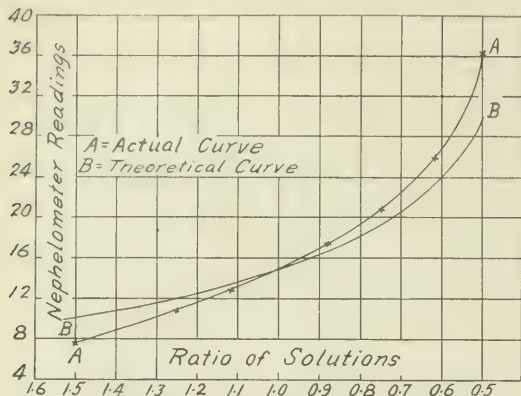


FIG. I—NEPHELOMETRIC CURVE FOR OIL OF PEPPERMINT

thus reducing the chance of error. It is in general easier because the correction curves are not the same for different oils.

The method works best on alcoholic solutions which do not contain over one per cent of the essential oil, so that standard or full strength extracts should be diluted with two or three times their volume of strong alcohol, and then the nephelometric determination made in the usual way.

Similar results were obtained in the cases of NUTMEG and ANISE OILS, these, when diluted, following the theoretical curve of the nephelometer even more closely than oil of peppermint and giving results agreeing closely with theory. Oil of anise gives a heavy precipitate with water and it was found best to precipitate 5 cc. of the extract with 5 cc. of water instead of the larger quantity used to precipitate the other oils.

EXTRACT OF ROSE, which is quite difficult to examine by ordinary methods, owing to the small amount of oil of rose present, is satisfactorily assayed by the nephelometric method, using 15 cc. of water to precipitate the oil from 5 cc. of extract and employing 0.4 per cent or 0.2 per cent alcoholic solutions as standards. In this case, for accurate results, the standard and the unknown should be of nearly the same strength since, as shown in Fig. II, the actual and theoretical values agree only for concentration ratios near unity.

The possibility of using one oil as a standard in the determination of other oils was taken into consideration and two strengths of extracts of the different oils which had been examined, 1 per cent and 0.5 per cent, were compared in the nephelometer, using in each case 25 cc. of water to precipitate the oil. Peppermint oil was taken as the standard and the figures given below show the wide divergence of re-

sults obtained, making doubtful the possibility of using any one oil as a standard.

OIL	LENGTH OF COLUMN			
	Peppermint	Nutmeg	Anise	Rose
1.0 Per Cent Solution	15.0	10.6	8.8	15.0
0.5 Per Cent Solution	15.0	9.6	8.0	15.1

An interesting fact, however, is that peppermint oil can be very well used as a standard in the valuation of rose extract.

#### DETERMINATION OF ESSENTIAL OIL IN CORDIALS

The determination by means of the nephelometer of the small quantities of essential oils found in cordials suggests itself as a natural sequence to the examination of alcoholic extracts. The problem differs somewhat in that the percentage of alcohol is usually less in the cordials than in the extracts, and they usually contain also a considerable proportion of sugar and are frequently highly colored.

The amount of alcohol was found to have but little significance, the weaker alcohol serving to hold in solution perfectly well the small amounts of essential oil used in these preparations. The effect of the sugar was found to be more pronounced, the result of its presence being either to prevent the precipitation of a part of the oil, or to alter the size of the oil globules in the precipitate, so that the amount of light reflected is less than that reflected from a solution of the same strength but containing no sugar. This was readily shown by comparing readings on an alcoholic solution containing 0.25 per cent of peppermint oil with solutions containing exactly the same amount of oil but varying proportions of sugar. The reading for the solution without sugar was 15.0; for solutions containing the same amount of oil, but with the sugar content gradually increasing from 5 per cent to 40 per cent, the readings increased correspondingly from 15.1 to 17.2.

The error due to the alcohol and sugar, however,

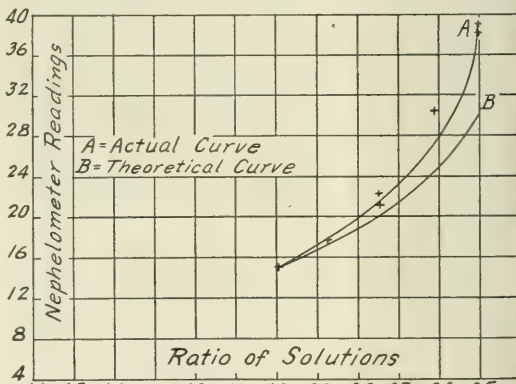


FIG. II—NEPHELOMETRIC CURVE FOR OIL OF ROSES

is readily corrected by adding to the standard approximately the same proportion of alcohol and sugar that are present in the sample being examined.

In the case of cordials that are colored, if the color is not too intense the same method may be employed, the matching of a tinted turbidity with a gray-white

one not being of great difficulty if the disparity of color is not great. With more deeply colored samples, however, separation of the oil by distillation is best, 100 cc. of the cordial being diluted with an equal volume of water and 100 cc. distilled. This procedure gives a colorless distillate of the same volume as the original sample and of approximately the same alcoholic strength, differing from it only in the absence of color and sugar.

Numerous experiments have shown that the distillation of the oil is quantitative, no special precautions being required except to distil rather slowly. The degree of accuracy obtained is shown in the following examples of artificial cordials containing either anise or peppermint oil, together with 25 per cent of sugar and 48 per cent of alcohol. They were highly colored with a mixture of Naphthol Yellow S and Indigo Carmine. The accuracy with oil of anise is somewhat greater than with peppermint:

	A	B	C	D
Per Cent Oil Present.....	0.16	0.33	0.20	0.45
Per Cent Oil Found.....	0.17	0.32	0.22	0.43

Typical results in the analysis of alcoholic extracts, containing amounts of oil unknown to the analyst are given below:

PER CENT	PEPPERMINT	ANISE	NUTMEG	ROSE
Oil Added....	0.88 0.40 0.198	0.625 0.33	0.375 0.31	0.325 0.317
Oil Found....	0.89 0.40 0.200	0.62 0.33	0.375 0.302	0.323 0.310

#### SUMMARY

If water is added to an alcoholic solution of many essential oils, the oil is precipitated as an emulsion which appears white, on account of the reflection of light from the minute globules of oil constituting the emulsion.

The amount of oil present may be determined by measurement of the amount of light reflected from a column of this emulsion. The reflected light is compared in a nephelometer with the light reflected from a solution containing a known amount of the same oil. The nephelometer used was an adaptation of the Duboscq colorimeter.

The general law of the nephelometer is that when two solutions give equal illumination in the eyepiece, the concentrations of the reflecting substance are inversely proportional to the lengths of the columns.

Peppermint oil, nutmeg oil, anise oil and oil of rose follow this law with slight variations which do not affect the usefulness of the method.

All of these oils can be determined with great accuracy by the nephelometric method in concentrations up to one per cent and, by suitable dilution with alcohol, in higher concentrations. The nephelometric reading is not affected by slight variations in the chemical composition of the oil, hence it is not necessary that the standard employed should be from exactly the same source as the oil being determined.

This method as described is not applicable to those essential oils which do not form an emulsion on adding water to their alcoholic solutions.

There is no single oil that can be used as a standard for the determination of all these oils, because the emulsions formed by adding the same amount of

water to alcoholic solutions of different oils of equal strength differ widely in the amount of light reflected. The only oil that it was found possible to use as a substitute was peppermint oil for rose oil on account of the fact that these two oils show approximately equal reflecting power under the same conditions.

In applying the method to cordials two factors influence the amount of light reflected: (1) percentage of alcohol and (2) percentage of sugar. Their influence is large enough to make it necessary to use a standard containing approximately the same percentage of alcohol and sugar, but their effect does not change rapidly with small increases in their concentration and thus approximate equality of standard and unknown is all that is necessary.

Colored cordials can be examined directly provided the color is not so deep as to make the end-point obscure.

Deeply colored cordials can be determined by first distilling off the alcohol and oil and comparing the distillate with a standard extract.

In general, it may be said the nephelometric method is a rapid, simple and accurate method for the determination of small amounts of many essential oils, requiring ordinarily less than half an hour for its completion.

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#### REAGENTS FOR USE IN GAS ANALYSIS

#### III—THE SPECIFIC ABSORPTION OF ALKALINE PYROGALLOL IN VARIOUS PIPETTES

By R. P. ANDERSON

Received August 30, 1915

The development of a pipette in which gases may be absorbed rapidly and completely by the proper reagents without the necessity of shaking has proceeded along two lines. There is (1) the form of pipette in which absorption is hastened by increasing the surface of reagent that is in contact with gas and (2) the form in which the same result is obtained by passing the gas through the reagent in such fashion as to secure intimate contact. Under (1) there is included the Orsat<sup>1</sup> pipette and its many variations; under (2) there are many distinct pipettes, including those of Hankus,<sup>2</sup> Nowicki-Heinz,<sup>3</sup> and Dennis.<sup>4</sup> It has been demonstrated<sup>5</sup> repeatedly that the Orsat pipette, or its modifications, is unsatisfactory for the absorption of oxygen by alkaline pyrogallol prepared in the usual fashion. Since rapid and complete absorption is a function of the composition of the reagent as well as of the construction of the pipette in which it is to be employed, it was thought desirable, on the introduction of new proportions of pyrogallol and potassium hydroxide for the preparation of alkaline pyrogallol,<sup>6</sup> to ascertain the behavior of this modi-

<sup>1</sup> *Chem. News*, **29** (1874), 177.

<sup>2</sup> *Österr. Chem. Ztg.*, **47** (1899), 81; *J. f. Gasbel.*, **49** (1906), 367.

<sup>3</sup> Designed by Nowicki, *Österr. Zeit. f. Berg. Hutt.*, **63** (1905), 337; improved by Heinz, *J. f. Gasbel.*, **49** (1906), 367.

<sup>4</sup> *THIS JOURNAL*, **4** (1912), 898.

<sup>5</sup> See Dennis' "Gas Analysis," p. 78.

<sup>6</sup> *THIS JOURNAL*, **7** (1915), 587.



fied reagent in various pipettes regardless of their usefulness with the old reagent. In the following article there are given the results of experiments that were made to determine the specific absorption<sup>1</sup> of the modified reagent in the four pipettes that have been mentioned, together with some observations on the convenience and ease of manipulation of the reagent in the various pipettes and the attempts that were made to adapt the reagent to them.

The construction of each pipette is shown in Fig. 1. A measured amount of the modified alkaline pyrogallol was placed in each and the specific absorption of the reagent was determined for samples containing

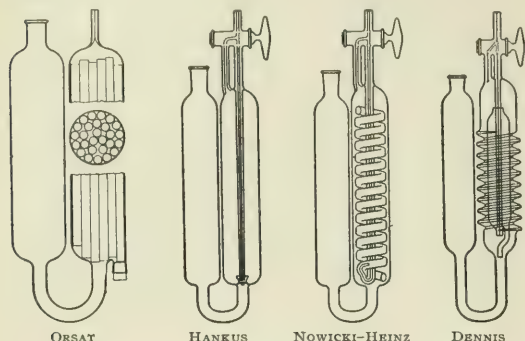


FIG. 1

20.9 per cent oxygen, using the method of manipulation which was found by experiment to be best adapted to the pipette. The procedure that was followed resembled that employed in similar determinations with the Hempel pipette<sup>2</sup> and consisted of the analysis

the customary manner, is probably due in part to the formation of a thick film of reagent on the glass tubes in the pipette, as a result of the high viscosity of the reagent.

A comparison of each of the four pipettes under discussion as regards the time consumed in their manipulation and the specific absorption that is thus obtained shows that the Orsat pipette is superior to any of the others for the absorption of oxygen when the modified reagent is employed. Allowing 15 seconds for the passage of a sample of gas either to or from the Orsat pipette and 30 seconds for the return of gas from the other pipettes, it is seen that in the case of the Orsat pipette only 1½ minutes is required from the time the gas leaves the burette until it has been returned, while the corresponding time in the case of the Hankus, Nowicki-Heinz, and Dennis pipettes is 5½, 2½, and 2½ minutes, respectively. Further, the specific absorption that may be obtained from either the Nowicki-Heinz or the Dennis pipette in the 2½ minute interval is small as compared with that obtained in the Orsat pipette for the 1½ minute interval. In fact, it seems probable that, when the modified reagent is employed, the Orsat pipette is superior to any form in which the gas is made to bubble through the reagent, since the Nowicki-Heinz and Dennis pipettes, with which the comparisons were made, are undoubtedly the most efficient pipettes that operate on that principle.

The convenience of manipulation is not all that might be desired, however, in the case of any of the pipettes that were studied. One source of trouble that is common to each is the formation of a deposit

TABLE I—SPECIFIC ABSORPTION OF MODIFIED ALKALINE PYROGALLOL(g)

METHOD OF MANIPULATION	TYPE OF APPARATUS USED			
	Orsat	Hankus	Nowicki-Heinz	Dennis
One-minute contact	22.1(b)	0	5.1	7.1
One passage occupying 2 minutes(c)	0	0	24.8	28.0
Two passages occupying 1 minute each(c)	0	21.3	30.5	31.8
Two passages, first occupying 2 minutes, second 1 minute(c)	0	0	0	0
Three passages, first occupying 2 minutes, others 1 minute each(c)	0	0	0	0
Four passages, first occupying 2 minutes, others 1 minute each(c)	0	0	0	0

(a) This modified reagent is prepared by dissolving 15 g. of pyrogallol in 100 cc. of a solution of potassium hydroxide of 1.55 specific gravity and contains 13.5 g. of pyrogallol and 71.5 g. of potassium hydroxide to 100 cc. of solution.

(b) The first sample to be analyzed requires a two-minute contact.

(c) The time of returning gas to burette is not included.

of samples of air, alternated with the admission of pure oxygen to the reagent in order to shorten the routine work of the experiments. The results that were obtained are shown in Table I.

It will be seen from a comparison of the results of Table I with those given by Dennis<sup>3</sup> that the time necessary for the complete absorption of oxygen in air, using new reagent, has been shortened by changing its composition. The order of the pipettes as regards the time necessary for complete absorption has been changed also by using the modified reagent. The Orsat pipette required the longest time with the reagent employed by Dennis and the shortest time with the reagent under consideration. The surprising activity of the latter reagent in a pipette which has been shown to be very unsatisfactory when employed in connection with alkaline pyrogallol prepared in

on the inner surface especially at the upper end where the constriction occurs. The presence of this deposit makes it difficult to determine the exact position of the surface of the reagent when the gas is being drawn back into the burette and causes the retention of minute bubbles of gas during the same operation. The separation of a precipitate also causes more or less additional trouble, the nature of which varies with each individual pipette.

In the case of the Hankus pipette, the precipitate accumulated in an amount sufficient to clog temporarily the small openings in the glass plate at the bottom of the central capillary tube by the time a specific absorption of about 18 has been reached. From this point on, the pipette became increasingly difficult to manipulate and finally the attempt to exhaust the reagent was abandoned at a specific absorption of 21.3.

In the Nowicki-Heinz pipette, the accumulation of

<sup>1</sup> THIS JOURNAL, 7 (1915), 587.

<sup>2</sup> Loc. cit.

<sup>3</sup> THIS JOURNAL, 4 (1912), 898.

precipitate tended to clog the spiral tube with the result that occasionally gas would escape from the opening at the bottom of the spiral and bubble up through the reagent. Also, on returning the gas to the burette for measurement, it was found frequently that gas would be retained in the spiral and liberated some little time after the volume of the sample had been read. This objection became more and more serious, until finally the reagent was discarded before it had become exhausted.

The accumulation of precipitate in the Dennis pipette gradually increased the resistance offered to the passage of gas until, in some cases, a portion of the sample was forced into the leveling arm of the pipette when only two minutes were allowed for the complete transfer of the sample to the pipette. In the case of the pipette from which the data in the table were obtained, it was possible, by careful manipulation, to exhaust the reagent to the point where it would no longer absorb oxygen completely in a reasonable length of time without much trouble from this source.

In the Orsat pipette, the precipitate clogged the lower ends of the outer glass tubes with the result that, as the precipitate increased in amount, it became more and more difficult to introduce a sample of gas into the pipette without loss of gas into the leveling arm of the pipette. Also, at about the time when absorption failed to be complete with one-minute contact, small bubbles of gas were frequently retained in the pipette as the gas was withdrawn. For these reasons, no attempt was made to determine the specific absorptions for longer contact of the gas with the reagent.

The formation of a precipitate which appears to contain the various oxidation products of alkaline pyrogallol<sup>1</sup> is the cause of practically all of the difficulties of manipulation of the modified reagent in the pipettes that have been employed. In an effort to further modify the reagent so that this objection might be removed without too great a sacrifice of specific absorption, experiments were performed to ascertain the effect on the formation of precipitate of variations in the amounts of pyrogallol and potassium hydroxide.

The effect of varying the amount of pyrogallol was first determined. It was known from previous work<sup>2</sup> on alkaline pyrogallol that, within certain limits, a decrease in the amount of pyrogallol would cause a nearly proportional decrease in the specific absorption of the reagent, but it seemed possible that a reduction in the amount of pyrogallol might prevent the formation of precipitate and thus result in a more satisfactory reagent. Accordingly solutions were prepared which contained  $\frac{1}{3}$  and  $\frac{2}{3}$  of the usual amount of pyrogallol and these were exhausted as previously described. It was found that there was no apparent advantage in using less pyrogallol, the amount of precipitate being, as far as the eye could judge, proportional to the amount of oxygen which

the reagent had absorbed and independent of the amount of pyrogallol employed.

The relation of the amount of alkali to the formation of precipitate and to the specific absorption of the reagent was next considered. It seemed probable that the formation of a precipitate in alkaline pyrogallol could be retarded or prevented by using less potassium hydroxide in the preparation of the reagent. Such a procedure would probably lessen the specific absorption of the reagent. To obtain information on these points, solutions were prepared using alkali of specific gravity 1.50 and 1.45. These solutions were exhausted in the usual manner, first in the Hempel pipette for use with mercury and then in the Orsat and Dennis pipettes. The results of the determination of specific absorption are shown in Table II, data on the original solution being included for purposes of comparison.

TABLE II—SPECIFIC ABSORPTION OF ALKALINE PYROGALLOL IN HEMPEL PIPETTE FOR ORSAT PIPETTE FOR DENNIS PIPETTE FOR

Specific gravity of alkali	HEMPEL PIPETTE FOR		ORSAT PIPETTE FOR		DENNIS PIPETTE FOR	
	1-min. shaking	2-min. shaking	1-min. contact	2 contacts 1 min. each	2-min. passage	2 passages 1st-2 min. 2nd-1 min.
1.55.....	27	30	22	..	7	28
1.50.....	5	24	12	29	3	24
1.45.....	0	6	0	24	0	9

The reagent prepared from alkali of 1.45 specific gravity showed much less precipitate than the others, but the specific absorption of this reagent is much too low for general use. Considerable precipitate was formed in the reagent prepared from alkali of 1.50 specific gravity and this caused a certain amount of inconvenience of manipulation, much less, however, than follows from the use of the original solution. The drop in specific absorption that accompanies the use of alkali of 1.50 rather than 1.55 specific gravity is quite pronounced except when the Dennis pipette is employed. Of the two reagents, it appears that the one containing the smaller amount of alkali is better suited for use in this pipette, since the gain in convenience of manipulation seems to more than offset the small loss in specific absorption.

From the results of the experiments that have been described, it may be said that the modified alkaline pyrogallol is not well suited for use in pipettes that have been designed for the absorption of oxygen without shaking, nor can it apparently be readily adapted for convenient use in these pipettes without considerable loss in specific absorption. It seems feasible, however, to adapt the pipettes to the modified reagent, and a modification of the Orsat pipette in which the accumulation of precipitate does not interfere appreciably with its manipulation is described in the following article.

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#### PIPETTES ESPECIALLY ADAPTED FOR USE WITH ALKALINE PYROGALLOL

By R. P. ANDERSON  
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It has been shown in the foregoing article that the Orsat pipette is probably superior for the absorption of oxygen by alkaline pyrogallol to any of the pipettes that have been suggested as a substitute for it in the

<sup>1</sup> See Berthelot, *Ann. chim. phys.*, [7] 15 (1898), 294.

<sup>2</sup> *Loc cit.*



Orsat apparatus, provided certain proportions of pyrogallol and potassium hydroxide are employed in the preparation of the reagent. The inconveniences attendant upon its use are inconveniences of manipulation, due to the formation of a precipitate, which it was not found possible to eliminate by changing the composition of the reagent without undue loss in specific absorption.

In the form of Orsat pipette shown in Fig. I, the accumulation of precipitate is not a serious objection to its use. The construction of the upper end of the pipette is such that very little precipitate clings to it and no trouble is found from the retention of gas at this point, as is the case with the usual form of the Orsat pipette. The perforated porcelain cone forms a support for the glass tubes and has the advantage over the horizontal perforated plate sometimes employed that the precipitate cannot collect and clog the lower ends of the glass tubes. Gas can be passed rapidly into this pipette, even when considerable precipitate has accumulated, without danger of its being forced into the leveling arm. The length of the cylindrical portion of the left-hand tube is 13 cm. and its diameter, 3.6 cm. Thin-walled glass tubes about 5 mm. in diameter are employed to increase the surface of the reagent in contact with a gas sample and 27 of these are required to fill the pipette.

On account of the differences in manipulation of the pipette in question and the Hempel pipette, the proportions of pyrogallol and potassium hydroxide that were recommended as the result of previous work<sup>1</sup> for the preparation of alkaline pyrogallol for use in the latter pipette, are not necessarily the most desirable for use in the former. An increase in the amount of pyrogallol in the solution results in a reagent that foams appreciably on shaking, but since the manipulation of the proposed Orsat pipette does not involve shaking, it would seem that higher concentrations of pyrogallol might be employed, thus resulting in an increase in specific absorption. To test the truth of this assumption, the specific absorption of each of a series of solutions of alkaline pyrogallol was determined using the modified Orsat pipette. The solutions were prepared by dissolving a definite amount of pyrogallol in 200 cc. of a solution of potassium hydroxide of specific gravity 1.55, the one obtained by using 30 grams of pyrogallol being the solution suggested for use in the Hempel pipettes where the gas sample is shaken with the reagent. The values of specific absorption were obtained at room temperature (20–24° C.), for samples of gas 100 cc. in volume containing 20.9 per cent oxygen, and for one-minute contact of gas and reagent. The results follow:

Grams pyrogallol to 100 cc. alkali.....	15	20	25	30
Specific absorption of the solution.....	25.0	31.2	36.1	37.8

The saturation of each reagent was stopped at the point where there was a noticeable retention of gas between the glass tubes in the pipette due to the clogging of some of the smaller openings by precipitate, and the values of the specific absorption given in

the table were obtained from the volume of gas absorbed up to that point. This retention of gas seems to occur at or slightly before the time when absorption fails to be complete for one-minute contact of gas with the reagent. The increase in specific absorption that results from the increased concentration of pyrogallol is pronounced<sup>1</sup> up to a concentration of 25 grams of pyrogallol, and since there is but little advantage in using still more pyrogallol, the solution containing 25 g. of this constituent was chosen as being the most desirable for use in this pipette. Dissolving 25 grams of pyrogallol in 100 cc. of a solution of potassium hydroxide of 1.55 specific gravity results in a volume of about 118 cc. and there are thus 21.2 grams of pyrogallol and 66.6 grams of potassium hydroxide to 100 cc. of the proposed reagent.

From a comparison of the specific absorption ob-

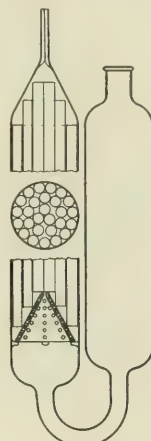


FIG. I

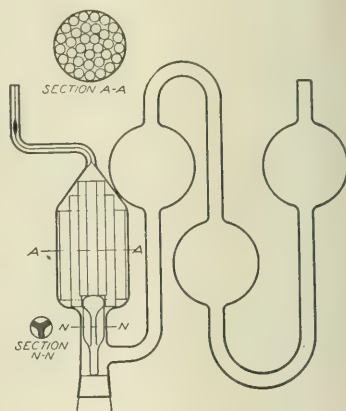


FIG. II

tained in this modified Orsat pipette using the above reagent with that<sup>2</sup> obtained in the Hempel double pipette using the reagent best adapted to it, it appears that there is considerable advantage in using the former pipette; further, the fact that no shaking is required emphasizes the superiority of the proposed pipette; therefore, it seems desirable to adapt this modification of the Orsat pipette for use in a frame such as ordinarily is employed to hold a Hempel double pipette for solid and liquid reagents. The form that is suggested is shown in Fig. II. It differs from the usual Hempel double pipette for solid reagents in having a smaller cylindrical bulb and a much more gradual constriction at its top. It was found that the cylindrical portion of the usual Hempel double pipette of this form is much larger than necessary when thin-walled glass tubes are used as contact material and in this connection it is desirable to have as small a bulb as possible in order to decrease the volume of the space between the upper ends of the tubes and the top of the bulb. The cylindrical portion of the bulb is 7 cm. and its diameter 5 cm. The construction of the glass part at the bottom of the bulb is such that the glass tubes are held in position

<sup>1</sup> Loc. cit. See particularly Curve II in Fig. 4.

<sup>2</sup> Loc. cit. 25 for one-minute shaking.

<sup>1</sup> THIS JOURNAL, 7 (1915), 587.

and at the same time they can not readily become clogged with precipitate. This form has the advantage over that in Fig. I that the glass tubes are removable. If it is desired to eliminate the rubber stopper at the base of the pipette, the construction of the lower end of the cylindrical bulb can be made identical with that in Fig. I. An opening<sup>1</sup> (not shown in the figure) between the first and last two bulbs which is closed by a small cork or rubber stopper is a great convenience in filling and cleaning the pipette.

The specific absorption that may be obtained in this pipette is practically the same as that obtainable with the pipette shown in Fig. I, *viz.*, 36.1 for the reagent prepared as suggested and exhausted under conditions that are there specified.

It was found that the pipettes that have been described are not well adapted to the analysis of samples of nearly pure oxygen,<sup>2</sup> and for this reason no determinations of specific absorption for gas samples containing 90 per cent oxygen, such as have been published for the Hempel pipettes, were made. When a gas sample high in oxygen is placed in contact with the reagent in either of these pipettes in the usual manner, rapid absorption occurs up to what apparently corresponds to the exhaustion of the film of reagent upon the glass tubes and the inner wall of the pipette; thereafter absorption is slow unless the remaining gas is passed into the burette and returned in order to moisten the contact material with fresh reagent. Even with this latter procedure, considerable time is consumed in effecting complete absorption, partly because of the intermittent contact of gas and reagent, and partly because of the decrease in the amount of contact material in proportion to the size of the gas sample as the latter becomes small and occupies only the upper portion of the pipette above most of the glass tubes. Therefore, it is believed that when the analysis of gases high in oxygen is frequently made, the Hempel pipette should be employed. On the other hand, when such samples are met with infrequently, as is usually the case, the longer time required for their analysis will not prove a great objection, especially if the pipette is shaken to hasten the absorption when the volume of the sample has become too small to uncover the tops of the glass tubes.

#### SUMMARY

I—Pipettes especially adapted for use with alkaline pyrogallol are shown in Figs. I and II. These pipettes are constructed in such fashion that the formation of precipitate, a characteristic of alkaline pyrogallol of high specific absorption, is not objectionable until the reagent has nearly become exhausted.

II—It has been found possible to employ a reagent containing a higher concentration of pyrogallol than that recommended for use in the Hempel pipettes. This reagent is prepared by dissolving 25 grams of pyro-

gallol in 100 cc. of a solution of potassium hydroxide of 1.55 specific gravity, which results in a volume of about 118 cc. There are thus 21.2 grams of pyrogallol and 66.6 grams of potassium hydroxide to 100 cc. of the solution.

III—The specific absorption of the above reagent for 1-minute contact is about 36 when treated in the proposed pipettes at room temperature (20°–24° C.) with gas samples 100 cc. in volume containing 20.9 per cent oxygen. This is a decided gain both in specific absorption and convenience of manipulation over the results that have previously been obtained with the Hempel pipette (specific absorption 25, for 1-minute shaking). No determinations of specific absorption for samples of nearly pure oxygen were made, since complete absorption can not be obtained in these pipettes in less than 4 or 5 minutes unless shaking is employed to facilitate the removal of last traces of oxygen.

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#### REAGENTS FOR USE IN GAS ANALYSIS IV—PHOSPHORUS IN SOLUTION

By R. P. ANDERSON AND W. BIEDERMAN

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Centnerszwer<sup>1</sup> has proposed that a solution of phosphorus be employed to replace solid phosphorus as an absorbent for oxygen in gas-analytical work, since the behavior of the latter reagent is appreciably influenced by temperature, percentage of oxygen in the mixture, and the presence of certain other gases. Castor oil was chosen as the solvent for phosphorus because it possesses a negligible vapor pressure at ordinary temperatures and because it dissolves the products of the oxidation of the solute.

It was thought desirable to study further the solution which Centnerszwer recommends, with the idea of determining how long a time is required for the complete absorption of oxygen under ordinary conditions and what specific absorption may thus be obtained. Accordingly, solutions of phosphorus in castor oil were prepared by the method which he employed, which is as follows: About 230 cc. of castor oil and 3 grams of well-dried phosphorus are placed in a flask of 250 cc. capacity, a well-fitting stopper is loosely placed in the neck of the flask, and its contents heated in an oil bath to 200°. The flask is then removed from the bath and dried with filter paper, and, after tightly inserting the stopper, it is wrapped in a towel and vigorously shaken to effect complete solution of the phosphorus. When cool, the solution is transferred to a pipette and is then ready for use. The precaution of wrapping the hot flask with a towel before shaking, as specified by Centnerszwer, is an important one as regards the safety of the operator, since considerable pressure is developed when the shaking is started, especially if the castor oil does not almost entirely fill the flask, and in one instance the flask was shattered by the pressure produced.

Samples of air were brought into contact with the reagent at 25° C. in Hempel pipettes for solid and liquid

<sup>1</sup> This construction is shown on a special pipette for use with cuprous chloride, designed by the United Gas Improvement Co., in the catalogs of Eimer & Amend and A. H. Thomas Co.

<sup>2</sup> This appears to hold true for all pipettes in which the gas sample is not shaken with the reagent.

<sup>1</sup> Chem. Ztg., **34** (1910), 494.



reagents. It was found that the absorption of oxygen took place slowly and was in no case complete in a reasonable length of time. In a typical experiment, the absorption at the end of 3 minutes amounted to 8.4 per cent, at the end of 6 minutes 14.8 per cent, and at the end of 9 minutes 20.4 per cent. Increasing the time of contact of the gas and reagent did not result in any appreciable change in the volume of the sample. That the absorption of oxygen was actually incomplete was shown by treatment of the residue with alkaline pyrogallol, whereupon a further decrease of 0.4 per cent was obtained, thus indicating approximately the correct percentage of oxygen in air. It appears, therefore, that the solution of phosphorus in castor oil is not suitable for the gas-analytical determination of oxygen at ordinary temperatures. No attempt was made to maintain the reagent at an elevated temperature in order to obtain complete absorption, since it is believed that such a procedure would complicate the determination of oxygen unnecessarily. Assuming that complete absorption can be obtained with this reagent at elevated temperatures, there seems to be no reason why it should be preferred to alkaline pyrogallol properly prepared.<sup>1</sup> In fact the latter reagent is much more convenient to prepare, and by its use practically complete absorption of oxygen can be obtained at room temperatures in a much shorter time.

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#### THE UTILIZATION OF CULL FLORIDA CITRUS FRUITS<sup>2</sup>

By F. ALEX. McDERMOTT

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In the packing of citrus fruits, a considerable proportion of the fruit coming into the packing houses is unfit for shipment, and must be discarded; this discarded fruit constitutes the culls, and may amount, during poor seasons, to as much as 10 per cent of a given lot of fruit, though ordinarily the proportion is not so high. The usual causes of culling are extreme over- or under-size, stem-end rot, traumatic injuries to the peel, and blue molds. A few of these culls are disposed of at low prices for quick sales in the local markets, while a good proportion are consumed by the local cattle or simply allowed to decay on the ground. A considerable number of these culls have the flavor and food value unimpaired, if utilized immediately. The main problems offered were (a) to find a satisfactory process by which the juice of these culls could be preserved for at least two years, without conflict with the national or state pure food laws, and (b) to develop a method by which the flavoring oil could be removed from the peels in such a manner that the product would meet the commercial requirements for such an oil, and could sell,

as a domestic product, in competition with the imported Italian oil. The recovery of the citric acid formed one of the minor problems.

A large number of experiments were made with different processes to determine their effect on the stability of the juice. As had already been observed, it was soon found that simple pasteurization of the juice was not sufficient to protect it from further change; for a short time after pasteurization, usually less than two weeks, the juice kept without apparent change, but after the lapse of this time a change of color became evident, the juice darkening and finally becoming muddy; this change in color was accompanied by a deterioration in flavor, which eventually became offensively acid. All specimens did not change to the same degree, but it was found impossible to correlate this difference between specimens with differences in acidity or sugar content. Such darkened specimens appeared to be sterile, no organisms being shown by inoculations on standard agar or on sterilized orange juice, or under microscopic examination. The effect seemed to be due to chemical action, but although a large number of tests were made, these failed to indicate just what change had taken place in the darkened juice. It was found, however, that the removal of the air dissolved in the juice and that in the container above it, followed by pasteurization, was sufficient to prevent this deterioration of the juice for a considerable time—in fact all failures which occurred within two years could be traced to air having gained access to the juice through leaks which developed in the stoppers on long standing under varying conditions of temperature. It was found further that, as would naturally be expected, it was the oxygen of the air which was active in producing this change, although replacing the air with pure oxygen did not produce as rapid and strong a darkening as would be expected, the effect being but little different from that of air alone.

It may be of interest to note here that the most common organized contamination of orange juice, which was encountered in this work, was a strain of the wild yeast ("Kahmhefe") *Willia anomala*, and it is this organism which is responsible for the development of the ester odor (apparently ethyl acetate) which may so frequently be noticed in orange juice which has stood some hours at room temperature; the yeast was kindly identified for me by Dr. Alb. Klöcker, of the Carlsberg Laboratory, Copenhagen. Acetic acid bacteria were also found occasionally, in every case observed being secondary to the wild yeast, and on long standing various molds developed. The common blue molds of the peel of the orange, *Penicillium italicum* and *P. olivaceum*, appeared to be unable to grow on the sterilized juice, and all attempts to inoculate them directly from infected fruit on this medium resulted instead in the growth of the *Willia*.

The simplest method of effecting the removal of the air from and above the juice in the containers seemed to be to replace it by some non-oxidizing gas, and of those commercially possible, carbon dioxide appeared to be the best. A very large number of

<sup>1</sup> THIS JOURNAL, 7 (1915), 587 and 8 (1916), 131.

<sup>2</sup> Author's abstract of a rather extensive report on the utilization of the cull citrus fruits from the packing houses in Florida, covering the author's work on this subject during the period from October, 1911, to August, 1913, under the auspices of the Florida Citrus Exchange, at the Mellon Institute of Industrial Research, of the University of Pittsburgh. Publication has been withheld, up to this time, in accordance with the fellowship agreement; complete publication of the entire report will be made at a later date.

specimens of orange and grapefruit juices were prepared, in which the juice was charged with carbon dioxide at atmospheric pressure, and the air above the liquid replaced with the dioxide; the bottles were then sealed with paraffined stoppers, pasteurized, and the joint between the stoppers and the necks kept covered with paraffin while cooling. This system of sealing, while by no means perfect, gave a considerable number of specimens which remained without apparent change for two years or more. Charging with  $\text{CO}_2$  under pressure, without removal of the air present, did not afford protection against deterioration. It was found that pure nitrogen, hydrogen or methane (washed natural gas) gave as good results so far as preservation was concerned, as did the carbon dioxide, but owing to their lower solubility, they were somewhat more difficult to deal with than the dioxide. Nitrous oxide, as might be expected, gave results about like those of pure oxygen. So far as flavor is concerned, the hydrogen was superior to any of the other gases, though of course harder to handle. The carbon dioxide gave a slightly unnatural tang to the juice, suggesting incipient fermentation to some who tasted it.

Sealing *in vacuo* was also tried, and eventually proved to be the most satisfactory method of meeting the difficulty. Early experiments using sealing bottles showed that the juice retained its flavor best when pasteurized under as complete a vacuum as possible, the usual process being to exhaust the container to about 28.5 inches vacuum, while immersed in water at a temperature slightly above the boiling point at this pressure; the contents were then allowed to boil a little while under the reduced pressure, to drive out dissolved gases, the liquid then cooled, and the bottle sealed. Such preparations kept excellently, as long as the bottles remained sealed; breakage of the seal was followed by discoloration and deterioration of flavor, as in the fresh juice. Later experiments were made using the method of vacuum sealing with a rubber gasket and cap, which has been so widely applied recently in the preparation of food products, especially by the Beech Nut Company. It was found that equally good results were obtained, the main difference in operation being that the juice in the container was heated to a point slightly above that at which it would boil at the vacuum employed, then the container placed in the sealing machine, exhausted, ebullition permitted for a minute or so, and then the jar sealed and pasteurized. Of course, these seals fail occasionally, and such failures were always evidenced by discoloration of the juice.

What has been said heretofore has referred mainly to orange juice; the juice of the grapefruit undergoes exactly the same discoloration and change of flavor, on simple pasteurization in air, as does the orange juice. Lemon juice, however, seems to be a somewhat different proposition, as it is reported in the literature that repeated simple pasteurization is all that is necessary to prevent deterioration; no direct experiments were made with lemon juice, but it was found that the repeated pasteurization (pasteur-

ized at 63–65° C. on two or even three successive days) was insufficient to inhibit this change in orange juice.

The temperature of pasteurization is an important factor in the flavor of the juice. Temperatures below 60° C. were insufficient to prevent the development of the spores of *Willia*, and with subsequent fermentation, while at temperatures above 70° C., the flavor began to be noticeably that of cooked juice, and lacked the freshness of the untreated product. Pasteurization at 63–65° C., for 15 minutes, provided the entire volume of the juice reached that temperature, gave the most satisfactory results, so far as flavor was concerned. Sterilizing at 100° C., and autoclaving at pressure are out of the question when preservation of the natural flavor is to be considered; autoclaving without the replacement of the air by a non-oxidizing atmosphere usually caused immediate darkening, in addition to the deterioration of flavor.

For the best flavor it was found that all of the fruit should not be peeled before expressing the juice; the juice from all peeled fruit was flat and uninviting, but if five to ten per cent of the oranges were left unpeeled, the juice had about the correct flavor. Of course, the addition of the expressed oil from the peel is possible, but experiments indicated that this did not give as satisfactory a flavor as the retention of unpeeled fruit in the lot to be pressed. For grapefruit juice, it was found necessary to peel completely all the fruit, and to supply the flavoring by adding five to ten per cent of unpeeled oranges; retention of the grapefruit peels produced a liquid of extreme bitterness.

The clarification of the juice is a serious problem. For commercial purposes it would seem best that the juice be nearly clear, although this is not a natural condition for orange juice. The juice, however, does not yield readily to the ordinary methods of clarification or filtration; of many methods tried, the best results were obtained with DeLaval clarifiers, the juice being taken first through a clarifying bowl to remove the greater part of the suspension, and then through a filtering centrifuge. The liquid so obtained is not water-clear, but contains comparatively little suspension. An alternate procedure is to pasteurize out of contact with the air in large containers, and allow to settle, then draw off the clear supernatant liquid after several weeks, bottle like fresh juice, and treat the residue by centrifugal methods. Chemical clarification by means of formaldehyde or alcohol is possible, but obviously not desirable.

Both orange and grapefruit juices may be evaporated under conditions of greatly reduced pressure, to a thick sirup, and this sirup may, in either case, be dried to a brittle, glassy, and very hygroscopic solid. It is essential for the retention of a good flavor, however, that the temperature in these evaporation and drying processes shall at no time exceed 60° C., which condition makes the drying extremely slow. The products so obtained may be dissolved in water, and beverages thus made up from them; it cannot be said that



the flavor of these beverages is quite up to the standard of fresh juice preserved as above indicated, but it is still quite close to the normal taste of orange juice, if the evaporation has been carefully done. Of course, the vacuum treatment removes the flavoring materials from the juice, and it is necessary to add oil for flavoring purposes, better at the time of making the beverage than before pasteurization in the vessel. The concentrated juice will keep under the same conditions as the fresh, *i. e.*, after pasteurization in the absence of free oxygen; the dried material cannot be pasteurized, as it fuses together at pasteurizing temperatures, but pasteurization is not necessary, provided water and air are excluded.

There is a considerable literature, especially of patents, regarding the preservation of fruit juices, but it is thought inexpedient to include any of these references in this abstract.

The recovery of the flavoring oils from the peels of citrus fruits is at present carried on mainly by rather crude methods in Italy and Sicily, under conditions of cheap labor with which American packers cannot compete. A process for recovering this valuable oil from the peels of Florida oranges must therefore be one which will handle a large number of peels at very little cost. Various mechanical methods of pressing, rolling, abrading, etc., were tried without much promise of success. Soaking methods, in which the ground peel is covered with water, to the surface of which the oil rises and is there drawn off, gave low yields of fair quality oil, but while simple, these processes are rather inefficient. After considerable experimentation it was found that a very satisfactory oil could be produced by grinding the peel, submitting the ground material to a current of water vapor at greatly reduced pressure and condensing and separating the oil. Ordinary Florida oranges yielded about 0.5 cc. of oil per peel, while the late Valencias gave from 1 to 1.5 cc. per peel. The liberation of the oil appears to be favored by previous partial drying of the peel. The oil obtained from Florida oranges as above indicated, has been used repeatedly in cakes and candies, when dissolved in alcohol, and has given excellent results. It appears to be up to the requirements of the existing legislation.

As is well known, the flavoring oils from citrus fruits rapidly deteriorate on exposure to the air, especially in the light, acquiring a very offensive turpentine-like odor. It was found during this research that this could be obviated by the addition to the oil of about 10 per cent by volume of absolute alcohol; oil so treated was allowed to stand exposed to diffused daylight at room temperatures for many months, without deterioration. It is not to be recommended, however, that such oils be kept under these conditions; keeping in the dark in a cool place is far better, even with protecting agents present. The use of 1.5 to 2 per cent of olive oil has also been recommended for this purpose; this gives some protection, but is not as good as the alcohol. Sealing in an atmosphere of carbon dioxide is also effective in protect-

ing the oil for a long time. On the whole, however, the addition of absolute alcohol gave the best results, and it seems that it would be well to admit of this treatment of such oils for their preservation in the United States Pharmacopoeia and other standards.

The recovery of the citric acid from the juice of Florida citrus fruits (for the sake of the acid alone) is scarcely worth while, in view of the small amount available, rarely over 0.7 per cent in the orange, or 1.5 per cent in the grapefruit. As a matter of scientific interest, however, it was found that *Wehmer's Citromyces* molds would grow on the sterilized juice in the presence of calcium carbonate, and convert a considerable proportion of the residual sugar into citric acid. The commercial application of such a process seems rather hypothetical.

From the results of this investigation it appears, then, that the preservation of the juice of the orange and grapefruit is practicable, the method depending on pasteurization out of contact with air, and that the recovery of the flavoring oil from the peels may be accomplished commercially by methods of vacuum distillation, but that the recovery of the citric acid for itself alone is not practicable.

Since this abstract was prepared, a valuable and interesting paper by Will<sup>1</sup> has appeared, relating to the utilization of these culls in the California citrus industry.

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## ON THE CHEMICAL CONSTITUTION OF THE PROTEINS OF WHEAT FLOUR AND ITS RELATION TO BAKING STRENGTH

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### INTRODUCTION

The most generally accepted definition of "baking strength" of a wheat flour is that put forward by Humphries and Biffen,<sup>2</sup> in 1907, which states that a "strong wheat is one which yields flour capable of making large, well-piled loaves;" a definition similar to that of Jago,<sup>3</sup> who states that "strength..... is defined as the measure of the capacity of the flour for producing a bold, large-volumed, well-risen loaf." Since the value of wheat (other things being equal) depends on the so-called "strength" of the flour which may be made from it, it is obviously of great importance that complete knowledge be obtained concerning the factors which cause strength, and to this end an enormous amount of scientific work has been done, especially during the last twenty years. In spite of the fact that some of the foremost investigators of the world have bent their energies to this task, the problem is not yet completely solved, although considerable light has been thrown on the subject. It is not yet possible to correlate baking strength with any chemical or physical factor to such an extent that a simple laboratory test or group of tests will always

<sup>1</sup> THIS JOURNAL, 8 (1916), 78-86.

<sup>2</sup> "The Improvement of English Wheat," *Jour. Agr. Sci.*, 2 (1907), 1-16.

<sup>3</sup> "Technology of Bread Making," Chap. XV, p. 291, 1911.

furnish an infallible guide, but it is necessary to mill the wheat into flour and have a sample of it actually baked into a loaf of bread by an expert baker, before its strength can be accurately ascertained.

#### FACTORS WHICH MAY INFLUENCE BAKING STRENGTH

Almost every known constituent, or group of constituents, and almost every known physical and chemical property of flour has been investigated with respect to its possible relation to baking strength, but as yet no one is believed to have discovered a limiting factor or group of factors which completely solves the problem. Moreover, there is a general disagreement among many of the leading investigators as to the importance which should be attached to each factor or set of factors, and two workers frequently have arrived at exactly opposite conclusions after having investigated practically the same problem; however, much of this confusion is caused by the use of different methods of analysis.

A brief review of some of the more important work which has been done will serve to bear out the preceding statement, as well as to indicate the many sides from which the question of flour strength has been studied.

**GLIADIN-GLUTENIN RATIO**—As soon as Osborne and Voorhees,<sup>1</sup> in 1893, established the composition and properties of the wheat proteins, attention was attracted to gliadin and glutenin, the two conspicuous and characteristic proteins of wheat, which were shown to make up the gluten, the more or less elastic binding material which enables flour to be made into the dough with its characteristic elastic, gas-retaining property, and which may be separated from the starch and soluble proteins by the well-known process of washing the dough in a stream of water. Fleurent,<sup>2</sup> in 1896, claimed that flour strength depends on the proportion of gliadin to glutenin present in the gluten of the flour. He concluded from his experiments that the optimum ratio was 75 parts of gliadin to 25 of glutenin or 3:1. He assigned certain limits, outside of which flours were said to be of poor baking quality. Snyder,<sup>3</sup> in 1899, published similar results, although he fixed his ideal ratio at 65:35. He also states<sup>4</sup> that the quality rather than the quantity of gluten is the important factor, because he was able to add up to 20 per cent starch to flour without decreasing its baking quality. Regarding the quantity of gluten in flour, the amount of gliadin present, the ratio of gliadin to glutenin, and the relation of these to baking quality, it suffices to say that the results of different investigators quite frequently are not concordant. However, as mentioned before, this is in a considerable measure due to different analytical methods employed by different workers.

**CRUDE GLUTEN**—The crude gluten determination, which consists essentially of washing the gluten free

from starch and soluble material by means of water, and weighing the gluten, both in a wet and dry state, was for a long time considered of great value, but Snyder and Norton,<sup>1</sup> in 1906, Chamberlain,<sup>2</sup> in 1906, and others showed that it gave but little information which might not be gained from a determination of total nitrogen or alcohol-soluble nitrogen. Nevertheless, it is still used extensively by millers and bakers, and in technical laboratories.

#### PHYSICAL STATE OF GLUTEN AND SUGAR CONTENT

In 1907, Wood<sup>3</sup> published the results of a thorough and systematic study of the chemistry of flour strength. He concluded that there is no difference in the chemical constitution of gliadin and glutenin from strong and weak flours, and decided that strength (particularly shape of loaf) is much more closely related to the physical state of gluten, which in turn is profoundly affected by the presence of electrolytes. He showed that minute quantities of acids and bases tend to "disperse" gluten, making it weak and inelastic, while small quantities of neutral salts have the opposite and consequently beneficial effect. Furthermore, he found that the volume of a loaf of bread is proportional to the rate of carbon dioxide evolution resulting from diastatic activity of yeast in the later stages of fermentation. In other words, he concludes that loaf volume depends on the amount of available sugar in the later stages of fermentation. Alway and Hartzell,<sup>4</sup> in 1909, however, performed experiments which led them to say, in contrast to Wood's findings, "there is clearly no direct connection shown between the size of the loaf and the volume of gas evolved. The thirteen flours which gave the largest loaves evolved on the average somewhat less gas than the other thirteen flours." Shutt<sup>5</sup> states that from his experimental evidence he was unable to find any relation between size of loaf and sugar content.

**ENZYMES**—Comparatively less study has been made of the enzymes of flour and their relation to strength. Perhaps the most prominent work in this field is that which was done simultaneously but independently by Baker and Hulton,<sup>6</sup> and by Ford and Guthrie,<sup>7</sup> in 1908. They point out that both proteoclastic and amyloclastic enzymes are present in flour and in many instances may exert a profound influence on its bread-making qualities. Baker and Hulton state that "it is obvious that the strength of a flour must be closely connected with the gluten, although no doubt the presence of enzymes, soluble carbohydrates, and mineral constituents all play a part." Koch,<sup>8</sup> in 1914, found no difference in the quantity of diastase in strong and weak flours, after extracting them with

<sup>1</sup> "Crude Gluten," *J. Am. Chem. Soc.*, **28** (1906), 8-25.

<sup>2</sup> "Properties of Wheat Proteins," *Ibid.*, **28** (1906), 1657-1667.

<sup>3</sup> "The Chemistry of Strength of Wheat Flour," *Jour. Agr. Sci.*, **2** (1907), 139-161 and 267-277.

<sup>4</sup> Neb. Exp. Sta., 23rd Annual Report, 1909.

<sup>5</sup> "Flour—The Relationship of Composition to Bread Making Value," *Canadian Miller and Cerealst*, **5** (1913), 176-178.

<sup>6</sup> "Conditions Affecting the Strength of Wheaten Flour," *Jour. Soc. Chem. Ind.*, **27** (1908), 368-376.

<sup>7</sup> "The Amyolytic and Proteolytic Ferments of Wheaten Flour and Relation to Baking Value," *Jour. Soc. Chem. Ind.*, **27** (1908), 389-393.

<sup>8</sup> "The Diastase and Invertase Content of Wheat Flour and Their Relation to Baking Strength," Thesis for Master's Degree, University of Minnesota, June, 1914.

<sup>1</sup> "The Proteids of the Wheat Kernel," *Am. Chem. J.*, **15** (1893), 392-471; *Ibid.*, **16** (1894), 524-535.

<sup>2</sup> "Sur une method chimique d'appréciation de la valeur boulangere des farines de blé," *Compt. rend.*, **123** (1896), 755-758.

<sup>3</sup> *Minn. Exp. Sta. Bull.*, **63** (1899).

<sup>4</sup> U. S. Dept. Agr., *Bull.* **101** (1901).



water at 0° according to the method of Thatcher and Koch.<sup>1</sup>

**CONCENTRATION OF HYDROGEN IONS**—H. Jessen-Hansen,<sup>2</sup> in 1911, finds a close relationship between the concentration in hydrogen ions and baking strength, and asserts that there is an optimum hydrogen-ion concentration for flour, the poorer flours having lower concentrations. He attributes the beneficial effects of neutral salts and "flour improvers" on flour to the fact that they raise the hydrogen ion concentration.

**SOLUBLE PROTEINS**—There does not seem to have been a very considerable amount of work done regarding the rôle of the soluble proteins as a factor in baking strength. Snyder,<sup>3</sup> in 1897, says "When any of the wheat proteids except gliadin or glutenin are extracted the expanding and bread-making qualities of the flour are not affected." The conclusions of Bremer,<sup>4</sup> in 1907, are also to the effect that the soluble proteins have little bearing on flour strength. Rousseaux and Sirot,<sup>5</sup> in 1913, consider the ratio of total nitrogen to soluble nitrogen as a valuable index to baking value and have determined an ideal ratio for flours according to their method, as well as the limits between which strong flours must fall in this respect.

**GENERAL CONSIDERATIONS**—Numerous other results of careful and valuable research might be cited, but the above serve to indicate the confusion existing in the present state of our knowledge regarding the factors involved in flour strength, and is intended to serve this purpose rather than constitute anything like a complete summary of all the work which has been done in this field. Numerous summaries of this sort have been published in text-books and articles dealing with methods of milling and baking technology, such as that of the Jagos,<sup>6</sup> and a repetition of them here would serve no useful purpose. It is believed, moreover, that the above discussion indicates nearly all of the view-points from which the problem of the chemistry of flour strength has been attacked. The situation is very well expressed by Bailey<sup>7</sup> when he says: "Perhaps one of the reasons that a greater degree of success has not attended these endeavors is the fact that it has been attempted to discover one constituent (or group of constituents) which is the sole determining factor. It does not seem reasonable to believe that in so complex a substance as wheat flour the percentage of one constituent can be regarded as solely indicative of baking quality. Rather must we study these various compounds in their relation to one another, in an effort to arrive at their single and combined effects."

<sup>1</sup> "The Quantitative Extraction of Diastases from Plant Tissues," *J. Am. Chem. Soc.*, **36** (1914), 759-770.

<sup>2</sup> "Studies on Wheat Flour. Influence of H-ion Concentration on Baking Value of Flour," *Compt. rend.*, **10** (1911), 170-206.

<sup>3</sup> *Minn. Exp. Sta. Bull.*, **54** (1897).

<sup>4</sup> "Hat der gehalt des Weizenmehls an Wasserlöslichen Stickstoff einer Einfluss auf seiner Backwert?" *Ztschr. Unter. Nahr. Genuss.*, **13** (1907), 69-74.

<sup>5</sup> "Les matières azotées solubles comme facteur d'appréciation des farines," *Compt. rend. Acad. Sci.*, **166** (1913), 723-725.

<sup>6</sup> *Loc. cit.*

<sup>7</sup> "Relation of the Composition of Flour to Baking Quality," *Canadian Miller and Cerealists*, **5** (1913), 208-209.

#### PURPOSE OF THIS INVESTIGATION

In a series of investigations of the various factors which may influence the strength of wheat flour, now in progress in the Division of Agricultural Chemistry of the University of Minnesota, it was proposed to study the chemical constitution of the various proteins in flour with a view toward ascertaining more definitely than has yet been done, whether or not the proteins of a strong flour may differ in their chemical constitution from those of a weak flour, since the physical properties of their glutens are found to differ so markedly.

Wood,<sup>1</sup> in 1907, following Osborne and Harris' modification of Hausmann's method, subjected samples of gliadin and crude gluten (composed chiefly of gliadin and glutenin) of flours of different strength, to hydrolysis for 8 hours with strong hydrochloric acid. He then steam-distilled the products of hydrolysis with magnesia and determined the percentage of nitrogen given off as ammonia. Finding a close agreement in the different samples he concluded that gliadin and glutenin of all wheat flours are of the same chemical composition. Since the work of Wood,<sup>1</sup> a more detailed method of protein analysis, which gives further insight into the constitution of the protein molecule and is capable of yielding quantitative results, has been presented by Van Slyke,<sup>2</sup> who has incidentally shown that the hydrolysis of gliadin with strong hydrochloric acid is not complete at the end of 8 hours. It was therefore decided to make further study of the chemical constitution of flour proteins in the light of better methods of analysis now available.

#### METHODS OF STUDYING CHEMICAL COMPOSITION OF PROTEINS

It has been shown repeatedly that for practical considerations all of the nitrogen of flours of the higher milling grades may be regarded as in the proteins. The chemical structure of the proteins has been clearly demonstrated by Fischer<sup>3</sup> and a host of other workers since, so that it needs no elaborate discussion here. Briefly stated, the facts appear to be that the protein molecule is made up of a number of amino acids, there being some 18 or 20 of these which occur in natural proteins. These are probably linked together by anhydride combinations between the amino group of one amino acid and the carboxyl group of another. This is indicated by the nature of the products formed (amino acids) when the protein is subjected to hydrolysis. Moreover, it appears that the characteristic chemical and physical nature of individual proteins depends largely on the nature and number of the various amino acids of which they are composed. In a comparison of the chemical constitution of proteins, then, it is necessary to split the molecule by hydrolysis into its "bausteine" (characteristic units) and determine the relative proportions of these which are formed in each case. There is no known method of ascertaining

<sup>1</sup> *Loc. cit.*

<sup>2</sup> "The Analysis of Proteins by the Determination of the Chemical Groups Characteristic of the Different Amino Acids," *J. Biol. Chem.*, **10** (1911), 15-55.

<sup>3</sup> "Untersuchungen über Aminosäuren, Polypeptide und Proteine," Berlin, 1899-1906.

the exact manner in which these units are grouped together in the various proteins, since even the sensitive anaphylaxis reaction is not specific in the case of many vegetable proteins, as has been demonstrated by Wells and Osborne,<sup>1</sup> who found that animals sensitized with gliadin of either wheat or rye will react with hordein of barley, a protein known to have a different chemical constitution, and that gliadin and glutenin, known to be different as regards the relative proportions of the various amino acids in their molecule, react anaphylactically with each other.

#### METHOD USED IN DETERMINING PRODUCTS OF PROTEIN HYDROLYSIS

Van Slyke's method gives the most detailed insight into the protein molecule of any known method which, at the same time, indicates quantitatively the distribution of its component units. Accordingly, the Van Slyke method, in some cases slightly modified, was used in this investigation. The method, which is an extension of the principle of the Hausmann method, consists of a division of the protein molecule into various groups, or units, after prolonged hydrolysis with hydrochloric acid, and the determination of the percentage of nitrogen in each individual group, thus ascertaining the distribution of the total nitrogen in the protein. Briefly, the groups determined are: (1) ammonia or amide nitrogen, which is considered

work. Their sources and relative baking values, as measured by loaf volume, are indicated in Table I.

#### THE PRODUCTS OF PROTEIN HYDROLYSIS FROM ENTIRE FLOUR

Osborne<sup>1</sup> and his associates have shown that there are five proteins present in flour, *viz.*, gliadin, glutenin, albumin, globulin and proteose, the latter being of little significance. The first two named compose the gluten, already referred to, while the others are soluble in dilute salt solutions and are, for the most part, removed in the familiar process of "washing out" the gluten.

Since the proteins are, for all practical considerations, the only nitrogen compounds in the higher grade flours, it was decided to submit first, in all cases, a sample of the entire flour to prolonged hydrolysis with strong hydrochloric acid, and determine the distribution of nitrogen in the various units. Should the results vary in different flours, it would be necessary to obtain the different proteins and ascertain their composition in a similar manner. If they should show the same chemical constitution then they must be present in the flour in varying amounts to account for the difference when analyzed collectively, as is done in the hydrolysis of the entire flour. That the latter is true has, of course, been concluded by numerous investigators who have extracted flour proteins with specific

TABLE I—DISTRIBUTION OF NITROGEN IN THE PRODUCTS OF HYDROLYSIS OF ENTIRE FLOURS

Sample No.	FLOUR	SOURCE	BAKING STRENGTH Loaf volume	TOTAL N Per cent	PER CENT OF TOTAL NITROGEN			
					Ammonia N	Humin N	Basic N	Mono-amino acid N
B401	Pillsbury Patent	Northern Spring Wheat	Good	2.035	20.81	5.32	8.10	65.77
B438	Patent Biscuit Flour	Soft Missouri Wheat	Poor	1.67	18.85	5.62	9.25	65.65
B439	Patent Flour	Nebraska Turkey Wheat	Good	1.928	21.01	4.92	8.56	65.51
B440	Patent Flour	Hard Wheat, Prosser, Washington	Medium	2.170	21.47	5.00	7.88	65.65
B441	High Gluten, Low Strength Flour	North Dakota Wheat	Poor	2.13	21.03	5.16	8.74	65.07
B444	Very High Gluten Flour	Kansas Experiment Station	Medium	2.55	23.00	5.42	7.08	64.50
B445	"Fortyfold" Soft White Wheat	Troy, Idaho	Very Poor	1.260	18.21	7.51	9.00	65.28
B452	Patent Flour	Ritzville, Washington	Poor	1.917	19.87	5.63	8.03	66.47

to be derived from  $-\text{CONH}_2$  or  $-\text{CONHOC}-$  groups linked to the carboxyl groups of the dicarboxylic acids in the protein molecule (glutamic and aspartic acids); (2) humin nitrogen, from the dark-colored pigment and slight amount of insoluble matter always formed in the hydrolytic products of acid hydrolysis of proteins; (3) the amino nitrogen of the mono-amino acids, which corresponds to all of the mono-amino acids excepting proline and oxy-proline; (4) the non-amino nitrogen of the mono-amino acids, which corresponds to the proline and oxy-proline; and (5) to (8) the nitrogen corresponding to each of the individual di-amino acids, *i. e.*, arginine, lysine, histidine, and cystine, respectively. Thus, eight units of the protein molecule may be estimated quantitatively, the determination of histidine nitrogen and lysine nitrogen being subject to a larger experimental error than the other units, which may be determined with the exactness required by ordinary quantitative procedure.

#### FLOURS USED IN THE INVESTIGATION

Eight flours of the higher grades (as separated in the process of milling) from various sources and of varying baking qualities were selected for the preliminary

solvents and have found their amounts to vary widely in different flours. The solvents most frequently used are: (1) alcohol—varying from 50 to 80 per cent, and (2) neutral salt solutions of different concentrations. The former was at first thought to extract only gliadin while the latter was considered to remove only albumin, globulin and proteose. Owing to the fact that solutions of varying strengths and different methods of extraction have been employed by different investigators, however, their results often disagree widely, and in many cases even fail to support the same general conclusions. Furthermore, it has been found that the solvents mentioned above are not as specific as was formerly supposed, and that alcohol extracts not only gliadin but also considerable of the "soluble proteins," the material so extracted depending on the strength of the alcohol, while salt solutions extract some gliadin as well as albumin and globulin, according to the concentration of the solution. Other physico-chemical factors undoubtedly enter as well. Olson<sup>2</sup> states that "the amount of gliadin extracted by 1 per cent sodium chloride solution approximately amounts to about 29 per cent of the total proteids," and "the nitrogen

<sup>1</sup> "Is the Specificity of the Anaphylaxis Reaction Dependent on the Chemical Constitution of the Proteins or on Their Biological Relations? The Biological Reactions of the Vegetable Proteins. II," *Jour. Infect. Dis.*, 12 (1913), 341-358.

<sup>1</sup> "The Vegetable Proteins" (1912), Plimmer's, Monograph, London, New York, etc.

<sup>2</sup> "Quantitative Estimation of Salt-Soluble Proteins in Wheat Flour," *This Journal*, 6 (1914), 212.



bodies soluble in salt solution are partly or wholly soluble in diluted alcohols varying with the concentration of sodium chloride used." That a study of the products of hydrolysis of the flour proteins both collectively and individually can furnish an indication of the proportions of these proteins in the flour, providing there is no difference in the chemical constitution of the same proteins in different flours, is evident from the following considerations: the percentage of ammonia nitrogen yielded on the hydrolysis of the individual proteins of wheat flour varies as follows, according to Osborne, gliadin 24.5, glutenin 18.8, leucosin (albumin of flour) 6.8, and globulin, 7.7. Since the figures for the ammonia nitrogen show wider variation than do those of any other units, and since also the estimation of this unit is probably accompanied by less error than that of any of the others, it may be supposed that its estimation in the proteins taken collectively and individually will indicate closely the relative amounts of the various proteins present, providing, as mentioned before, the same proteins of different flours do not vary in their chemical constitution.

In determining the distribution of nitrogen in the entire flour, 10-gram samples were hydrolyzed for 48 hours, and the "Hausmann" units determined. In the case of the entire flour the presence of a large amount of starch occasions a voluminous precipitate of "humin" material which made it impractical to attempt a determination of all the units of the Van Slyke method, since a large enough sample could not be used to insure the estimation of the smaller units with sufficient accuracy that the figures would be of much significance. The instructions of Van Slyke regarding the conditions for precipitating and washing the bases, however, were carefully followed.

In determining the total nitrogen in the hydrolyzed mixture, the presence of large amounts of "humin" substances resulting from the carbohydrates, and small amounts of fat, necessitated the slight modification of Van Slyke's method suggested by Gortner.<sup>1</sup> The above mentioned substances make it impossible to obtain an aliquot until after they have been removed in the processes of determining the ammonia and humin nitrogen. Consequently, the hydrolyzed mixture is evaporated *in vacuo* to remove most of the hydrochloric acid. The ammonia is distilled off as in the Van Slyke process (without removing the material from the distillation flask from which the acid was evaporated off), collected in standard acid, and estimated by titration; the humin filtered, washed, and submitted to Kjeldahl analysis for nitrogen, and total nitrogen determined in aliquot portions of the filtrate from the humin. This, added to the ammonia nitrogen and the humin nitrogen, gives the total nitrogen in the hydrolyzed sample. No correction was made in any of the analyses for the solubilities of the bases in the solutions from which they were precipitated, since the same conditions were observed in all cases and the results are strictly comparable.

The results given in Table I were obtained from the analyses of the eight samples of flour by the above-described process. The different flours vary significantly with respect to the ammonia nitrogen yielded on hydrolysis. The basic nitrogen or nitrogen of the diamino acids also shows a slight variation, this being inversely as the variation in ammonia nitrogen. The variations shown in the table are much greater than could possibly be due to experimental error and were confirmed by repeated determinations. Hence, there can be no doubt that these variations show actual characteristic differences in the nitrogen distribution in the different samples.

#### THE DISTRIBUTION OF NITROGEN IN GLIADIN, GLUTENIN, AND SOLUBLE PROTEINS

Hydrolysis of the entire flour having shown characteristic differences in the composition of the entire protein material contained in them, it appeared to be necessary to establish as definitely as possible whether or not the chemical constitution of the various individual proteins is the same in different flours. For this purpose two flours which differed widely in their origin, total nitrogen content, and baking strength were selected. Flour B401 is a typical Minnesota patent flour, milled from northern spring wheat, of fairly high nitrogen content and of good baking strength, while B438 is a patent biscuit flour, made from a softer Missouri wheat, low in total nitrogen and of poor baking strength. Gliadin was extracted from the gluten of the flours with alcohol and carefully purified by pouring the concentrated syrup from the clear alcoholic extract alternately into large volumes of water and strong alcohol and finally digesting with absolute alcohol and ether, according to the method of Osborne. Glutenin was also prepared according to Osborne's method which consists, briefly, of dissolving the residue left after the alcohol extraction of the crude gluten in a dilute solution of potassium hydroxide, neutralizing with hydrochloric acid to precipitate the glutenin, decanting the liquid and further extracting the precipitate repeatedly with alcohol to remove the remaining gliadin; finally digesting with absolute alcohol and ether. The preparations of glutenin in this work were not pure, being contaminated by small quantities of carbohydrates, owing to lack of facilities for obtaining clear extracts and filtrates at the time, but it is believed that all other nitrogen-containing bodies were removed, and that the preparations served the purpose of the investigation, namely, to ascertain whether there was any appreciable difference in the chemical constitution of the pure proteins. Considerable quantities of each of the two flours were then extracted with 1 per cent salt solution, the extracts were filtered as clear as possible and concentrated *in vacuo*. These extracts and weighed quantities of the gliadin and glutenin were then hydrolyzed for 48 hours with strong HCl. The gliadin and glutenin were analyzed according to the Van Slyke method, while only ammonia nitrogen was determined in the case of the soluble proteins. From the results shown in Table II (1, 2, and 3) it is readily seen that, after making allowance for the limits of experimental error

<sup>1</sup> "Studies on the Chemistry of Embryonic Growth. I. Certain Changes in the Nitrogen Ratios of Developing Trout Eggs," *J. Am. Chem. Soc.*, **35** (1913), 632-645.

of the method, there is no apparent difference in the chemical constitution of the proteins of typical strong and weak flours of the same market grade.

THE DISTRIBUTION OF NITROGEN IN CRUDE GLUTEN

More complete evidence that the gluten-forming proteins are of the same chemical constitution in different flours was obtained by analyzing thoroughly washed crude glutens of three flours of widely differing characteristics. The same two flours as in the immediately preceding experiments were used, and in addition, B444, a Kansas flour of exceedingly high nitrogen and gluten content, but of low baking strength, as shown in Table I. The results, obtained from the complete Van Slyke process as applied to the crude glutens from these three flours, appear in Table II (4) and indicate

TABLE II—DISTRIBUTION OF NITROGEN IN THE PROTEINS OF TYPICAL STRONG AND WEAK FLOURS

UNITS DETERMINED	(1) In the Gliadin Van Slyke's Method		(2) In the Glutenin Van Slyke's Method		(4) In Crude Glutens			
	PER CENT OF TOTAL N		PER CENT OF TOTAL N		PER CENT OF TOTAL N			
	B401 (Strong)	B438 (Weak)	B401 (Strong)	B438 (Weak)	B401 (Strong)	B438 (Weak)	B444 (Weak)	
Ammonia N.....	26.13	25.90	16.50	16.17	22.87	23.19	23.69	
Humin N.....	0.50	0.57	1.84	1.66	1.19	1.37	1.11	
Cystine N.....	0.37	0.29	0.18	0.18	0.46	0.70	0.43	
Arginine N.....	4.55	4.47	9.69	9.27	5.24	5.54	5.54	
Histidine N.....	6.77	5.62	5.47	7.59	2.79	1.28	1.50	
Lysine N.....	0.65	0.97	2.61	1.90	2.21	2.60	2.28	
In Filtrate from Bases:								
Amino N.....	53.46	54.10	53.59	53.38	55.21	56.15	55.14	
Non-amino N.....	7.44	7.55	9.52	9.35	9.54	9.88	10.13	
TOTAL.....	99.97	99.47	99.40	99.50	99.51	100.71	99.82	
			B401	B438				
			12.68	12.84				

(3)—Ammonia Nitrogen Yielded on Hydrolysis of the Soluble Protein.....

that not only are the gluten-forming proteins in flours of widely differing baking qualities of the same chemical constitution, but the ratio of gliadin to glutenin is probably the same, or very nearly so, in flours of the same market grade but very different baking strengths. With respect to this latter point, it may be said that since, as is shown above, gliadin yields 26 per cent of its nitrogen as ammonia nitrogen after hydrolysis, while glutenin yields only 16 per cent of its nitrogen in this fraction, the determination of ammonia nitrogen of the hydrolyzed glutens will certainly indicate any significant variation in the ratio of gliadin to glutenin in different flours, although the limits of experimental error are not narrow enough to indicate very small variations in this ratio. The data in Table II (4) indicate very clearly, therefore, that there is no significant variation in the gliadin-glutenin ratio in flours of such widely varying baking strength as those used in this investigation.

THE SIGNIFICANCE OF THE SOLUBLE PROTEINS IN AFFECTING THE NITROGEN DISTRIBUTION IN FLOUR

It is evident that the differences in the percentages of ammonia nitrogen and basic nitrogen yielded on the hydrolysis of the several entire flours, as shown in Table I, cannot be accounted for as being due to differences in chemical composition of the individual proteins since it has been clearly shown that these have the same chemical constitution.

It was thought at first that the varying percentages of starch in the different flours might cause differences in the percentage of ammonia nitrogen, since Mann,<sup>1</sup> in 1906, states "if in addition to the carbohydrate, ammonia or other nitrogenous substances are in solu-

tion, then the humins combine with the ammonia and thereby become nitrogenous." In order to ascertain whether varying proportions of starch would influence the results obtained by the Van Slyke method as used in these investigations, a sample of the flour B401, to which had previously been added 20 per cent of its weight of wheat starch, was hydrolyzed and the distribution of nitrogen in the products of hydrolysis determined. There was no significant change in the percentage of ammonia nitrogen when compared with the sample to which no starch was added, although there was a very noticeable increase in humin N and a corresponding decrease in basic N, as shown in Table III.

Further, it has recently been shown by Gortner and

Blish<sup>1</sup> that other carbohydrates than starch which might be present in flour do not affect the percentage of ammonia nitrogen obtained after hydrolysis, although they may, in many instances, increase the humin nitrogen by forming condensation products of humin-like nature with tryptophane.

The significant variation in the percentages of ammonia nitrogen in the different flours (Table I) must therefore be due to considerable variations in the amounts of soluble proteins present, since the gliadin-glutenin ratio does not differ enough to account for

TABLE III—EFFECT OF STARCH ON THE DISTRIBUTION OF NITROGEN IN THE PRODUCTS OF HYDROLYSIS OF FLOUR B401

MATERIAL USED	Per cent of the total nitrogen			
	Ammonia N	Humin N	Basic N	Mono-amino acid N
B401.....	20.81	5.32	8.10	65.77
B401 + 2 g. Starch.....	21.05	6.38	6.95	65.62

the difference in the percentages of ammonia nitrogen. As already shown, the "soluble proteins" (albumin and globulin) yield respectively 6.8 per cent and 7.7 per cent of ammonia nitrogen on hydrolysis, while the gluten yields about 23 per cent. It may be calculated, therefore, that flours containing the larger amounts of "soluble proteins" will yield the smaller percentages of their total nitrogen as ammonia nitrogen after hydrolysis. Accordingly, the flours showing the lower ammonia nitrogen figures as shown in Table I might be supposed to contain the larger percentages of their proteins in the form of albumin and globulin. Since there is no known method of quantitatively estimating the albumin and globulin in flour, owing to the fact that the extraction of the various proteins

<sup>1</sup>"On the Origin of the Humin Formed by the Acid Hydrolysis of Proteins," *J. Am. Chem. Soc.*, **37** (1915).

<sup>1</sup>"Chemistry of the Proteids," New York, 1906.



varies with the concentration of the solvents employed, the proportions of solvent to material extracted, and possibly other physico-chemical factors, the determination of ammonia nitrogen in hydrolyzed flour, flour extracts, and gluten should form a basis for a more exact knowledge of the proportions in which the various proteins occur in flours. Such methods are obviously unadapted to ordinary analytical use, but afford the best possible method of exact study and careful investigational work. For example, in Table II (3), the per cent of ammonia nitrogen yielded on hydrolysis of the extract with 1 per cent salt solution indicates clearly that protein other than albumin and globulin was extracted, since, as already pointed out, the per cent of ammonia nitrogen yielded by pure albumin and globulin should be lower. It is suggested also that to ascertain how much albumin and globulin are extracted by alcohol of any given percentage it should suffice to hydrolyze the alcoholic extract and determine the percentage of ammonia nitrogen in a similar manner.

Since this article has been in press, the results of a study of the purity of proteins extracted from flour by various solvents, using methods here indicated, have been published by Bailey and Blish.<sup>1</sup>

In order to substantiate the evidence that there is a relation between the ammonia nitrogen yielded on hydrolysis of flour, and the total quantity of soluble proteins in the flours in question, the latter were extracted with tap water (since it was thought desirable to use the same solvent as was used in washing out the glutes) and the percentage of "soluble nitrogen" in the total nitrogen of the flour estimated in the extract. Although protein material other than globulin and albumin is extracted in this process, the results should be comparative, and in the order as indicated above, that is to say, the previously indicated relationship between ammonia nitrogen of the hydrolyzed entire flour and the soluble nitrogen should be apparent. That this is true is indicated by the results obtained, as shown in Table IV.

TABLE IV—COMPARISON OF PERCENTAGES OF SOLUBLE NITROGEN IN ENTIRE FLOUR WITH AMMONIA NITROGEN AFTER HYDROLYSIS OF ENTIRE FLOUR

Sample No.	TOTAL NITROGEN	Per cent of total N	
		Soluble N	Ammonia N
B444.....	2.55	15.68	23.00
B440.....	2.17	18.20	21.47
B439.....	1.928	18.67	21.01
B401.....	2.085	18.94	20.81
B452.....	1.917	19.55	19.87
B441.....	2.130	20.42	21.03
B438.....	1.67	26.86	18.85
B445.....	1.26	28.96	18.21

Inspection of Table IV shows that, with the single exception of B441, as the percentage of ammonia nitrogen increases, the percentage of soluble nitrogen decreases, as was expected from the theoretical considerations already discussed.

#### CONCLUSIONS

I—The individual proteins of strong and weak flours are identical in their chemical constitution, as determined by Van Slyke's method for the analysis of proteins.

[Since this went to press, the attention of the writer

<sup>1</sup> "Concerning the Identity of the Proteins Extracted from Wheat Flour by the Usual Solvents," *J. Biol. Chem.*, **23** (1915), 345-357.

was called to a study of some of the physical constants of gliadin from flours of varying strengths, by Gróh and Friedl,<sup>1</sup> in which they conclude that proteins of different flours have the same constitution.]

II—The ratio of gliadin to glutenin is much more nearly constant in flours of different baking qualities than has heretofore been supposed.

III—There is a far greater variation in the percentages of the so-called "soluble proteins" (albumin and globulin) in flours.

IV—Since the various proteins in the same flour differ widely in their content of ammonia nitrogen, the determination of ammonia nitrogen in flours, in extracts of flours made with various solvents, and in the crude gluten of flours, after their previous complete hydrolysis with strong mineral acid, can be made to serve as an accurate indication of the amounts of the various proteins present, since the proteins of widely different flours have been shown to have the same chemical constitution.

Acknowledgment and sincere thanks are herewith extended to Professor R. W. Thatcher under whose supervision this work was done, also to Dr. R. A. Gortner and Professor C. H. Bailey for many valuable and helpful suggestions.

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#### THE ANALYSIS OF MAPLE PRODUCTS, V

##### Miscellaneous Observations on Maple Syrup Incidental to a Search for New Methods of Detecting Adulteration<sup>2</sup>

By J. F. SNELL  
Received August 20, 1915

In the course of a search for new and improved methods of detecting adulteration in maple syrup, the author and his associates have made a number of miscellaneous observations which may be suggestive or otherwise useful to other investigators in this line.

#### I—EFFECTS OF SOME REAGENTS

It is well known that lead subacetate produces a heavy precipitate in maple syrup and the normal acetate one not so heavy. In the "malic acid value" determination, alcohol and calcium chloride are employed together as precipitants. It appeared to the author not improbable that a systematic search would reveal other precipitating reagents whose behavior might prove equally useful in the examination of maple products. Mr. J. M. Scott made some desultory experiments in this direction and has recorded in his notes "indifferent" results with ether, zinc acetate, uranium acetate, cadmium chloride, bismuth nitrate, copper nitrate and cupric chloride. Mercuric acetate gave a flocculent precipitate which settled on standing and was light yellow in color. Silver nitrate in 50 per cent solution gave a white precipitate which darkened on standing. The author has also observed that barium salts give no precipitate in maple syrup although they do so in solutions of the

<sup>1</sup> *Biochem. Ztschr.*, **66** (1914), 154.

<sup>2</sup> Presented at the 51st Meeting of the American Chemical Society, Seattle, Aug. 31-Sept. 3, 1915. Previous papers of this series—*THIS JOURNAL*, **5** (1913), 740, 993; **6** (1914), 216, 301.

ash. Alcohol by itself gives a precipitate containing calcium, potassium and organic matter. By far the greater part of the total calcium and of the total potassium of the syrup are precipitated by the addition of a suitable quantity of alcohol. It was Mr. Scott's intention to investigate this alcohol precipitate further, but his removal to another position prevented his returning to the point.

## II—EXPERIMENTS WITH SILVER NITRATE

Silver nitrate having been found to give a decided precipitate in maple syrup and none in a syrup made from white sugar, it was thought that a "silver number" might be determined by a method analogous to the Winton method with lead subacetate. Mr. Scott made a number of experiments towards this end. The idea was to add an excess of a standard solution of silver nitrate, filter off the precipitate, determine the residual silver volumetrically, and calculate from the results a "silver number" representing the quantity of silver precipitated by 100 grams of the syrup (or, alternatively, by 100 grams of the dry matter of the syrup). It was found, however, that the longer the solution containing the excess of silver was allowed to stand (and standing appeared to be necessary to allow the precipitate to collect) the lower was the quantity of residual silver. In other words, precipitation of silver continued during a period of several hours. For example, in one series of experiments 50 cc.  $N/10$  silver nitrate were added to 25 cc. syrup and the mixture made up to 100 cc. Filtered 20 cc. aliquots, taken, respectively, after 1, 2, 4 and 6 hours, required the following quantities of  $N/10$  sodium chloride to precipitate the residual silver: 8.00 cc., 7.55 cc., 7.40 cc. and 7.20 cc.

It is conceivable that a method using silver nitrate might be worked out, but obviously this circumstance of a slow reaction in the solution resulting in the precipitation of silver would have to be taken into account. The slow reaction would appear to be worthy of study also for its theoretical interest. Has it any connection with the darkening of the precipitate? Is it a reduction? What constituent of maple syrup is it which reacts thus with silver nitrate?

Some experiments with a  $N/50$  silver nitrate solution, made by Mr. N. C. MacFarlane, are reported in Sections V and VI below.

## III—A LEAD SUBACETATE METHOD BASED ON THE WINTON AND CANADIAN METHODS

In Paper II of this series<sup>1</sup> reference was made to some experiments in which an endeavor was made to combine the advantages of the Canadian and the Winton methods of detecting adulteration of maple syrup by the use of lead subacetate.<sup>2</sup> The outcome of these experiments, made by Mr. Scott, was a method in which 25 grams syrup were treated with 10 cc.<sup>3</sup> of lead subacetate solution of sp. gr. 1.25, enough water added to bring the volume to 100 cc. and, after

standing three hours and filtering, a 10 cc. aliquot taken for determination of unprecipitated lead as in the Winton method. Comparison with a blank, using a syrup made from granulated sugar,<sup>1</sup> enabled one to calculate the amount of lead precipitated by 100 grams of the maple syrup. This quantity of lead was to be the "lead number" of the proposed method.

For comparison with the Canadian and Winton methods this proposed lead number was determined upon twenty of the syrups whose analysis was reported in Paper III<sup>2</sup>—viz., ten of those which gave high, and ten of those which gave low, Canadian and "modified" Winton lead values.<sup>3</sup> The values obtained by the projected method were in all instances lower than those given by the modified Winton method. The ranges of variation of the three lead numbers in these twenty syrups, expressed in percentage of the minimum, were found to be:

	Per cent
Canadian Lead Number .....	316(a)
Modified Winton Lead Number .....	190
Proposed Lead Number .....	200

(a) The syrup which gave the highest Canadian lead number was not included among the twenty. Hence the range of this value among the twenty syrups is a little smaller than that among the 126 reported in Paper III.

Inasmuch as the lead number determined by the original Winton method (using 25 grams syrup and not reducing to the dry basis) has a narrower general range of variation than the value obtained by reducing the results to the dry matter basis,<sup>4</sup> it appeared not improbable that if the comparison were made between the true Winton and the proposed method, the advantage in favor of the former would be more considerable than that in favor of the modified Winton number. Determination of the true Winton number upon nine of the twenty syrups corroborated this conjecture, the ranges of the values among these nine syrups being as follows:

	Per cent of minimum
Canadian Lead Number .....	192
Modified Winton Lead Number .....	149
Proposed Lead Number .....	149
True Winton Lead Number .....	119(a)

(a) This is exactly the same range of variation as is shown in McGill's analysis of 47 samples (see Paper III, Table VI, *Loc. cit.*, p. 221). Bryan's results on 481 samples showed a range only slightly higher, viz., 135 per cent (*Loc. cit.*). But if McGill's results and Bryan's are taken in conjunction, the true Winton value shows a range of 286 per cent of the minimum value. One cannot help suspecting, however, that there was some difference in manipulation in the two laboratories which resulted in the Canadian obtaining uniformly lower results than the American.

These results indicate that the proposed lead method, although having a decided advantage over the Canadian lead method in the matter of the range of the value in pure syrups would not be the equal of the Winton method in this respect.<sup>5</sup>

## IV FALLING OFF OF VALUE DUE TO DILUTION WITH SUCROSE

**SYRUP**—If the proposed new lead subacetate method proved to yield a value which shared with the Canadian

<sup>1</sup> *Loc. cit.*, p. 997.

<sup>2</sup> Snell and Scott, *This Journal*, 6 (1914), 216.

<sup>3</sup> Using the quantities of syrup containing 5 grams and 25 grams dry matter, respectively, as prescribed in the Canadian pure food standards.

<sup>4</sup> See Table VI of Paper III, *Loc. cit.*, p. 221.

<sup>5</sup> The author desires to reiterate his opinion that the original Winton method, without reduction to the dry basis, is better than any of the modifications of it which have been proposed. Comparison with a blank is, however, essential, and the suggestion is here repeated that a syrup made from (commercial) pure cane sugar be employed in the blank determination. See Paper II, *Loc. cit.*, p. 997.

<sup>1</sup> Snell and Scott, *This Journal* 5 (1913), 993.

<sup>2</sup> *Loc. cit.*, p. 996.

<sup>3</sup> Experiments were also made with 15 cc. of the lead subacetate solution. The range of variation of the lead values so obtained was, however, 64 per cent of the minimum as compared with 200 per cent in the method with 10 cc.



lead value the advantage of falling off rapidly when the maple syrup is adulterated with a sucrose syrup of the same density, it might be worth recommending in spite of its apparent inferiority to the true Winton lead number in the matter of range of variation. The diminution of the new lead value was compared with that of the Canadian and true Winton values in three syrups, determinations of all three lead numbers being made on the pure syrups and on mixtures of each with sucrose syrup in such proportions as to give syrups containing 90, 80, 70, 50 and 30 per cent of maple syrup. In the first of the three syrups there was little choice among the three methods except in the mixture containing only 30 per cent of maple. For this mixture the Canadian lead value was only 18.7 per cent, the Winton value was 22.1, and the proposed lead number 33.4 per cent of the corresponding values for the pure maple syrup. In other words, the proposed lead method showed itself inferior to either of the old methods. In the other two syrups the proposed method showed a distinct advantage over the Winton method and for some of the mixtures appeared to be even slightly better than the Canadian method.

On the whole this projected lead value had compared sufficiently favorably with the established methods to justify further investigation, had we not hit upon another lead subacetate method which appears much superior to any hitherto proposed and which will form the subject of the next paper of this series.

#### V—LEAD CONTENT OF THE "CANADIAN LEAD" PRECIPITATE

Mr. J. M. Scott determined the quantity of lead in the Canadian lead precipitates from 8 samples of maple syrup, representing a wide range of Canadian lead number. The precipitate was washed as directed in the Canadian lead method, *i. e.*, four or five times with hot water. It was then dried, weighed and subsequently decomposed with aqua regia, after which the lead was converted into lead sulfate in the usual way and weighed as such. The results obtained are shown in Table I.

TABLE I—"CANADIAN LEAD" PRECIPITATES

No.	SOURCE OF SYRUP	DESCRIPTION	Canadian lead No.	Per cent Pb in ppt.
1	Canada	Composite of 54 syrups	3.44	69.41
2	Canada	Mixture of several syrups	4.40	70.11
3	Dutton, Ont.	Middle run, pan, white of egg	1.74	69.62
4	Brome, Que.	Early run, pan	2.86	68.66
5	Hillsburgh, Ont.	Early run, evaporator	2.01	68.51
6	Wardsville, Ont.	Early run, evaporator	2.33	68.50
7	Orangeville, Ont.	Middle run, evaporator, milk	5.08	68.25
8	Neustadt, Ont.	Early run, kettle, eggs	4.10	66.95
AVERAGE OF NUMBERS 3 TO 8,			3.02	68.415

The results indicate a fairly definite composition in the precipitate, the variation in lead content being just over 3 per cent of the total weight. There appears to be no definite relation between the quantities of precipitate yielded by the syrup (Canadian lead numbers) and the composition of the precipitates. In view of the fact that this precipitate has sometimes been erroneously assumed to consist of normal lead malate, it is worth noting that the latter salt in the anhydrous condition contains only 61.00 per cent of

lead. It is possible that a basic malate<sup>1</sup> may be the essential, or at all events an important, constituent of the precipitate, but evidence to that effect has not yet been adduced. It is our intention to make a study of the organic non-sugar constituents of maple syrup which will embrace a more complete analysis of the lead precipitate as well as of the other precipitates obtainable from maple syrup and not from syrups made from pure sucrose.

#### VI—ATTEMPTS TO DETERMINE INORGANIC CONSTITUENTS VOLUMETRICALLY

If among the non-sugar constituents of maple syrup one could be found showing a reasonable degree of constancy in all genuine syrups, a convenient method of determining that constituent would obviously constitute a useful method of detecting adulteration.<sup>2</sup> It appeared a possibility that among the inorganic constituents one might be found answering the requirements.

The recorded analyses of the ash of maple syrup and sugar are comparatively few and the only complete analyses known to the writer are those of Hortvet,<sup>3</sup> embracing only two sugars and two syrups. The constituents which have been determined in a larger number of samples—*viz.*, potash, lime, phosphoric acid and sulfuric acid—all show very wide variations in individual syrups. Jones<sup>4</sup> found the potash in a maple sugar ash as low as 18.26 per cent while Bryan<sup>5</sup> obtained results in syrups ranging from 24.55 to 54.54. For lime Bryan obtained results running from 13.20 to 36.36; for phosphoric acid, 1.08 to 12.90; for sulfuric acid, 0.00 to 6.18 per cent. The results obtained by the other investigators all fall within the above limits. Mr. J. M. Scott in 1913 made complete analyses of the soluble and insoluble portions of the ash of a syrup compounded of about sixty genuine Canadian syrups. This analysis will probably be published in a future paper of this series dealing with the ash. From its data and the ratio of the soluble to the insoluble ash in the same composite syrup (which ratio happens to be unity) the composition of the total ash can be calculated.

It is as follows:

K <sub>2</sub> O...	29.07	MgO....	2.34	CO <sub>2</sub> .....	33.75	SO <sub>3</sub> .....	1.37
Na <sub>2</sub> O...	1.97	Fe <sub>2</sub> O <sub>3</sub> ...	1.82	SiO <sub>2</sub> .....	1.22	Cl.....	1.46
CaO...	25.88	Mn <sub>2</sub> O <sub>3</sub> ...	0.81	P <sub>2</sub> O <sub>5</sub> .....	0.15	Insol. in HF...	0.17
TOTAL, after deducting oxygen-equivalent of the chlorine.....							99.68

It will be noted that the quantity of phosphoric acid found is only one-seventh of the minimum percentage hitherto reported, thus extending the range of variation for this constituent.

It is clear, then, that none of the four ash constituents which have been extensively studied is suitable

<sup>1</sup> Otto's basic lead malate (Liebig's *Ann.*, **127**, 177) contained 73.8 per cent of lead, while the salt he obtained by adding the neutralized or nearly neutralized acid to a boiling excess of lead acetate solution contained 75.83 per cent of lead in its anhydrous condition, which is equivalent to 73.5 per cent in the monohydrate, which Otto found to be stable at 100° C.

<sup>2</sup> According to Hortvet, the protein (N × 6.25) content is fairly constant and has some value in this direction. So far as the writer is aware, but little attention has been paid to this suggestion of Hortvet's.

<sup>3</sup> Hortvet, *J. Am. Chem. Soc.*, **26** (1904), 1541.

<sup>4</sup> Jones, Vermont Agr. Expt. Station, *18th Annual Report*, 1904-5, p. 331.

<sup>5</sup> Bryan, Bureau of Chem., U. S. Dept. Agr., *Bull.* **134**, pp. 82-89.

for our purpose. Magnesia shows less variability (2.34 to 4.65) in the five instances in which it has been determined, but no easy method of determining it in presence of the other constituents of the syrup suggests itself.

The fact that Hortvet found extremely small quantities of chlorine in the ashes he analyzed suggested that a chlorine determination might be useful, particularly in case raw cane sugar or refined molasses were employed in adulterating.<sup>1</sup>

Mr. Scott's results, however, showing a very material chlorine content in a composite of so many samples, rather discouraged our hopes as to chlorine. Nevertheless, some experiments in titrating the diluted syrups with  $N/50$  silver nitrate were made by Mr. N. C. MacFarlane. Quantities of syrup containing 10 grams of solid matter were treated with 200 cc. water, 10 cc. lead subacetate solution (sp. gr. 1.25) and 10 cc. saturated potassium chromate, the assumption being that the lead would precipitate the organic matter precipitable by silver and at the same time decolorize the liquid, thus enabling the potassium chromate left in solution to act as an indicator in the titration for chlorine. The precipitate was washed with hot water and the filtrate (including washings) titrated with  $N/50$  silver nitrate. Nine genuine syrups took from 0.82 to 4.60 cc. of the silver nitrate. The same method, applied to 3 samples of raw cane sugar, gave 4.32, 5.14 and 9.08 as the number of cc. of silver nitrate required for 10 grams dry matter. A sample of beet sugar crystals gave 1.94 and a sample of cane molasses 51.99. The method, accordingly, offers little advantage except in the case of adulteration with molasses.

Experiments were also made in which the syrups were treated with alumina cream instead of lead subacetate. Syrup containing 10 g. solid matter was treated with 200 cc. water and 10 cc. alumina cream. The precipitate was washed with cold water and the filtrate and washings titrated with  $N/50$  silver nitrate, using potassium chromate as indicator. The same nine pure syrups as before took 1.01 to 6.40 cc. of the silver nitrate solution. In 12 other genuine maple syrups results were obtained ranging from 2.80 to 8.38. The raw cane sugars took 9.85, 3.64 and 7.52 cc. respectively, the beet sugar 2.23 and the molasses 57.00. The results by the two methods did not run parallel. In general, more silver nitrate was required after the alumina cream than after the lead subacetate treatment, but there were exceptions to this rule.

In view of the probability that the phosphorus in maple syrup is largely in organic combination, it was thought that in spite of the wide variability of the phosphoric acid content of the ash, the amount of phosphorus in the syrup itself precipitable by uranyl acetate might prove to be reasonably constant. Mr. MacFarlane made some titrations which appeared to indicate a fair degree of constancy in this value in the same nine syrups as were used in his experiments with silver nitrate. The results obtained with the

raw sugars, however, were very similar to those with the maple syrups. It is doubtful whether the method employed—titration of 20 cc. syrup with a uranyl acetate solution of which 1 cc. is equivalent to 5 mg. of  $P_2O_5$ —was suitable for the measurement of such small quantities of phosphoric acid and it is possible that further investigation along this line might be useful.

#### VII—ELECTROTITRIMETRIC EXPERIMENTS

The interesting paper of F. H. Hesselink van Suchtelen and Arai Itano,<sup>1</sup> pointing out that measurements of electrical resistance might be employed for the detection of the end-point in precipitation titrations, suggested to us that we might titrate syrups with silver nitrate without previous treatment with lead subacetate or alumina cream, using the electrical resistance as indicator in place of potassium chromate. It was, indeed, found possible to get a definite end-point in this way—indicated by a break in the curve on the plot of electrical resistance with volume of silver nitrate added: 3 cc. syrup were diluted to 30 cc. and  $N/50$  silver nitrate added from a burette, the electrical resistance being measured with a dip electrode after the addition of each cc. of the reagent. Fifteen genuine syrups gave end-points at 0.20 to 1.95 cc. silver nitrate. The range of variation is, therefore, too wide to render the method useful.

Similar experiments were made with  $N/10$  barium nitrate solution. With this reagent, as might be anticipated from the fact that no precipitate is produced, the resistance-volume curves showed no break.

It then occurred to us that the electrical resistance might be employed to detect the end-point in a titration with lead subacetate solution. Mr. MacFarlane, who had conducted the experiments reported above, made a number of experiments in this line, finally adopting a procedure in which a solution of lead subacetate prepared by diluting a solution of sp. gr. 1.246 (at 15° C.) with ten times its volume of water<sup>2</sup> was added from a burette to 3 cc. syrup diluted to 30 cc. This method applied to 14 samples of pure syrup gave results varying from 4.5 to 6.8 cc. of the lead subacetate solution—a range of 51 per cent. Later Mr. G. J. Van Zoeren applied this method to 24 syrups of the season of 1915, obtaining results ranging from 4.0 to 5.4. The total range among the 38 syrups is, accordingly, 70 per cent of the minimum.

The dip electrode used in the above experiments was of one of the common forms made for use with poor conductors.<sup>3</sup> A new electrode was designed by Mr. Van Zoeren which can be used for both the conductivity test described in Paper I of this series and the volumetric lead subacetate test to be described in Paper VI. A description of this electrode will be published in the *Journal of the American Chemical Society*.

The new electrode being larger than that previously used it became necessary to employ a larger volume of liquid than Mr. MacFarlane had used: 60 cc. were

<sup>1</sup> Practical men in Canada appear to be of the opinion that raw sugars and molasses are not commonly used as adulterants, but I have not thought it advisable to ignore the possibility.

<sup>2</sup> van Suchtelen and Itano, *J. Am. Chem. Soc.*, **36** (1914), 1793.

<sup>3</sup> This solution has a density of 1.025.

<sup>4</sup> Baird and Tatlock's Catalogue, 1914, No. 5313T.



found to be a suitable quantity of the diluted syrup for the purpose. Experiments were then made in which the concentration of the syrup and subacetate solutions were varied. The results are shown in Table II. The procedure adopted on the basis of these experiments will be described in the next paper. Applied to the same 24 syrups of the season of 1915 as were tested by Mr. MacFarlane's procedure, the Van Zoeren procedure gave results ranging from 4.8 to 6.0. This range amounts to 22 per cent of the mean (5.55) or 25 per cent of the minimum as against 30 per cent of the mean (4.70) or 35 per cent of the minimum for the MacFarlane procedure.

TABLE II. TITRIMETRIC EXPERIMENTS WITH LEAD SUBACETATE

Density of subacetate solution	Cc. syrup diluted to 100 cc.	No. of syrups tested	Range of lead numbers	
			Actual	In per cent of minimum
1.050	10	6	No definite breaks	
	15	23	2.5-4.5	80
	20	8	2.4-4.7	96
1.033	5	16	In 5 instances no breaks	
	8	12	4.0-5.9	41
	10	16	4.7-6.5	38

## SUMMARY

1—Silver nitrate added to maple syrup gives a white precipitate which darkens on standing. The precipitation of silver continues during a period of several hours.

2—Mercuric acetate added to maple syrup produces a light yellow precipitate.

3—Alcohol produces a precipitate containing most of the calcium and potassium.

4—A moderately successful attempt was made to combine the advantages of the Winton and Canadian lead subacetate methods.

5—The Canadian lead precipitates from six syrups showed a lead content of 66.95 to 69.62 per cent; average, 68.42. The precipitate from a composite of 54 syrups contained 69.41 per cent of lead, while that from another mixed syrup contained 70.11 per cent.

6—Titration of maple syrup with *N/50* silver nitrate (1) directly, using electrical resistance measurements to detect the end-point, (2) after treatment with lead subacetate or alumina cream, using potassium chromate as indicator, yielded definite but not useful results.

7—Titration with uranyl acetate gave no useful results.

8—Titration with lead subacetate solutions using electrical resistance as indicator led to a useful method of testing the syrup for purity, which is described in the next paper of the series.

9—A complete analysis of the ash of a composite of about sixty genuine syrups shows more chlorine and less phosphoric acid than the analyses previously recorded.

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## A COMPARISON OF METHODS FOR THE DETERMINATION OF SOIL PHOSPHORUS

By W. O. ROBINSON

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Hillebrand<sup>1</sup> outlines the main points of this determination in the following statement: "It is some-

times possible to extract all the phosphorus from a rock by simple digestion with nitric acid, but quite as often if not oftener this fails; hence the necessity of resorting to one of the longer methods of extraction \* \* \* Whatever method is used, great care is required to secure accurate results." This statement applies to soils with the further complication that organic matter is invariably present, sometimes in amounts large enough to require special treatment.

## METHODS OF SOLUTION OF THE SOIL

Washington<sup>1</sup> and Fry<sup>2</sup> have called attention to the presence of apatite inclusions in quartz as affecting the determination of phosphoric acid. Protected in this way the apatite would not, of course, be soluble in acids other than hydrofluoric. Further, there are many phosphate minerals such as variscite, wavellite, and xenotime, which, from the standpoint of determinative mineralogy, are classed as insoluble in acids. These minerals have not been reported as occurring in soils, but there is a possibility of it. Fry<sup>3</sup> cites a number of analyses showing that in most cases the total phosphoric acid is not dissolved by acid digestion: from 4 to 100 per cent is extracted. Obviously a method of simple acid digestion will not be generally reliable when applied to soils.

FISCHER'S METHOD—Fischer,<sup>4</sup> however, has modified an acid digestion method so that it appears to extract the entire amount of phosphorus. The salient feature of this process is an intervening ignition between two acid treatments. Briefly the procedure is as follows: 5-10 grams of soil are treated with 50 cc. of *aqua regia* in a covered quartz dish of appropriate capacity. After the action has ceased the cover is removed and the mass evaporated to dryness. It is then ignited (ostensibly long enough to destroy organic matter) and again treated with *aqua regia*, evaporated to dryness and taken up with nitric acid. Fischer claims that the process gives slightly higher results than the fusion method,<sup>5</sup> though he proves there is an almost negligible amount of phosphorus left in the insoluble residue. He points out that a larger sample can be conveniently used with his method than with the fusion method, thereby securing a fairer sample of the soil. The author has tested this method on a variety of soils. The samples were well ground and mixed so that but one gram was employed in each case. After the second *aqua regia* treatment, the mass was evaporated once with nitric acid, heated on the hot plate to browning to dehydrate the silica, then taken up with the requisite amount of nitric acid. The results, and for comparison, those obtained by other methods, are given in Table I.

Fair agreement is shown, considering the determina-

<sup>1</sup> "The Chemical Analysis of Rocks," Wiley & Sons, New York (1910), p. 162.

<sup>2</sup> THIS JOURNAL, 5 (1913), 664.

<sup>3</sup> Loc. cit.

<sup>4</sup> Intern. Mitt. f. Bodenkunde, 2 (1913), 541.

<sup>5</sup> Probably due to the difficulty of precipitating small amounts of ammonium phosphomolybdate in presence of much  $\text{NaNO}_3$  in the fusion method since Cain and Hostetter [J. Soc. Chem. Ind., 4 (1912), 250] have shown that aqueous solutions of  $\text{NaNO}_3$  have a strong solvent effect on the phosphomolybdate when vanadium is present.

tion, and one method can be classed as accurate as another.

Mr. W. H. Fry, of this Bureau, kindly examined soils Nos. 27 and 31 and found that approximately 0.8 per cent of No. 27 was made up of quartz grains with apatite inclusions. Similarly about 0.1 per cent of the soil grains of No. 31 contained apatite inclusions. He further reported that the insoluble resi-

TABLE I—COMPARISON OF DIFFERENT METHODS FOR THE DETERMINATION OF PHOSPHORUS IN SOILS

Soil No.	Results in Percentages $P_2O_5$		WASHINGTON METHOD	FISCHER'S METHOD
	$Na_2CO_3$ alone	$Na_2CO_3 + NaNO_3$		
25			0.18-0.18	0.16-0.17
27	0.11-0.10	0.10-0.10	0.10-0.08	0.12-0.10
28	0.10-0.11	...	0.08-0.09	0.08-0.10
29	0.11-0.11	...	0.10-0.10	0.10-0.10
30			0.08-0.09	0.09-0.08
3220	4.90	5.12	4.98-4.97	4.93

due of soil No. 25 showed but a single inclusion, which was apparently apatite but could not be absolutely identified. The fresh sample contained comparatively many inclusions. The evidence is, therefore, that apatite inclusions in quartz do not escape solution by this method.

**THE FUSION METHOD**—The method of fusing the soil with sodium carbonate is a standard one. It requires more attention than the other methods and is subject to one inherent error, as previously pointed out, *i. e.*, the solubility of small amounts of ammonium phosphomolybdate in aqueous solutions of  $NaNO_3$ .<sup>1</sup> If the sesquioxides are in excess, the  $P_2O_5$  can be precipitated with them and separation of the  $NaNO_3$  made in that way. This requires another operation and, except for very small percentages, is not necessary.

In many soils the silica separated from the fusion need not be driven off with HF, and the residue brought into solution and added to the main solution. The silica, separated from 5 soils containing from 0.05 to 0.13 per cent  $P_2O_5$ , contained, in every case, an insufficient amount of  $P_2O_5$  to weigh. If, however, the soil contains comparatively large amounts of iron, cerium and titanium as well as phosphoric acid, the separated silica may contain considerable phosphorus. For the sake of precaution, therefore, in every case the separated silica must be worked over.

Soils high in organic matter must be previously burned with magnesium nitrate or evaporated with nitric acid and ignited, taking care to avoid glowing, before they are fused. In such cases and if graphite or other reducing substances be present, some oxidizing material should be put in the flux to insure complete conversion of the phosphorus to orthophosphate.

**WASHINGTON'S METHOD**—In laboratories where platinum evaporating dishes are available, Washington's method<sup>2</sup> of making the solution is by far the neatest. With soils the sample must first be evaporated with nitric acid and ignited to destroy organic matter and render the soil easier to decompose. No phosphoric acid is lost by this procedure, provided it is carried out in such a manner that there is no glowing during

ignition. Numerous experiments show that the addition of magnesium nitrate, previous to ignition, is unnecessary for the reason that nitric acid dissolves enough bases to hold the phosphoric acid during the ignition.

In the following experiments one gram of soil containing 0.04 per cent of phosphoric acid and 0.29 per cent organic matter was used. A known amount of phosphoric acid was added in each case. The mixture was evaporated with nitric acid and ignited. The results are shown in Table II.

TABLE II—VOLATILIZATION OF PHOSPHORIC ACID DURING IGNITION

Added + amount in soil	Grams $P_2O_5$			
	Found	0.0104	0.0304	0.0304
Found	0.0106	0.0104	0.0301	0.0305

When 0.5 gram of sugar was added to the above mixture and the ignition hasty and attended with glowing, there was an apparent loss of from 30 to 11 per cent of the phosphoric acid present.<sup>1</sup>

In nearly a score of soil analyses made by this method only a negligible trace of phosphorus has been detected in the part of the soil insoluble in hydrofluoric and nitric acids.

Sulfuric acid must not be used in place of nitric acid in this method for fear of driving off phosphoric acid during the ignition or volatilization of the acid.

#### DISCUSSION

Where platinum dishes are not available or it is wished to avoid the use of hydrofluoric acid, Fischer's method of making the solution will be found satisfactory. The evaporation from quartz or porcelain<sup>3</sup> is slow, it is true, but does not require the constant attention of the analyst.

To further test the efficiency of Fischer's method of solution the following experiment was tried: A sample of variscite with a small amount of gangue was ground fine and well mixed. Although the mineral is reported to be insoluble it is only comparatively so: 0.5 gram of the powdered mineral when boiled two hours with 30 cc. nitric acid and 5 cc. hydrochloric acid gave 12.80 per cent  $P_2O_5$  soluble in acids. The sample contained 25.98 per cent  $P_2O_5$ . To 1 gram samples of soil containing 0.09 per cent  $P_2O_5$ , 0.0142 and 0.0800 gram of the powdered variscite were added. In the two portions there was 0.0046 and 0.0217 gram  $P_2O_5$  present. Fischer's method of solution gave 0.0047 and 0.0218 gram. The solution of the variscite was effected by ignition as is indicated by Morse's<sup>4</sup> work.

#### INFLUENCE OF VANADIUM

The author has previously shown<sup>4</sup> that soils contain appreciable amounts of vanadium, running from 0.01 to 0.08 per cent, and sometimes nearly as much vanadium as phosphorus. Brearley and Ibbotson<sup>5</sup> and Cain and Hostetter<sup>6</sup> have shown that in case of steels

<sup>1</sup> If phosphoric acid can be converted during ignition, to a form not changed to ortho-phosphate by two evaporations with nitric acid, it is possible that some escaped precipitation in this way during the experiment. See Leavitt and LeClerc, *J. Am. Chem. Soc.*, **30** (1908), 391, 617.

<sup>2</sup> The porcelain must be capable of standing the ignition.

<sup>3</sup> *J. Am. Chem. Soc.*, **25** (1903), 280.

<sup>4</sup> U. S. Dept. Agr., *Bull.* **122** (professional paper), 1914.

<sup>5</sup> "The Analysis of Steel Works Material," London (1902), p. 163.

<sup>6</sup> *This Journal*, **4** (1912), 250.

<sup>1</sup> Vanadium is ever present in soils.

<sup>2</sup> "The Chemical Analyses of Rocks," Wiley & Sons, N. Y. (1910), 162.



the vanadium has a tendency to prevent the precipitation of phosphoric acid. The former state that the phosphorus determinations in vanadium-bearing steels are low, notwithstanding the fact that vanadium is precipitated and weighed with the phosphomolybdate. Cain and Hostetter propose to precipitate the vanadium completely by co-precipitation with the phosphorus. They found that about ten times as much phosphorus as vanadium should be present to secure the complete precipitation of the latter. They show that the presence of vanadium in the molybdate precipitate can easily be recognized on account of the orange or brick color of the precipitate. The solution is colored a deep straw and precipitation is delayed or entirely prevented.

Using Woy's method of precipitation, one gram of soil containing 0.19 per cent  $P_2O_5$  gave 0.12 and 0.16 per cent when 0.0025 gram of  $V_2O_5$  had been added, and when 0.1 gram  $V_2O_5$  had been added no precipitate appeared after 48 hours' digestion. More reagents, further digestion and mechanical agitation produced a precipitation of 0.08 and 0.04 per cent in other gram samples.

In the following experiments the final volume in which the precipitation was made contained 5-7 per cent nitric acid by weight or volume,<sup>1</sup> 5 per cent ammonium nitrate, and to this was added 10 cc. of nearly neutral ammonium molybdate.<sup>2</sup> The precipitation took place at 65°-70° and the liquid was digested for two hours. It was cooled before filtering. Table III shows the results.

TABLE III—INFLUENCE OF VANADIUM ON THE PRECIPITATION OF AMMONIUM PHOSPHOMOLYBDATE

No.	1	2	3	4	5
Grams $V_2O_5$ present.....	0.0000	0.0010	0.0015	0.0025	0.0050
Grams $P_2O_5$ present.....	0.0018	0.0018	0.0018	0.0018	0.0018
Grams $P_2O_5$ found.....	0.0019	0.0019	0.0018	0.0020	0.0010

In these as well as in all other determinations described in this paper the yellow precipitate was dissolved in dilute ammonia and slowly precipitated with magnesia mixture,<sup>3</sup> enough strong ammonia added to make the liquid from 5-7.5 per cent  $NH_3$  and the beaker allowed to stand three hours in a cool place with occasional stirring.

In laboratories where precipitation by shaking or mechanical stirring can be conveniently carried on, the method of Cain and Tucker<sup>4</sup> for precipitating phosphoric acid in presence of vanadium is both accurate and rapid. The vanadium salts are reduced to the vanadyl condition by means of ferrous sulfate and sulfurous acid. In this reduced condition vanadium is not carried down with the yellow precipitate. Reoxidation of the vanadyl salts by nitric acid is prevented by keeping the temperature from 15°-20° C. Completeness of the precipitation is assured by shaking.

The author has tried this method of separation

<sup>1</sup> Nitric acid, sp. gr. 1.42, is about 70 per cent  $HNO_3$ .

<sup>2</sup> Nearly neutral ammonium molybdate is preferable for it keeps its strength, and further, since, using this method of precipitation, the solution is strong with nitric acid throughout the precipitation, there is less danger of absorption or occlusion of the bases.

<sup>3</sup> Too large an excess is to be avoided: 2 cc. above the actual amount required for precipitation in 100 cc. of liquid is sufficient.

<sup>4</sup> This Journal, 5 (1913), 647.

with soil solutions containing known amounts of vanadium and phosphoric acid. Precipitation was made in 125 cc. wide-mouth assay flasks closed with a rubber stopper. Precipitation was complete in 15 minutes. With these soil solutions the addition of sulfurous acid was not necessary: 0.08 gram of ferrous sulfate was present in all cases. The results are shown in Table IV.

TABLE IV—SHOWING THE SEPARATION OF VANADIUM AND PHOSPHORIC ACID BY MEANS OF FERROUS SULFATE

No.	1	2	3	4	5
Grams $V_2O_5$ present.....	0.0008	0.0013	0.0028	0.0103	0.0153
Grams $P_2O_5$ present.....	0.0058	0.0058	0.0054	0.0062	0.0058
Grams $P_2O_5$ found.....	0.0057	0.0058	0.0052	0.0062	0.0058

By taking precaution to make the precipitation of the phosphomolybdate complete by means of comparatively large excesses of reagents, and by digestion and mechanical agitation, the influence of the amount of vanadium ordinarily found in soil can be avoided without reducing the vanadium, provided the yellow precipitate is converted to magnesium ammonium phosphate. The method of titrating the precipitate with standard alkali calls for conditions which are against complete precipitation<sup>1</sup> and even though a second precipitation be made there is still some vanadium present and the results are apt to be low. Should the liquid, after the addition of the ammonium molybdate, turn a strong straw color and the precipitation be not complete after a half hour's digestion, there is an excess of vanadium present. In such cases if longer digestion, etc., do not satisfy the analyst that precipitation is complete, a known amount of phosphoric acid must be added and the digestion continued. It is important, of course, not to add too large an amount of phosphoric acid lest the accuracy of the subtracted amount be under suspicion.

#### INFLUENCE OF TUNGSTEN AND TITANIUM ON THE PRECIPITATION OF PHOSPHORUS

Small amounts of tungsten and titanium<sup>2</sup> interfere with the determination of phosphorus in the usual way in the course of iron and steel analysis.

With soils tungsten would not interfere unless it carried down phosphorus with it when precipitated by acids in removing the silica. The effect of the amounts of titanium usually found in soils is negligible when the gravimetric method is employed. Titanium is more difficult to wash out of the yellow precipitate than the other bases. In steel analysis titanium retards precipitation and in some cases may come down with the phosphomolybdate.

#### INFLUENCE OF VANADIUM ON THE PRECIPITATION OF AMMONIUM MAGNESIUM PHOSPHATE

A composite precipitate of magnesium pyrophosphate from about 30 soils was tested for vanadium and showed only the merest trace. Solutions containing 0.0050 gram  $V_2O_5$  and 0.00864 gram  $P_2O_5$  were treated with magnesia mixture in the usual manner and allowed to stand 6 hours; 0.0088 gram

<sup>1</sup> To avoid the influence of molybdic acid.

<sup>2</sup> J. M. Camp, "Methods for the Commercial Sampling and Analysis of Alloy Steel," U. S. Steel Corporation, 1915, p. 28; J. W. Mellor, "A Treatise on Quantitative Inorganic Analysis," Vol. 1, p. 594, J. B. Lippincott Co., Phila., Pa.

$P_2O_5$  was found. When the precipitation for the same amounts had stood 17 hours, however, there was apparently 0.0145 gram  $P_2O_5$ . From these experiments it appears that with the small amounts of vanadium and phosphorus occurring in soils, a satisfactory separation can be made with magnesia mixture provided the precipitate does not stand more than 3-4 hours. No experiments have been carried out on larger amounts.

#### THE NATURE OF THE MIXED YELLOW PRECIPITATE

It was first assumed that vanadium replaced the phosphorus in the yellow precipitate. Later consideration showed, however, that this was unlikely, for the precipitation of vanadium is complete<sup>1</sup> when phosphoric acid in amounts somewhat less than ten times the amount of vanadic acid is present, and Brearley and Ibbotson have shown that the results obtained by weighing the yellow precipitate are low when vanadium is present. To test this point mixtures of phosphoric and vanadic acids were precipitated under conditions outlined in *Bull.* 107 (revised) of the Bureau of Chemistry of this Department, and titrated with standard alkali. The results are given in Table below.

TABLE V.—SHOWING THE ACIDITY OF THE PHOSPHOMOLYBDATE PRECIPITATE OBTAINED IN THE PRESENCE OF VANADIUM

No.	1	2	3	4
grams $P_2O_5$ present.....	0.00432	0.00432	0.00432	0.00432
grams $V_2O_5$ present.....	None	0.00125	0.00250	0.00500
grams $P_2O_5$ found.....	0.00432	0.00396	0.00337	0.00298

The latter determinations showed incomplete precipitation. The precipitation was made complete when the phosphorus coming down was estimated gravimetrically. The amount of phosphoric acid recovered was added to that found by titration, making the final figures for Experiments 2, 3 and 4: 0.0045, 0.0045 and 0.0042, respectively. It thus appears that the acidity of the yellow precipitate is not increased by the presence of vanadium and that volumetric determinations of phosphorus in presence of vanadium are apt to be low. Apparently the vanadium replaces the molybdenum instead of the phosphorus as indicated by Blum.<sup>2</sup>

#### COMPOSITION OF THE FEATHERY PRECIPITATE

When the phosphomolybdate precipitate is dissolved in ammonia there is sometimes a white precipitate resembling ferric phosphate which fails to dissolve. Allebrand<sup>3</sup> states that this is a compound of phosphorus and recommends the addition of a small amount of citric acid or in case this fails to dissolve it, fusion with sodium carbonate. Hornberger<sup>4</sup> finds this precipitate contains titanium and phosphorus. It may be ferric, titanium or aluminum phosphates and hydroxides in mixtures of these, depending on the composition of the solution. It is a combination of phosphorus with the above bases that have been absorbed or not thoroughly washed away. If the solution is made sufficiently acid before the precipitation and nearly neutral ammonium molybdate added with stirring, one need not fear the formation of this precipitate

unless the concentration of phosphoric acid and bases is large. In such cases a second precipitation is the most expedient procedure.

One gram of soil from the Hawaiian Islands, containing 4.95 grams  $P_2O_5$  and large amounts of iron, aluminum and titanium, was precipitated in small volume without much stirring and the residue insoluble in ammonia set aside and analyzed. It contained 0.0017  $Al_2O_3$ , 0.0058  $TiO_2$  and 0.0016  $Fe_2O_3$ , combined with phosphorus. Two precipitations on the same amount conducted in a like manner yielded a precipitate containing 0.0004  $TiO_2$ , 0.0001  $Fe_2O_3$ , no  $Al_2O_3$  and an almost negligible amount of phosphorus. The precipitate obtained from some American soils contained only a trace of titanium and was largely aluminum.

The feathery precipitate deliberately obtained in small amounts from eight samples of soil weighed from 0.0004 to 0.0008 gram. In three cases only did the precipitate of  $Mg_2P_2O_7$  obtained from the above precipitates exceed the blank determination and these by 0.0001 gram only.

When precipitation of the phosphomolybdate is carried on in such a manner that it does not adhere to the sides of the beaker or flask and washing is thorough, the feathery precipitate can easily be avoided in soil determinations.

#### CONCLUSIONS

I—The fusion methods, Washington's method and Fischer's method, of treating the soil for the determinations of phosphorus, give accurate results.

II—Vanadium interferes with the phosphorus determinations in soils. This influence can be avoided by reducing the vanadium with ferrous sulfate and precipitating at low temperatures by shaking. With soil solutions it is not necessary to add sulfurous acid to prevent the reoxidation of the vanadyl salt. The influence of vanadium is also avoided by using the gravimetric method, provided precautions are taken for complete precipitation and the ammonium magnesium phosphate precipitate is not allowed to stand too long.

III—Tungsten and titanium do not interfere with the determination of phosphorus in soils, by the gravimetric method, provided precautions are taken to make the precipitation complete.

IV—The composition of the feathery precipitate is dependent on the nature of the bases in the solution before precipitation. Proper precipitation and washing of the yellow precipitate prevents the formation of the feathery precipitate or reduces it to a negligible amount.

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#### SOME NEW METHODS FOR THE ANALYSIS OF LIME-SULFUR SOLUTIONS<sup>1</sup>

By ROBERT M. CHAPIN

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#### INTRODUCTORY

The important substances contained in lime-sulfur solutions are calcium polysulfides and calcium thio-

<sup>1</sup> Published by permission of the Secretary of Agriculture.

<sup>1</sup> Cain and Hostetter, *Loc. cit.*

<sup>2</sup> *J. Am. Chem. Soc.*, 30 (1908), 1858.

<sup>3</sup> *U. S. Geol. Survey, Bull.* 422 (1910), 145.

<sup>4</sup> *Landw. Vers. Sta.*, 82 (1913), 299.



sulfate. In addition, theoretically at least, the solutions may be either basic through the presence of free calcium hydroxide, calcium hydroxysulfide, etc., or acidic (regarding hydrogen sulfide as an "acid") through the presence of free hydrogen sulfide, calcium hydrosulfide, etc. Dilute solutions of sulfides of calcium are notably hydrolyzed, and since both base and acids are diatomic, the possible molecules and ions are numerous and complex. The writer takes the position that analytical figures<sup>1</sup> inherently dependent upon or modified by degree of dilution can be of little value since such figures can afford no fixed basis for comparison between manufactured products of unequal degrees of concentration, and are still less applicable to the diluted solutions used in practice. The important problem in this connection is to determine the balance between the positive and the negative constituents; that is, to ascertain quantitatively whether a solution contains excess lime or excess hydrogen sulfide. The present paper describes methods for determining the concentration of total (sulfide) base, of total (sulfide) acid and of excess base or acid.

#### DESCRIPTION OF METHODS

The methods are all titration methods, performed with  $N/10$  solutions upon 10 cc. of lime-sulfur solution.<sup>2</sup> Moreover, they all ultimately measure either  $\text{CaA}_2$  or  $\text{M}_2\text{S}_x$ . Therefore the figures of the titrations are directly comparable and for the purpose of the present study the results are best given in that form without calculating to percentages of the actual substances present. The determinations are designated and defined as follows:

**I—SULFIDE-BASE FIGURE**, representing cc. of  $N/10$  base present in 10 cc. of solution, whether existing as "free lime" or as various possible calcium sulfides.

**II—REACTION FIGURE**, representing cc. of  $N/10$  base or acid (hydrogen sulfide) present in 10 cc. of solution *in excess* of the quantity necessary to form neutral salts of the formula  $\text{CaS}_x$ . If the solution contains an excess of base the reaction figure carries a plus sign; if an excess of acid, a minus sign.

**III—SULFIDE-ACID FIGURE**, representing cc. of  $N/10$  acid ( $\text{H}_2\text{S}_x$ ) present in 10 cc. of solution, whether existing free or as various possible calcium sulfides.

Lime-sulfur solutions are affected by exposure to air. Hence a sample is best preserved<sup>3</sup> by distribution among small, wholly filled and well sealed bottles, kept in a dark, cool place. The solution is to be clarified by sedimentation, never by filtration. A clean, dry pipette must be used for measuring each portion, for the skin of solution adhering to the walls of a pipette after drainage may undergo sufficient change to in-

fluence appreciably the composition of another charge immediately drawn into it. Lastly, the charge should always be delivered from the pipette into an appropriate liquid previously placed in the container in which the titration is to be executed, keeping the tip of the pipette constantly just under the surface of the liquid until necessary to raise it for drainage at the end.

#### DISCUSSION AND EXECUTION OF METHODS

**I. SULFIDE-BASE FIGURE**—The method employed is the obvious one, well described by Tartar and Bradley,<sup>1</sup> of titration with standard acid in presence of an appropriate indicator not sensitive to hydrogen sulfide. Into a 100 cc. Erlenmeyer flask containing 30 cc. water, is pipetted 10 cc. of the sample. The liquid is slowly titrated with  $N/10$  hydrochloric acid until the yellow tint has gone, then one drop of methyl orange is added and the titration continued to a clear endpoint. In a duplicate the addition of methyl orange is delayed as long as possible, to avoid bleaching or adsorption of the indicator—with a slight orange tint—by freshly precipitated sulfur. Instead of the methyl orange recommended by Tartar and Bradley, congo-red, recommended by Ramsay,<sup>2</sup> may be employed and may be preferred by some. It should be added similarly just before the end of the titration and just enough (it is necessary to dilute the ordinary indicator solution) is to be used to produce a distinct scarlet. As the titration progresses the scarlet becomes less intense, merely through coagulation of the sulfur in the background, but the purity of the tint remains until the end, where distinct modification occurs.

If the sample is a bath much used for dipping cattle or sheep both methyl orange and congo-red fail, but another indicator, sodium nitroprusside, appears reliable even in very dirty solutions. In a general way it has long been known that sodium nitroprusside, in the presence of hydrogen sulfide, is an indicator of neutrality, but the writer is unaware of its previous practical application in alkalimetry. Into 30 cc. of water in a 100 cc. beaker is pipetted 10 cc. of the sample, and the liquid is slowly titrated with  $N/10$  hydrochloric acid until the yellow color, which in case of used dipping baths may partly be due to extraneous matter, has become faint. A drop of the liquid is transferred to a white spot plate and treated with one drop of a 0.2 per cent solution of sodium nitroprusside, recently prepared and kept in an amber bottle. If the titration is still far from complete the well known violet will quickly develop and soon fade. If the color is doubtful or does not appear, enough of the well stirred liquid to nearly fill one of the cups of the spot plate is transferred thereto with a medicine dropper and immediately treated with one drop of the indicator solution. The medicine dropper is conveniently kept in a small beaker of distilled water, which serves to rinse it between tests. The end of the titration is indicated by the failure of a dirty green turbidity (in no way resembling the former clear violet) to appear within fifteen minutes

<sup>1</sup> Compare certain methods of Thompson and Whittier, *Del. Coll. Agric. Exper. Sta. Bull.* 105, June 1, 1914.

<sup>2</sup> The writer's concern with lime-sulfur solutions is confined to those used for dipping cattle and sheep under official regulations (B. A. I. Order 210 and Amendments). The regulations set standards of strength of 2 per cent and 1.5 per cent of "sulfide sulfur." Accordingly, the methods are adjusted for convenient work on samples from the field—which are often small—of such approximate strength. Increasing the quantity of sample and using stronger solutions for titration might very likely improve accuracy in some of the methods.

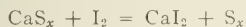
<sup>3</sup> The writer has previously noted (*Dept. Bull.* 163) that samples of dipping baths through which cattle and sheep have passed in large numbers are subject to deterioration even when sealed from air.

<sup>1</sup> *THIS JOURNAL*, 2 (1910), 271.

<sup>2</sup> *Journal of Agricultural Science*, 6 (1914), 476.

quiet standing in diffused daylight. It is naturally best to make a preliminary coarse titration, and then, by subsequent repetitions, to narrow the location of the end-point to the desired degree of definiteness. In such subsequent titrations not more than three tests should be made during any one, and these tests should be carried through without any intermediate delays to see whether color is going to develop or not. The writer will not now undertake any discussion of the rationale of the color production<sup>1</sup> or of its application to anything but the titration of lime-sulfur solutions. Where he has found the titration precise, the end-point sharp to less than 0.10 cc. of *N*/10 acid, and consistent with the end-points yielded by the other two indicators. Indeed, working to 0.1 cc. on pure solutions, it is easier to be positively assured of the attainment of the end-point when using sodium nitroprusside than when using either methyl orange or congo-red, though its application is so tedious that the two latter indicators will be preferred where practicable.

II. REACTION FIGURE—Some years ago Harris<sup>2</sup> proposed to determine "monosulfide sulfur" by simple titration with *N*/10 iodine until the original yellow color just disappears. He bases the validity of his method on the supposition that "the reaction



takes place to completion before the reaction between the iodine and calcium thiosulfate commences." In view of the considerable investigation by different chemists to which Harris' work has been subjected, it is surprising that no one has yet noted the obvious fallacy upon which the method is based. For, passing over the truth of Harris' unproven assumption of a selective action whereby iodine reacts more readily with calcium polysulfide than with calcium thiosulfate, it ought to be plain enough that such a selective action can lead to quantitative results only when complete admixture is made instantaneously. During actual titration, especially toward the end, when the concentration of calcium polysulfide has become relatively small, the iodine solution, as it drops from the burette, must be regionally in great excess with respect to calcium polysulfide and must then necessarily react with any contiguous molecules of calcium thiosulfate.

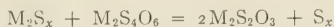
The only possible way in which Harris' method can afford uniformly dependable results is through the assumption of the reaction represented by the equation  $\text{CaS}_x + \text{CaS}_4\text{O}_6 = 2\text{CaS}_2\text{O}_3 + \text{S}_x$ , whereby any tetrathionate formed by the action of iodine upon thiosulfate is at once decomposed by polysulfide and the original amount of thiosulfate regenerated. As a matter of fact this reaction has been known for many years and is noted in the larger treatises. But the conditions under which Harris' method are executed are such that the above noted reaction does not always progress normally, and for this and other reasons<sup>3</sup> the method cannot be regarded as trustworthy.

<sup>1</sup> The phenomenon is possibly dependent upon the presence of thiofate (cf. Casolari, *Rend. soc. chim. ital.*, [2] 5 (1914), 294; *C. A.*, 9 (1915), 1435.

<sup>2</sup> *Mich. Agric. Coll. Exper. Sta. Tech. Bull.*, 6, Jan., 1911.

<sup>3</sup> Compare McDonnell, *Bur. Chem. Bull.* 162, p. 38, Nov., 1913.

Considering now the equation



it is evident that one result of the reaction is to exchange for the weak and volatile acid, hydrogen sulfide, an equivalent amount of relatively strong thio-sulfuric acid. Consequently if a strictly neutral solution of sodium tetrathionate be added in excess to a lime-sulfur solution, the resulting liquid becomes titratable with use of the ordinary indicators appropriate for moderately strong acids. The resultant figure for acidity or alkalinity must be the figure for acidity or alkalinity of the original lime-sulfur solution.

Preliminary investigation revealed that the reaction progresses normally only in alkaline solutions, not in presence of free hydrogen sulfide. On the other hand, alkalies decompose solutions of tetrathionates with production of acidity and iodine-absorbing power. The dilemma was avoided by rendering the solution alkaline to a small degree with ammonia only. Under such properly adjusted conditions, which are easily produced, the reaction progresses rapidly and normally without the occurrence of appreciable decomposition of excess tetrathionate.

Since the tetrathionate solution undergoes slow decomposition in any event, it should be prepared only in the quantity and at the time needed. Into a 250 cc. conical flask bring an excess (ordinarily about 25 per cent more than the titration for "sulfide-base figure") of *N*/10 iodine and mix in *N*/10 sodium thiosulfate until the color is nearly discharged. Add a little *N*/10 hydrochloric acid to destroy any iodate, rinse down the sides of the flask and cautiously titrate with *N*/10 thiosulfate against a white background till the yellow tint just vanishes. Add 5 cc. of 10 per cent ammonium chloride, dilute to 100 cc., add one drop methyl red indicator solution (0.2 per cent methyl red in alcohol), titrate with *N*/10 caustic soda to alkalinity, then carefully bring back to a distinct orange with *N*/10 hydrochloric acid; pipette in, while mixing, 10 cc. of the *N*/10 caustic soda. Now pipette in 10 cc. of the sample, mix well, and let stand three minutes, preferably stoppering the flask. Then add one drop more of methyl red, and titrate with *N*/10 acid to a distinct end-point. Determine the equivalence of 10 cc. of the *N*/10 alkali in terms of the *N*/10 acid and algebraically subtract it from the actual titration to obtain the "reaction figure." In duplicating the determination the amount of *N*/10 caustic soda should be adjusted—in multiples of 5 cc.—so that back titration with *N*/10 hydrochloric acid will require between 5 cc. and 10 cc. All the operations are to be carried through without intermediate delays.

III. SULFIDE-ACID FIGURE: METHOD A—Algebraically subtract the "reaction figure" from the "sulfide-base figure."

METHOD B—The liquid resulting from the determination of the "reaction figure" contains, in addition to the original thiosulfate of the sample, newly formed thiosulfate in amount exactly equivalent to the



$M_2S_x$  originally present in the sample. Therefore, after addition of starch the liquid is titrated with  $N/10$  iodine. From the resulting total iodine titration must be subtracted the thiosulfate titration,<sup>1</sup> in order to obtain the desired result.

**METHOD C**—Methods A and B, though preferable on the score of accuracy where they can be applied, fail on used dipping baths. For such baths Method C is the recourse, while in any case it affords a simpler and more direct road to the desired information. The method consists simply in titrating an ammoniacal dilution of the sample with standard tetrathionate, until an appropriate indicator no longer shows a trace of sulfide remaining.

To prepare the standard  $N/20$  tetrathionate, place a convenient quantity of  $N/10$  iodine in a dry capacious flask, and mix in  $N/10$  thiosulfate until the color of iodine becomes faint, then carefully finish from a burette until the yellow tint vanishes. If the normality of the iodine is  $a$  and the normality of the thiosulfate  $b$ , then, disregarding insignificant changes in molecular volumes, the normality of the tetrathionate is  $\frac{a b}{a + b}$ , or, if the two original solutions do

not differ in strength from each other and from true  $N/10$  by more than 5 per cent, the normality factor  $\frac{a + b}{4}$  is sufficiently close. The tetrathionate solu-

tion, being subject to slow decomposition, should be prepared not long before use, especially since it is so easily duplicated at any time from the original solutions.

Into 10 cc. of dilute ammonia (10 volume per cent of concentrated ammonia water) is pipetted 10 cc. of the lime-sulfur solution and the liquid, under constant stirring, is titrated with standard tetrathionate until the yellow tint disappears, or in case of used dipping baths, becomes faint. For finishing the titration a one per cent solution of nickel sulfate is used as an indicator, with a white spot plate and a medicine dropper, as in obtaining the end-point of the sulfide-base titration with sodium nitroprusside. But in this case it is better to place a drop of the nickel sulfate on the plate first, then to add enough of the solution under titration to fill the cup if color does not appear with the first drop. The end-point, passing from faint gray to faint bluish green, is much sharper than any the writer has been able to obtain with any indicator when a metallic salt solution is used as the titrating agent, largely because of the relatively small bulk of the precipitated sulfur compared with that of insoluble metallic sulfides. It is recommended, however, not to attempt to catch the end-point closer than within limits of 0.2 cc. of  $N/20$  tetrathionate. If two tests, 0.2 cc. apart, are respectively positive and negative, the true end-point may fairly be taken at the intermediate 0.1 cc. To this figure is then to be added a correction for the end-point of 0.2 cc.  $N/20$

tetrathionate. The fewer the tests and the less the time consumed in titration, the more accurate will naturally be the result. A 0.2 per cent solution of sodium nitroprusside, as an indicator, affords a more conspicuous color until just before the end-point and so may be useful in titrating very dirty solutions. But just at the end-point it is not quite so sensitive as nickel sulfate and yields a very evanescent color. Its use demands a slightly higher correction for end-point, probably 0.4 cc. of  $N/20$  tetrathionate.

## EXPERIMENTAL

**I. COMPARISON OF INDICATORS FOR SULFIDE-BASE DETERMINATION**—The personal factor involved in the use of indicators limits the value of experimental results, but since a new indicator is here proposed it is necessary to give some evidence of its probable reliability. The samples were prepared by diluting highly concentrated proprietary preparations. The pairs of figures for nitroprusside indicator show the limits within which the end-point was located in each titration.

TABLE I—COMPARISON OF INDICATORS FOR SULFIDE-BASE TITRATION  
Results expressed in cc.  $N/10$  HCl per 10 cc. sample

Sample	Methyl orange	Congo-red	Sodium nitroprusside
A.....	21.60	21.55	21.50-22.00
		21.55	21.60-21.80
	21.62	21.45	21.50-21.60
	Av., 21.61	Av., 21.52	Av., 21.60
B.....	20.70	20.64	20.50-20.70
	20.63	20.64	20.60-20.70
	Av., 20.67	20.69	20.70-20.80
		Av., 20.66	20.60-20.70
			Av., 20.68

The spot plate must be left at rest full fifteen minutes before a final decision is made. On long standing the positive tests tend to fade to a brownish tint, while the negative tests take on a transparent greenish tint, but these changes in no respect affect the sharp location of the end-point. For plain sodium sulfide solutions the nitroprusside indicator is not so satisfactory.

**2. DECOMPOSITION OF TETRATHIONATE IN ALKALINE SOLUTIONS**—A tetrathionate solution was prepared by nearly decolorizing  $N/10$  iodine with  $N/10$  thiosulfate, then adding a little hydrochloric acid to decompose any iodate, and finishing by titrating with thiosulfate from a burette, without starch. The solution was then made faintly orange to methyl red. Portions of 75 cc. of the neutralized tetrathionate

TABLE II—THE DECOMPOSITION OF TETRATHIONATE IN ALKALINE SOLUTIONS

Test No.	Temperature of Solution, 28° C.				N/10 I for titration
	Cc. of 10 per cent $NH_4Cl$ added	Cc. $N/10$ $NaOH$ added	Time of standing Minutes	Cc. $N/10$ HCl for titration	
1	0	10	10	1.13	7.52 cc.
2	5	10	10	9.97	1.5 drops
3	5	10	20	9.92	2 drops
4	5	10	40	9.90	3 drops
5	0	0	200	0	1 drop

solution were brought into 300 cc. glass-stoppered Erlenmeyer flasks and made to 100 cc. with or without the addition of ammonium chloride:  $N/10$  caustic soda was then pipetted in with thorough mixing, the flasks were stoppered and left standing definite periods. Finally the solutions were titrated, first with  $N/10$  hydrochloric acid and methyl red, then

<sup>1</sup> Method given in *Bur. Chem. Bull.*, 152 (1912), 70. In view of the usually small titration the writer always adds about 1 g. potassium iodide to the solution before titration to insure proper development of the end-point.

with  $N/10$  iodine and starch. The hydrochloric acid was standardized in a parallel manner, by titrating against 10 cc. of the  $N/10$  caustic soda in 100 cc. distilled water.

In the iodine titration of test No. 2 one drop of iodine yielded a very faint blue, but too faint to be comparable to an ordinary titration. The results indicate that in a regular determination, carried through according to directions, the error due to decomposition of tetrathionate can scarcely amount to more than one drop of either  $N/10$  hydrochloric acid or iodine.

3. TESTS OF METHODS I, II, IIIA AND IIIB ON LIME-SULFUR SOLUTIONS—An approximately double-strength dilution, prepared from a commercial concentrated lime-sulfur solution, was distributed among small bottles, well filled and sealed. Measured portions of this stock solution were then diluted with equal parts of water,  $N/20$  caustic soda, and  $N/20$  hydrochloric acid. These final dilutions were likewise distributed among small bottles, and analyzed within two hours after preparation. The standard solutions employed were all referred to the  $N/10$  hydrochloric acid as a base, the caustic soda by direct titration, the iodine in the following manner: Solutions of potassium iodide, 5 per cent, and potassium iodate, 0.5 per cent, were prepared, and, appearing slightly alkaline, were neutralized after the addition of methyl red. Neither solution gave color when treated with acid and starch. In mixing 25 cc. of the two solutions, and adding starch, no color developed, but after adding one drop of  $N/10$  hydrochloric acid to 25 cc. of the potassium iodate, then mixing with 25 cc. of the potassium iodide and lastly with starch, a pronounced blue appeared. The solutions having thus shown their neutrality, 25 cc. of the potassium iodide, 25 cc. of the  $N/10$  hydrochloric acid from a pipette, and lastly 25 cc. of the potassium iodate, were placed in a 200 cc. Erlenmeyer flask. The solution was then immediately titrated with  $N/10$  thiosulfate of proved neutrality, starch being added at the end. As the next step 25 cc. of the  $N/10$  iodine were pipetted into 50 cc. of slightly acidified water contained in a 200 cc. Erlenmeyer flask and the solution was immediately titrated with the  $N/10$  thiosulfate. In this way was obtained a direct comparison of the standard acid and iodine, which was a point of vital importance. Table III contains the results obtained, corrected to  $N/10$  standard.

The reason that only duplicate results are given for the "reaction figures" is that methyl orange was employed for the others, this indicator being later rejected together with its results, in favor of the more sensitive methyl red.

In considering the results of Table III, it is necessary to note that the titrations were sometimes performed in different dilutions of the stock solution prepared at different times, and that we are dealing with a material of poor keeping powers. The figures on the same line in Columns V and VI should check.

Solution B, compared with Solution A, provided no chemical reaction other than neutralization has occurred, should show a "sulfide-base figure" of 24.17 +

2.50 = 26.67. The actual figure is 26.40, that is, 0.27 less. Likewise the "reaction figure" of Solution B should be +2.50 — 1.01 = +1.49, but being actually only +1.20, it shows a loss of 0.29, closely agreeing with the loss on the "sulfide-base figure."

TABLE III—TESTS OF METHODS ON LIME-SULFUR SOLUTIONS

Preparation of solutions	I Sulfide base figure; methyl orange	II Reaction figure	III Total iodine titration	IV Thiosulfate titration	V Sulfide-base figure; Method A (I-II)	VI Sulfide-acid figure; Method B (III-IV)
A—Stock solution diluted with an equal volume of water..	24.20 24.25 24.15 24.07	—1.02 —0.99	25.97 25.88 25.93 25.93	0.65 0.65		
Mean,	24.17	—1.01	25.93	0.67	25.18	25.26
B—Stock solution diluted with an equal volume of $N/20$ NaOH.....	26.30 26.50 26.40 26.42	+1.17 +1.23	26.01 26.00 26.01 25.99	0.85 0.84 0.88		
Mean,	26.40	+1.20	26.00	0.86	25.20	25.14
C—Stock solution diluted with an equal volume $N/20$ HCl.	21.80 21.74 21.63 21.70	—3.10 —3.13	25.71 25.64 25.63 25.57	0.65 0.67 0.68 0.69		
Mean,	21.72	—3.12	25.64	0.67	24.84	24.97

The apparent loss is largely, at least, explicable through the formation of thiosulfate which has evidently occurred as shown by the figures for the thiosulfate titration.

Comparing the results for Solution C and Solution A, the former ought to show a sulfide-base figure of 21.67, while the actual figure found is 21.72, in good agreement. It ought also to show a reaction figure of —3.51, but actually shows only —3.12, a loss of 0.39. This loss is of course mainly attributable to the escape of hydrogen sulfide which is likewise shown by the loss of 0.29 in the total iodine titration.

Altogether the writer is unable to discover any fundamental weaknesses in the methods not inherent in most titration methods as executed under practical conditions. That the results in Columns V and VI, which represent the same value obtained by two distinct methods, do not show greater horizontal differences, in view of the character of the solutions operated upon and the number of titrations involved, must indicate the substantial accuracy of all the methods.

4. APPLICATION OF THE REACTION METHOD AND THE SULFIDE-ACID METHOD TO HYDROGEN SULFIDE SOLUTIONS—Inasmuch as Solution C of Experiment 3 showed the poorest check between the results of Columns V and VI, and since it was known that the reaction between sulfide and tetrathionate progresses normally only in alkaline solutions, it seemed that the methods could be given the severest test by attempting to apply them to a water solution of hydrogen sulfide. Therefore such a solution was freshly prepared in an amber bottle and diluted so that 50 cc. required about 10 cc. of  $N/10$  iodine on direct titration. The tests tabulated in Table IV were then carried through in the order given.

The hydrogen sulfide solution evidently became significantly weaker between the successive tests. But the close agreement between the reaction figure



and the iodine titration in both Test B and Test C indicates that the methods are reliable when applied to solutions of hydrogen sulfide. In fact they made a better recovery of the hydrogen sulfide than the direct titration method, by the ratio of about 100 to 88.

TABLE IV—TESTS ON AQUEOUS HYDROGEN SULFIDE

Procedure	Reaction figure	Iodine titration
A—Into a 500 cc. Erlenmeyer flask containing 250 cc. water were poured from a cylinder 50 cc. of sample, starch added, and the liquid titrated at once		9.06
B—Into a 500 cc. Erlenmeyer, neutral tetrathionate was prepared in usual way from 15 cc. $N/10$ I. 10 cc. of 10 per cent $NH_4Cl$ being added. After diluting to 50 cc., 25 cc. of $N/10$ $NaOH$ were introduced, followed by 50 cc. of sample. Stood three minutes before titration.	10.22	10.29
C—A repetition of B, except stood 6 minutes before titration.	10.09	10.05
D—A repetition of A.		8.72

Moreover, the iodine titration of the thiosulfate progresses decidedly more smoothly, rapidly and with a sharper end-point than the iodine titration of the original hydrogen sulfide. The method accordingly seems to offer promise in certain other estimations of soluble sulfides or hydrogen sulfide.

5. METHOD C FOR SULFIDE-ACID FIGURE—The sample was a diluted proprietary preparation. The factor for the thiosulfate solution against the  $N/10$  iodine was found to be 0.997; therefore the factor for the tetrathionate solution was  $0.499 \times N/10$ .

TABLE V—COMPARISON OF SULFIDE-ACID FIGURES BY METHOD B AND METHOD C

Test No.	I Total iodine titration	II Thiosulfate titration	III Figure by Method B (I-II)	IV Tetra- thionate titration	V Figure by Method C (IV $\times$ 0.499)
1.....	23.82	0.98	.....	45.5-45.7	.....
2.....	23.79	0.98	.....	45.5-45.7	.....
Mean,	23.81	0.98	22.83	45.6+0.2 = 45.8	22.85

An attempt was made to determine directly the correction for end-point thus: To 10 cc. of dilute ammonia (1 : 9) in a 100 cc. beaker was added from a capillary pipette 0.10 cc. of the same lime-sulfur solution; then 50 cc. distilled water were run in from a burette as in titration. The clear liquid was distinctly yellow and gave a plain positive test with nickel sulfate. There was then added 0.20 cc. of  $N/20$  tetrathionate, after which a test with nickel sulfate yielded a positive result, but so faint that it is questionable whether it would have been detected in presence of the usual

amount of precipitated sulfur. After addition of 0.4 cc. tetrathionate the test with nickel sulfate was negative. A repetition gave an identical result. The theoretical titration would, of course, be 0.46 cc. It seems therefore that a correction of about 0.2 cc.  $N/20$  tetrathionate may fairly be added to compensate for insensitiveness of indicator and slight oxidation which must necessarily result from the action of the air during titration.

Though Table V showed excellent results for Method C, there still remained the possibility that the method might not be trustworthy for solutions containing an excess of lime on account of possible appreciable decomposition of tetrathionate in alkaline solution before reaction with sulfide had gone to completion. Therefore 10 cc. portions of a lime-sulfur solution were titrated with tetrathionate after being diluted as follows: (a) with 10 cc. dilute ammonia, as in the regular method, (b) with 10 cc. concentrated ammonia, (c) with 10 cc.  $N/10$   $NaOH$  and 1 cc. concentrated ammonia. Several repetitions of the titrations gave exactly the same result for all, namely, an end-point between 52.5 and 52.7 cc. standard tetrathionate. Evidently the titration is entirely trustworthy when carried out on solutions strongly alkaline with ammonia, or alkaline to saturation with calcium hydroxide, the conditions produced under (c).

#### CONCLUSIONS

The methods described appear scientifically sound, being based on definite reactions and—assuming the absence of sulfites—involving no significant errors of which the source and probable magnitude cannot be estimated. They also appear practically applicable for use in the laboratory, some of them affording the desired information even for dirty dipping baths through which cattle and sheep have passed. The operations, though perhaps appearing numerous at first sight, are simple and rapidly executed when once the procedure has been grasped, while the standard solutions required are only those commonly at hand in all laboratories. Some of the methods appear to offer promise for the determination of hydrogen sulfide or compounds thereof in other materials.

BIOCHEMICAL DIVISION, BUREAU OF ANIMAL INDUSTRY  
U. S. DEPARTMENT OF AGRICULTURE  
WASHINGTON

## LABORATORY AND PLANT

### THE PRODUCTION OF AMMONIA FROM CYANAMIDE<sup>1</sup>

By W. S. LANDIS  
INTRODUCTION

After working for many years on the problem of the fixation of atmospheric nitrogen in the form of cyanides and cyanamides, the outbreak of the Boer War forced Professors Frank and Caro of Berlin to turn their attention to the utilization of their products otherwise than in the field of precious metal extraction. A consequence of the then existing economic situation was the discovery of the process of transforming the

<sup>1</sup> Presented at 8th Annual Meeting of the American Institute of Chemical Engineers, January 12, 1916, Baltimore, Maryland.

cyanamide compounds into ammonia. United States Patent No. 776,314, granted November 29, 1904, most probably represents the first American publication on this subject.

According to the specifications of this patent various cyanamide compounds and derivatives, including the crude form of the calcium salt sold under the name of Lime Nitrogen, when treated with steam or water in the proportion of three molecules of water to two atoms of the nitrogen in the cyanamide salt, will yield ammonia. It is recommended in the specifications that the reaction be carried out at temperatures from

160–180° C. in a closed vessel, though the claims of this patent cover temperatures above 100° C.

There has grown around this process and its later refinements in the last fifteen years an extremely important ammonia industry. Naturally the greatest development has been in Europe, its home, and it is only within the past year that a plant comprising full-sized apparatus has been in operation in the United States. In attempting to catalog the various plants throughout the world which have been converting cyanamid into ammonia in large scale operations, I find that available information, particularly since the outbreak of the European War, is so incomplete that the listing in consequence was very inaccurate. It is certain, however, that the transformation of cyanamid into ammonia is successfully carried out in Norway, Germany, France, Switzerland, Italy and Japan, and, prior to the war, in Belgium, the bulk of the product going into ammonium sulfate for the chemical and fertilizer trade. Norway is producing large quantities of ammonia used in the Birkeland-Eyde plants for the production of ammonium nitrate; France has produced considerable quantities of anhydrous ammonia by this process; at the present time Germany is producing enormous quantities of nitric acid from this cyanamid-ammonia by a newly developed oxidation process, and is erecting cyanamid plants equipped with ammonia apparatus at various places.

The fixation of atmospheric nitrogen, chiefly due to our Government's policy in respect to water power development, has not been practiced in the United States. During the year 1914 contracts were let in Germany by the American Cyanamid Company for the equipment of the largest single ammonia plant then projected or operating in the cyanamid industry, but the outbreak of the European war interfered with the shipment of this apparatus, nearly all of which was seized by the German Government for the purpose of providing for its own explosive requirements. It was possible to bring only a small portion of this equipment over to the States, where it was set up and put into operation, and is now producing several tons of pure ammonia gas per day. This plant has been in continuous operation here for six months without any signs of trouble whatever and is considered to be most successful and satisfactory in every way.

#### RAW MATERIALS

The crude Cyanamid or Lime Nitrogen is now a well known commercial product. The Canadian factory supplying the United States and its insular possessions with this product has a capacity of fixing nitrogen equivalent to 90,000 lbs. of ammonia per day, and with the completion of certain additions now being made will be capable of supplying some 110,000 lbs. of ammonia each 24 hours. The demands for this product, most of which goes into the fertilizer industry, are so great that the plant is now operating at its full rated capacity. It is therefore evident that the supply of raw material for an ammonia industry is in no sense limited.

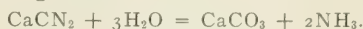
Crude Cyanamid or Lime Nitrogen, the reagent used

for the production of ammonia, is an electric furnace product, whose production has been described elsewhere by the writer.<sup>1</sup> This material as turned out of the furnace contains nearly 25 per cent nitrogen in the form of  $\text{CaCN}_2$ , 12 per cent  $\text{CaO}$  and 12 per cent carbon, with miscellaneous impurities derived from the various raw materials entering into its manufacture.

The other raw materials entering into the ammonia process are soda ash and hydrated lime. The quantities used are small, being approximately, 3.5 and 2 per cent respectively of the weight of Lime Nitrogen used. Steam and power requirements, which vary with the size of the plant, are discussed later.

#### CHEMISTRY

On treating Lime Nitrogen with steam, ammonia is produced from the calcium cyanamide according to the following reaction:



The reaction is almost quantitative when carried out on a large scale according to the process to be described later in detail. This reaction is exothermic in character, and while the exact heat of formation of calcium cyanamide has never been determined accurately it is believed that the heat evolution from the decomposition of the cyanamide alone amounts to between 200 and 300 lbs. cal. per pound of ammonia evolved. This plays an important part in the present method of carrying out the process, inasmuch as after once starting the reaction under proper conditions it will proceed of itself, and, in fact, with such great velocity that only complicated and highly developed apparatus can take care of the gaseous products.

The process as carried out in the plant operating in the United States is essentially that described in the specifications of United States Patent 1,149,633, dated August 10, 1915, "Process of Making Ammonia from Calcium Cyanamid."

In order to take advantage of the exothermic character of the reaction, as above stated, the process is made to take place in an autoclave partly under high pressure. This apparatus consists of a steel tank approximately 6 ft. in diameter, 21 ft. high and capable of operating under a working pressure of 300 lbs. per sq. in. It is provided with a powerful stirring apparatus. Into this autoclave is charged about 12,000 lbs. of mother liquor derived from a previous operation (fresh water to start), and Lime Nitrogen is slowly fed into this liquor under continuous agitation. As the Lime Nitrogen contains always a fraction of a per cent of undecomposed carbide, acetylene is evolved during this dissolving of the Lime Nitrogen. A proper ventilating system is provided to remove this acetylene at such dilutions as will be non-explosive even if subjected to a source of ignition. The charging is usually carried on over a period of an hour so as to insure a thorough incorporation of the Lime Nitrogen with the solution and the breaking up of all lumps in the slurry. When the Lime Nitrogen has all been added to the autoclave the reagents—soda and lime—are added

<sup>1</sup> THIS JOURNAL, 7 (1915), 433



for the purpose of increasing the efficiency of ammonia evolution, principally through prevention of the formation of polymeric forms of cyanamide compounds which are difficult of transformation into ammonia. The autoclave is then closed and steam is admitted for approximately 15 minutes, or until the pressure gauge on the autoclave registers 3 or 4 atmospheres, which indicates that the temperature in the autoclave

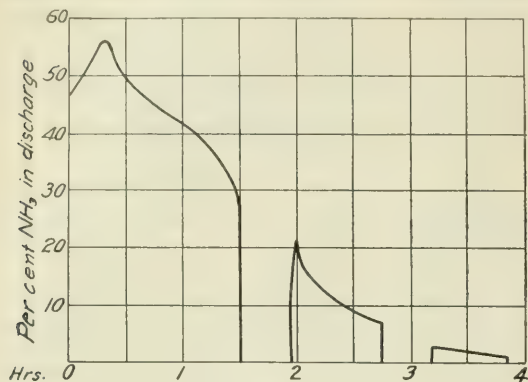


FIG. 1

has been raised sufficiently to start the reaction at a fair rate of speed. The reaction then proceeds of itself, generating ammonia and steam in the autoclave, and it is necessary to relieve this gas accumulation, by means of suitable valves, to avoid excessive pressures in the apparatus. The rate of reaction becomes cumulative as the temperature rises, and this relief of ammonia and steam must be permitted. Under normal working conditions the pressure in the autoclave will rise to about 12-15 atmospheres in the course of about 20 minutes, with the relief valve open. The pressure then drops off slowly, as the gas is discharged, the rate of discharge being usually regulated by the attendant at the valve so as to maintain a constant pressure in the ammonia line, and at the end of about one and a half hours from the start of the operation the evolution has usually stopped. Nearly all of the cyanamide in the charge has been decomposed during this first period of the operation, but the solution is still highly charged with ammonia, which it is necessary to expel. A very small amount of undecomposed Lime Nitrogen may be left, particularly of polymerized forms, which yield up ammonia only slowly. The steaming operation is then repeated, this time introducing steam until the pressure of the autoclave goes up to 6-8 atmospheres. The ammonia discharge valves are again opened until the autoclave is discharged, requiring a period averaging approximately one-half hour for this second discharge. In order to insure practically complete evolution of all the ammonia in the autoclave it is advisable to again repeat the steaming to 6-8 atmospheres for a third period, discharging as before. During this last period of steaming and discharge rarely over 2 per cent of the total ammonia as charged is evolved, and it can, therefore, be omitted if extraordinary demands on the capacity of the apparatus are made.

Extended studies of the course of this decomposition of Lime Nitrogen in the autoclave have been made both abroad and in this country, and are here reproduced in the form of charts. The discharge from the autoclave consists of a mixture of steam and ammonia, the composition progressively changing during the cycle. This variation in composition is shown for an actual operation carried out in this country in Fig. 1, in which the ordinates represent the percentage of  $\text{NH}_3$  by weight in the ammonia-steam mixture discharged from the autoclaves, and the abscissa the time after start of the operation, analyses of discharge being made at approximately three-minute intervals.

The rate at which ammonia is discharged from the autoclave under operating conditions varies with the imposed condition. It has been found that most requirements are met by discharging at such rate as to maintain a constant pressure of steam and ammonia in the main leading from the autoclave. Under such conditions the rates of discharge during a given operating cycle are represented by the curve in Fig. 2, in which the ordinates are the pounds of ammonia discharged per hour, and the abscissa again the various elapsed times from the start. In this case the charge in the autoclave was 7000 lbs. of Lime Nitrogen analyzing about 26 per cent equivalent  $\text{NH}_3$ .

Where a uniform supply of ammonia is required it can be obtained by the insertion of a special type of gasometer in the system. Also suitable grouping of a number of autoclaves and cyclical operation of the same will assist greatly in obtaining a uniform rate of production without the use of such gasometer.

In Fig. 3 is shown a curve of the pressures existing in an European autoclave, slightly smaller than the one described above, and operating on a charge of 8000 lbs. of Lime Nitrogen. The dotted lines represent

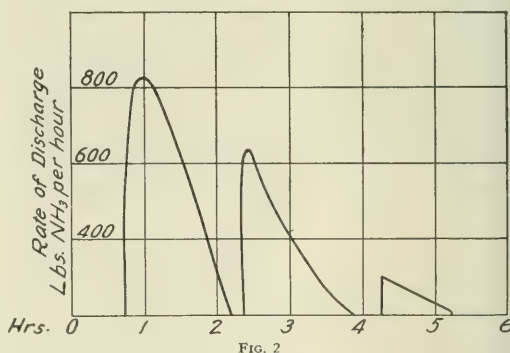


FIG. 2

the admission of steam, and the full lines the pressures as shown on the gauge on the autoclave. The ammonia discharge valves of the autoclaves are opened where the lines are indicated double.

At the close of the operation the bottom discharge valve is opened and the mud contained therein runs by gravity into large suction filters of the well known "Nutsche" type. Here the liquor is sucked off from the solid constituents, a thorough wash with water is given and the sludge removed to the dump. Under

normal operating conditions this sludge when dried contains less than 0.2 per cent of equivalent ammonia, and about 65 per cent of CaO in the forms of carbonate and hydrate. It is dark gray or black in color, due to the carbon present, and finds application as an agricultural lime. The liquor removed from the filter is used in dissolving the next batch.

#### HANDLING THE GAS

In the manufacture of ammonium sulfate, as carried out extensively abroad, the mixture of steam and ammonia coming from the autoclave is led directly into an absorber and produces a high-grade white sulfate. This production of sulfate is much simpler than from ammonia liquor. Where the introduction of the accompanying steam is not permissible, as in the production of certain ammonia salts which cannot be subjected to high temperatures, or where the process involves subsequent evaporation and crystallization, the ammonia-steam mixture coming from the autoclave is passed through a simple rectifying column provided with dephlegmator and condenser, and there is obtained therefrom a practically chemically

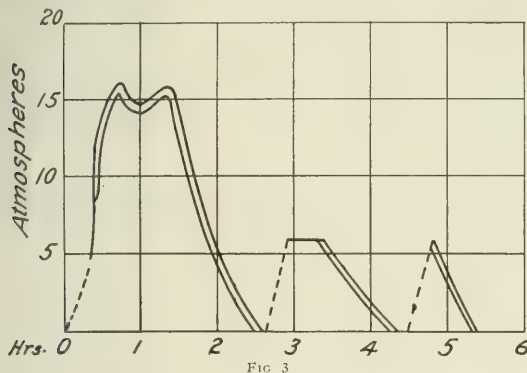


FIG. 3

pure ammonia gas, saturated with moisture at the temperature of the condensing water. This rectifying column is self-acting because of the large quantity of steam admitted with the ammonia-steam mixture, and requires no attention whatever in its operation, other than to shut off the cooling water to the condenser when not in use.

The ammonia derived from the column, as before mentioned, is practically chemically pure, and is used directly in a large number of chemical industries. The Birkeland-Eyde engineers absorb this ammonia gas in distilled water, forming a dilute aqua ammonia, which they add directly to their dilute nitric acid for the manufacture of ammonium nitrate, the product being of extraordinary quality. On the other hand, ammonium nitrate of equal grade may be produced directly from the ammonia gases dehydrated in the column without the water absorption step.

One of the large autoclave plants in France has been manufacturing anhydrous ammonia for years, and in addition to the above purification system they have installed an oil washer, charcoal filter and lime drying boxes before liquefaction. The oil washer, the writer was informed, was installed to remove some very

minute traces of an unknown organic compound, but he has inferred that the character and quantity of this impurity, from the manipulation of this apparatus, is largely mythical.

For the production of nitric acid from ammonia, the product as taken from the condensers attached to the ammonia column is so pure that no trouble is occasioned by the poisoning of the catalyzers used in its subsequent oxidation.

#### COMPLETE PLANT

I have with me assembled drawings of an autoclave plant of 16 autoclaves, such as supplied the Birkeland-Eyde Co., which is similar to those intended for this country. The rated capacity of the plant is 75,000 lbs. of ammonia gas per day. Owing to the present inability to obtain this apparatus from Germany, where it has been manufactured on an extensive scale, the American Cyanamid Company has re-designed the whole equipment, adapting it to American standards and manufacturing conditions, and is now building this equipment in the United States.

#### EFFICIENCY OF DECOMPOSITION

An extended study made by the writer a year ago of one of the European plants which had been in operation for a long time, showed that the transformation efficiency of the nitrogen in the Lime Nitrogen into ammonia was over 99 per cent. Our American plant is showing operating efficiencies, covering a period of several months, substantially equal to the above.

#### AUTOClave PLANT

An economical autoclave unit is one of eight working shells. As the operating load factor on these autoclaves is very close to 100 per cent it is not necessary to supply more than one spare shell to this eight-autoclave equipment to insure a full 100 per cent load factor. Such a plant of eight autoclaves would require a 300 h. p. boiler. It was the old practice abroad to set the safety valve on the autoclave shells at 20 atmospheres and operate the boiler at this same pressure. In our own designs here in the States we have successfully operated at 125 lbs. steam pressure without trouble and can take steam from a common plant main. Superheated steam is preferable for the purpose, but not absolutely necessary. There is in addition required for operating the Lime Nitrogen feeding device, the stirrers in the autoclaves, the vacuum pump and the air compressor, and miscellaneous sludge disposal equipment, a continuous motor load of approximately 100 h. p. (the connected motor load would probably average about 200 h. p. depending upon local conditions).

#### OPERATING COSTS

In the compilation of a cost sheet for the production of ammonia from Lime Nitrogen there is such great latitude in unit costs concerned that the writer is presenting rather full quantitative data to which he is appending assumed unit costs. In most cases the assumed unit costs are averages existing before the outbreak of the European war; to these an approximate return may be expected after its close. In



any case they may be readily corrected to meet local conditions.

LIME NITROGEN (20 PER CENT AMMONIA) is unquestionably the cheapest source of nitrogen (ammonia) in this country. The sales prices are dependent to an extent upon the quantities and deliveries contracted for. The freight is allowed at \$3.00 per ton of Lime Nitrogen shipped in special containers, which should cover the greater portion of territory in the United States lying within a 500 mile haulage radius of Niagara.

CAUSTIC LIME is to be air-slaked on spot, 2 per cent weight of Lime Nitrogen used assumed at \$6.00 per ton delivered.

SODA ASH: 3.5 per cent of weight of Lime Nitrogen at \$16.00 per ton delivered.

POWER: 100 h. p. continuous at 1c. per h. p. hour.

STEAM: at 30c. per 1000 lbs., 60 per cent weight Lime Nitrogen.

WATER: 2 U. S. gals. per lb. ammonia. As the larger part of this is used in condensers and coolers the greater proportion may be salt water. Assumed at 2c. per 1000 gals.

LABOR AND SUPERINTENDENCE: Assumed at 300 men-hours per day at 30c. per man-hour.

REPAIRS AND RENEWALS: \$1.50 per ton ammonia, a record of long time operations.

INTEREST: Assumed at 6 per cent on plant cost of \$120,000.

DEPRECIATION: On plant cost of \$120,000 depreciated in 10 years, say 8 per cent.

#### OPERATING COST OF AMMONIA PLANT

Capacity 30,000 Lbs. Ammonia per Day

Gas Saturated with Water at Cooling Water Temperatures

ITEM	QUANTITY	RATE	PER DAY	PER LB. AMMONIA
Freight		\$ 3.00	\$180.00	\$0.00600
Lime	1.20 tons	6.00	7.20	0.00024
Soda	2.10 tons	16.00	33.60	0.00112
Power	2400 h. p. hr.	0.01	24.00	0.00080
Steam	72 M lbs.	0.30	21.60	0.00072
Water	60 M gals.	0.02	1.20	0.00004
Labor	300 men-hrs.	0.30	90.00	0.00300
Repairs and Renewals			22.50	0.00075
Interest			20.00	0.00067
Depreciation			26.66	0.00089
Miscellaneous			24.67	0.00082

TOTAL CONVERSION COST (excluding NH<sub>3</sub> losses) \$451.43 \$0.01505

#### COST OF PLANT

On account of the varied building conditions existing throughout the country it is almost impossible to give a detailed estimate of the cost of plant. A recent projection of such costs made by this Company for a plant of this size, from which I have deducted the cost of land, foundations and sludge disposal, shows that an ammonia plant of the size herein described could be erected for about \$120,000. This plant is designed to produce as its final product an ammonia gas cooled to the temperature of the available water of the condensers, and, therefore, not strictly anhydrous. This figure further assumes that water and power are furnished the plant, and no provision is made for power or pumping plants.

Steel buildings with corrugated iron sides and roof, and of a type which have demonstrated themselves as fairly satisfactory for this service are included. The limitations imposed by building laws and choice of architecture may force one to materially modify this estimate, as cheaper forms of construction may be used. On the other hand, many may prefer a more elaborate type of building than provided in the above estimate, which would materially raise this figure.

#### SUMMARY

The large number of installations operating with perfect success in various parts of the world for a number of years have demonstrated the commercial possibility of making ammonia from Lime Nitrogen. The plant in its present highly developed state is extremely certain in its action and simple to operate. The efficiency obtained in the transformation of the nitrogen in Lime Nitrogen into ammonia gas is upwards of 98 per cent, or almost quantitative. The consumption of reagents is remarkably small, and they are cheap and easy to obtain in almost all parts of the world.

The quality of the ammonia produced by this process is not surpassed by any in the United States. It is chemically pure as produced and requires no further costly and tedious purification to render it available for the highest grade chemical products, or for the production of liquefied anhydrous product. The actual cost of production of this high-grade pure ammonia on a considerable scale, which enables one to take advantage of the lower prices at which Lime Nitrogen is offered, brings high-grade cyanamid-ammonia into the market almost as cheaply as the more impure forms already found there, and very much cheaper than it is possible to obtain an equal quality of ammonia from gas house liquor, the coke ovens, etc.

NEW YORK CITY

#### MANGANESE IN GROUND WATER AND ITS REMOVAL

By S. B. APPLEBAUM

Received June 10, 1915

Ground water as a source of municipal supply is constantly growing in importance. For many municipalities it is the only available source. For others, it is often the best alternative when a surface supply, formerly wholesome and potable, becomes sewage-polluted. In this respect, well waters rarely fail to meet the demands of modern sanitary science. It is only when engineering conditions of yield in dry periods and chemical considerations of the mineral composition of such waters are taken up that difficulties arise. The troubles resulting from the hardness or iron content of ground water and the most economical methods of removing these constituents are matters well understood. But the evil effects of manganese and the pressing need of its removal when it is found present do not seem to be fully appreciated by our water works engineers. Superintendents of municipal water works rarely, if ever, have their supplies tested for manganese and the ordinary effects of that element are often probably reported as iron troubles difficult to cure.

This article is a summary of the experience with manganese-containing waters of European cities, especially in the North German alluvial plains during the last decade. Further details and much valuable matter can be found in German publications by R. Gans, H. Luhrig and Weiss, extracts of which have been printed in the *Gesundheits-Ingenieur, Journal*

für Gasbeleuchtung und Wasserversorgung and the Chemiker-Zeitung.

#### FORMS OF OCCURRENCE OF MANGANESE IN WATER

Manganese, like iron, is a common element in the top layers of alluvial soils and in many plant and animal organisms. As a rule, manganese will be found to occur in all ground-waters containing considerable amounts of iron. But there are waters also which contain much manganese and little iron. The Dresden supply is a good example with from 0.6 to 1.0 p. p. m. of the former and only 0.1 p. p. m. of the latter. Being elements closely akin, both are found in water attached to the same two radicles, the bicarbonate and the sulfate. In the soil, manganese and iron are usually present in insoluble forms. But organic matter, by evolving free carbonic acid or hydrogen sulfide, assists in transforming these salts into the above-mentioned soluble forms. Of the two, the sulfate is the more troublesome, inasmuch as it is the more difficult to remove.

#### THE SANITARY AND TECHNICAL EFFECTS OF MANGANESE IN WATER

From a sanitary point of view it was known as early as 1891 that troubles with microscopic growths were to be attributed to manganese as well as iron. In Germany, Proskauer examined many of the growths in pipes and reservoirs and found them to contain manganese, especially the *Crenothrix*, *Gallionella* and *Chlamydothrix*. These organisms absorb the manganese into their sheaths and form long, fibrous, gelatinous masses, which cut down the effective area and increase the friction of the water conduits in which they lodge. Occasionally these growths are loosened by heavy currents and the water issues from the faucets in a most unsightly condition.

It is interesting to note that manganese in surface waters is deadly to fish life. It seems that the brownish cast of such waters shuts out sufficient sunlight to stunt fish growth and the oxides of manganese gradually accumulate in and clog up the fish gills. In other respects, the occurrence of manganese is of no very great sanitary significance. The usual amounts present in municipal waters do not affect taste or color and even the higher quantities present in old mineral waters of repute have never seemed to affect the health of persons drinking them.

It is for technical purposes that manganese in waters is of serious consequence. In laundries, bleacheries, dye-houses, paper-mills, etc., as little as 0.5 p. p. m. of manganous oxide will have a decidedly injurious effect on the quality of the materials coming into contact with the water. In the laundries, the wash will show distinctly yellow streaks on ironing. In bleacheries, the manganese of the water is oxidized during the bleaching period and precipitated on the goods, producing a muddy white effect and especially brown spots where the water has concentrated during drying. The same applies to the finer classes of white paper. Manganese has an injurious effect also on the fermentation processes of breweries and the color-baths of dye-houses.

#### EXPERIENCE OF CITIES

The wide occurrence of manganese in European waters may be seen from the number of old mineral waters containing it. Among others may be mentioned Baden-Baden, Bilin, Eger, Fachingen, Gieshubel, Homberg, Kreuznach, Marenbad, St. Moritz, Pyrmont, Salzbrunn, Tarasp and Wildungen.

The cities that have found manganese in their supplies and experienced troubles therefrom are:

HUTSCHEIN—Water has 1.2 p. p. m. of manganous oxide.

HANNOVER—Water has 0.22 p. p. m. of manganous oxide, and manganese algae growths were found in the street mains.

HALLE—Water contains 0.1 to 0.5 p. p. m. manganous oxide.

WIESBADEN—Water contains 0.1 to 1.3 p. p. m. manganous oxide.

STETTIN—Water contains 5.2 p. p. m. manganous oxide.

BRAUNSCHWEIG—Iron removal plants were found to precipitate manganese.

NEUSALZ—Iron removal plants were found to precipitate manganese.

BERNBERG—Water contains 3 to 4 p. p. m. manganese.

FRANKFORT A/O—High amounts of manganese in ground-water supply caused those supplies to be abandoned for the river Oder.

BRESLAU—An attempt was made to substitute a ground-water supply for that of the river Oder but a sudden temporary high increase in the manganese content prevented any further development of the project.

GLOGAU—Water contains 0.7 to 6.5 p. p. m. manganous oxide.

The experiences of the latter two cities are valuable enough to deserve special consideration:

BRESLAU is on the Oder river. Until 1871 the source of municipal water supply was the unfiltered river water. Increasing pollution and danger of contamination caused the installation of a filter plant in that year. This was soon outgrown and large covered filters were added in 1893. Even this extension did not succeed in reassuring the public, panic-stricken as it was after the cholera epidemic in 1892. A movement in favor of ground-water was set on foot. There was no doubt of the existence of considerable reserves of ground-water near Breslau, but its quality, as to iron content, had always been suspicious. Now that methods of iron removal were thoroughly understood and known to be certain in their action, a test plant of 25 small wells was installed. The results were fairly satisfactory and on the data thus obtained wells were bored to yield the total 15,000,000 gallons per day. The layout consisted of about three hundred 6-in. wells about 60 ft. apart, pumped through collecting mains to an iron-removal plant of tricklers and sand filters. The plant was put in operation in the latter part of 1904 and it was soon found that the maximum safe yield was only 10,000,000 gallons daily. The iron content of the water also gradually rose from 6 to 20 p. p. m. but the tricklers and filters took care of the increase without great difficulty. In the early part of 1906, during a season of drought, the water table was observed steadily to fall. On March 28, 1906, immediately after a flood of the Oder over the lands sur-



rounding the wells, the chemical composition of the water changed completely over night. The total solids trebled. The iron rose to 100 p. p. m., the manganese to 50 p. p. m., and the water was found to be slightly acid. The tricklers and filters made a strenuous effort to remove the impurities, but the manganese would not precipitate. After a short while the greater number of the wells returned to their normal condition. But a series of wells continued to deliver water unfit for use and had to be abandoned. It is interesting to note that a similar flood of the Oder, in February, 1906, reproduced the phenomena of March.

Much interesting research has been devoted to this so-called Breslau "calamity." Geologists, chemists and engineers have published volumes of theoretical matter. But the most probable explanation, in brief, is the abnormally low ground-water level, there being only about 2 ft. of water in the wells, assisted by the flood of the Oder over the well area. The iron and manganese were present in the soil in the form of sulfides, due to the action of hydrogen sulfide produced by organic matter. As the water level fell, air entered the soil and oxidized these sulfides to sulfates. The flood carried these soluble salts down into the ground water.

Since 1906 much experimental work, especially under the direction of Dr. H. Luhrig, has been carried out in Breslau to find a practical method of manganese removal. The results of these experiments will be summarized later.

GLOGAU is also on the banks of the Oder. But the municipal water supply from as far back as 1700 on, consisted of springs in the hills south of the city. With the growth in population, however, the springs became insufficient in capacity and a search for additional supply was begun. In 1906, therefore, test-wells were sunk on Dom Island in the Oder and a fair yield was obtained. The iron content, however, was from 15 to 20 p. p. m. and the manganese, as usual, was undetermined. Nevertheless, complete plans were drawn up for a municipal ground-water plant on Dom Island. Fortunately, Dr. Luhrig, who had been consulted, made his report before these plans were executed. He cited the troubles at Breslau and warned the authorities of Glogau against taking any hurried false steps. The City decided to investigate further, especially as to iron and manganese removal. An experimental station was built to handle 15,000 gallons per hour. This plant consisted of a four-storied building, the top story containing coke towers, the third an aerated-water reservoir, the second, closed sand filters, and the ground floor containing closed manganese removal filter. The latter, about 3½ ft. in diameter and 6 ft. high, was designed to pass only about 6000 gallons per hour. It contained a bed of manganese permutit 2 ft. deep, resting on gravel with a layer of marble in the top head. The station was put in operation in October, 1908, and proved satisfactory. In 1910 three more manganese permutit filters were added to take care of all the 15,000 gallons per hour.

During 1914 the Permutit Company of Berlin erected a municipal plant on Dom Island of about three times the capacity of the experimental station. This plant consists of six closed steel filters, 7 ft. 4 in. in diameter by 20 ft. high. These tall shells contain four decks, the upper two removing the iron by aeration under pressure and filtration, the lower two, marble and manganese permutit, removing the manganese. The tall filter represents an effort towards economy and compactness.

In 1913 a manganese permutit plant was also erected in Dresden. The municipal water contains 0.1 part per million of iron and 0.6 to 1.0 p. p. m. of manganese. The plant consists of six closed filters 10 ft. in diameter and about 15 ft. high, with a capacity of 10,000,000 gallons per day.

#### METHODS OF MANGANESE REMOVAL

I. AERATION AND FILTRATION—When the manganese is present in the form of the bicarbonate and is accompanied by a considerable amount of iron in the water, it can be removed by aeration and filtration. The aeration may be effected in tricklers or under pressure in a closed shell, the filtration following through fine sand. In most iron-removal plants of this nature an examination of the precipitate on the filters will show the presence of the manganese thus removed. In Stettin the open iron-removal plant was observed to reduce the manganese content of 5.2 p. p. m. to 0.27 p. p. m. A similar effect was noted in Wiesbaden.

The shortcomings of this method of manganese removal, however, are:

1—It will not remove any appreciable amount of manganese when the raw water contains very little iron.

2—It fails completely when the manganese is present as the sulfate, as at Glogau and Breslau.

3—Even under the most favorable conditions, the manganese is not entirely removed.

4—It usually involves double pumping of the water or pumping of air.

II. ADDITION OF LIME—This method was one on which Dr. Luhrig in his Breslau experimental work laid great stress. He removed the greater part of the iron by aeration and filtration and then added a slight excess of lime-water (2-4 per cent). The precipitates of iron and manganese thus formed were allowed to settle in basins and the settled water filtered through sand. The method is an old one and is thoroughly practical, but its disadvantages are:

1—The addition of lime-water requires the most careful chemical attendance to control the amounts needed as the composition of the raw water varies.

2—An excess of lime-water is needed to complete the reaction and this excess imparts a highly disagreeable taste to the water. In Breslau, the excess was successfully removed, either by the further addition of alum, of free carbonic acid, or by mixing the effluent with filtered river water. Either of the latter operations adds to the complexity of the method.

III. ADDITION OF PERMANGANATE—This was also one of the Breslau experiments. Permanganate is an oxidizing agent *par excellence*, and attacks the manganese in all forms. Like lime it is a reagent of old standing. With an average of 8 p. p. m. of  $\text{MnSO}_4$  in water, it will not involve a cost of treatment greater than 0.6 of a cent per 1000 gallons, but its disadvantages are similar to and greater than those of the lime method.

1—With manganese in the sulfate from one of the products of the oxidation is sulfuric acid. This has to be completely neutralized, preferably by filtration through marl, which increases the hardness of the water.

2—The chemical control and the attendance necessary is still more troublesome than with lime-water. A slight excess of permanganate is undesirable and an under-dose leaves manganese in the effluent.

IV. OZONE OR ELECTROLYSIS—Dr. Luhrig also experimented in the laboratory with ozone and electrolysis. Ozone is still more effective than permanganate as an oxidizing agent, but the precipitates formed are extremely fine, making it necessary to run the filters at slow velocities. Furthermore, the cost of treatment for plants on a large scale is still prohibitive, which is also the case with electrolysis.

V. FILTRATION THROUGH MANGANESE PERMUTIT—This method is the one that was successfully tried out in Glogau in 1908 and later made the basis of the municipal plant there installed.

Permutit is an artificial zeolite or complex alumina silicate, first made on a laboratory scale in Germany by R. Gans in connection with soil studies. Much research had been devoted to fertilizers and the manner in which the nutritive elements reached the plant roots. It was noted that the operation proceeded more rapidly and effectively in some soils than in others. Gans' theory was, in brief, that this transmission of potassium and ammonium involved a chemical reaction or exchange between the soil and the fertilizer which only the zeolite soils could accomplish. He prepared an artificial zeolite by fusing together quartz, aluminum silicate and alkali-carbonate at a temperature approximating that of the earth's natural furnace, to demonstrate this reaction. By thus omitting the inactive impurities a product was obtained many times more effective than the natural zeolite in exchanging the bases found in soil for those of the fertilizer. This power of exchange was found to be great enough to make permutit commercially applicable for water purification. Undesirable bases in water, like iron, manganese, calcium and magnesium can be easily exchanged for sodium by passing the water through a bed of permutit at rates greater than those of the usual rapid sand practice.

For manganese removal, the method that was successfully applied at Glogau and later at Dresden is a slight modification of the direct exchange reaction. The sodium permutit obtained from the usual melt in the furnace is treated with a dilute solution of manganoous chloride to form manganese permutit by exchange. The latter is then oxidized by a 2 to 3 per

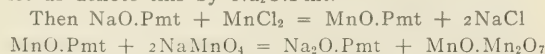
cent solution of permanganate. This treatment is carried out in the closed shell and the product thus formed is used directly as a filter bed for manganese removal.

The reactions that take place may be written as follows:

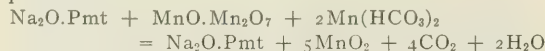
The most probable chemical formula for sodium permutit is



let us denote this by  $\text{Na}_2\text{O.Pmt}$ .



The higher oxides that are formed in the second reaction are finely divided and coat the porous grains of sodium permutit. They possess the intense oxidizing power which seems necessary for the complete precipitation of manganese, the permutit acting as a catalytic agent or a carrier of the active material. The following chemical reaction then takes place:



The filter bed becomes inactive when there are no higher oxides left on the permutit grains. When this happens permanganate is once again added and the bed is regenerated. The Glogau experimental filter above described passed 678,000 gallons between Jan. 15th, 1909, and Feb. 2nd, 1909, at a rate of 9.2 gallons per sq. ft. per minute with only one regeneration. About 8.8 lbs. of permanganate were used, giving 77,200 gallons per lb. of permanganate.

Besides regeneration, the only other attention given to the filter is a daily stirring up of the bed by means of a rake and a backwash. The water thus wasted averages about 1 per cent of the total amount filtered.

Assuming the cost of permanganate (potash preferably) to be 10c. per lb., the cost of chemical for treatment by manganese permutit ranges from 0.1 to 0.2 cent per 1000 gallons, depending upon the amount of manganese in the water. The cost of installation is not excessive on account of the high rates of filtration used. The rate at Glogau is about  $7\frac{1}{2}$  gallons per sq. ft. per minute. In Dresden the rate is 20 gallons per sq. ft. per minute.

The advantages of this method of manganese removal over those previously described may be summarized thus:

1—The compactness, due to high rates of filtration, saves floor space.

2—The pressure type of installation avoids any extra pumping.

3—The absence of any continuous chemical feed reduces the necessary attendance to that of a rapid sand plant.

4—The effluent has no corrosive tendencies on pipe. (Aeration is frequently followed by pitting due to dissolved oxygen in the water.)

5—The manganese, in whatever form it may be present, is completely removed.

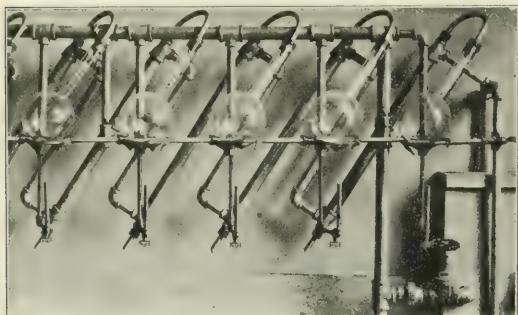


# ANOTHER MODIFICATION OF THE BARNARD-BISHOP STILL

By JACK J. HINMAN, JR.

Received September 15, 1915

The writer of this note has used both forms of the still described by Barnard and Bishop.<sup>1</sup> This type of still has many advantages which recommend it for use in a laboratory where a large number of distillations must be made. It allows the use of flasks varying greatly in size and may be placed upon a table close to the wall, allowing the greater part of the table top to be used for other work. The entire apparatus is held upon three vertical pipes and there is no confusion of water- and gas-tubing to litter the table. The burners may be readily turned to one side, raised or lowered. The modified still described herein was constructed for use in running ammonia determinations in water analysis. The changes made



from the old design were intended to give greater rigidity, better arrangements for centering the flames beneath the flasks, and also to allow the use of cooling water under greater pressure.

In the old type of still, a tapped 1-in. iron pipe acted as gas main and support for the burners and flasks. The difficulty of tapping the pipe and threading it accurately made the brass tubes somewhat insecure and rendered it almost impossible to make them lie in the same plane. This pipe is replaced in the new still by one composed of short sections of 1-in. pipe and 1-in.  $\times$  1-in.  $\times$   $\frac{1}{2}$ -in. tees. Into the tees ( $8\frac{1}{2}$  in. apart on centers) are screwed 11 in. pieces of  $\frac{1}{2}$ -in. iron pipe into which are slipped 12-in. pieces of  $\frac{1}{4}$ -in. brass tube which are threaded into  $\frac{1}{4}$ -in. brass elbows. A  $3\frac{1}{2}$ -in. brass nipple connects each of these with a Bunsen burner by means of an ordinary  $\frac{1}{8}$ -in. brass ell gas cock. A packing joint is made between the  $\frac{1}{2}$ -in. iron pipe and the brass tube by means of an ordinary valve stuffing box. A ring is soldered to the end of the brass tube to prevent its slipping through the packing and to hold it more rigidly upright. Two other 1-in.  $\times$  1-in.  $\times$   $\frac{1}{2}$ -in. tees carry 11-in. sections of  $\frac{1}{2}$ -in. pipe plugged with solder, which are connected to the condensers by ells and short nipples, and act as supports. The three upright 30-in. sections of 1-in. gas pipe which support

the entire apparatus are screwed into 1-in.  $\times$  1-in.  $\times$  1-in. tees. Two of these pipes are plugged with solder while the one at the right, which is shown in the picture, carries the 1-in. gas valve. All three are fastened to the table by 4-in flange plates.

The ordinary retort rings used in the old still are replaced by socket clamps and rings on 7-in. shafts. In order to fit on the  $\frac{1}{2}$ -in. gas pipe supports it was necessary to use the large sort of clamp used in physics laboratories. The clamps are fastened to the support to the right of the burner which is to be used. The last one is attached to the  $\frac{1}{2}$ -in. waste water pipe. This arrangement admits of easy centering of the flames under the flasks in any position, a thing which was not always possible with the variations in nipple-lengths and threading when the ring and burner had the same support and had a common center of movement.

The condensers are made of  $13\frac{1}{2}$ -in. pieces of 1-in. gas pipe, fitted with 1-in.  $\times$   $\frac{1}{2}$ -in.  $\times$   $\frac{1}{2}$ -in. tees and valve packings to hold the  $\frac{1}{4}$ -in. block tin inner tubes. They are joined with  $\frac{1}{2}$ -in. pipe. Where the condensers are supported, 1-in.  $\times$  1-in.  $\times$   $\frac{1}{2}$ -in. tees are inserted and fastened to the supports by means of short nipples. The condensers are set at an inclination of about  $60^\circ$  with the horizontal. We prefer the inclined condenser to the vertical because there seems to be less tendency to sputter. The block-tin inner tube extends  $2\frac{1}{2}$  in. below and  $11\frac{1}{2}$  in. above the end of the packing boxes. The tin pipe is easily bent by hand into the desired shape. The ends were cut off at an angle in a miter box. The cooling water passes through all the condensers and is wasted into a sink. The use of 1-in.  $\times$   $\frac{1}{2}$ -in.  $\times$   $\frac{1}{2}$ -in. tees instead of 1-in.  $\times$  1-in.  $\times$   $\frac{1}{2}$ -in. tees makes a neater appearance and in connection with the valve packing allows the use of water under the full pressure of the city mains.

Our still bank consists of 15 units. It has been in constant use for about 18 months and it has not been necessary to replace a packing. It has been found possible to make fifteen determinations at one time on the hottest summer days with the tap water at  $18^\circ$  C. without using the full pressure of the mains at any time. The water distilled over at the rate of about 10 cc. a minute and all tubes were cool.

The apparatus was constructed by the university's plumbers. New material was used throughout. The cost of material was roughly as follows:

Tin pipe.....	\$19.35
Brass tube and fittings.....	6.77
Iron pipe.....	7.50
Tees and ells.....	6.00
Valves and unions.....	2.75
Burners.....	3.00
Rings and clamps.....	19.19
Flange plates.....	0.28
Packing boxes.....	5.66
Total.....	\$70.50
Cost per unit.....	\$ 4.70

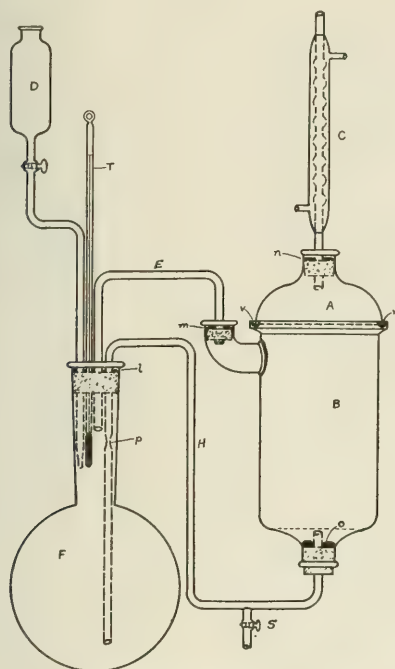
<sup>1</sup> Barnard and Bishop, *J. Am. Chem. Soc.*, **28** (1906), 1999; Bishop, *This Journal*, **7** (1915), 693.

## A LARGE FAT EXTRACTOR

By CARL L. A. SCHMIDT

Received December 11, 1915

Nearly all the types of fat extractors which have been described have been designed for the purpose of quantitatively determining fat in some particular substance rather than merely freeing a substance of its fat content so that the fat-free residuum may be used. The quantitative determination of fat can usually be made on a comparatively small sample and for such purposes the various types of fat extrac-



FAT EXTRACTING APPARATUS (1/4 ACTUAL SIZE)

tors on the market are well adapted. But when the fat from several pounds of material must be extracted, as is generally the case in the preparation of vegetable proteins, in order to obtain even a comparatively small yield of protein, recourse is generally had to some home-made type of fat extraction apparatus, since there are no extractors on the market adapted for this particular purpose.

Benson and Thompson<sup>1</sup> have described an extractor used by them in extracting tannin from sawdust. A somewhat similar apparatus was used by C. H. McCharles, of this University, for the extraction of fat from vegetable substances used in the preparation of pure proteins. I have made an extractor similar in principle by using a filtering bell jar and the top of a vacuum desiccator, both having ground glass joints. But a ground glass joint, even when clamped, will not prevent leakage of ether vapor. The apparatus described below has mercury seals at

<sup>1</sup>Benson and Thompson, *This Journal*, 7 (1915), 916.

all connections, thus preventing any leakage of ether vapor. In addition to its use in extracting fat from several pounds of material, the apparatus may be used in the recovery of the ether used in the extraction and it is even adapted for the distillation of anhydrous ether.

The extraction apparatus consists essentially of two parts, a large glass distilling flask, *F*, and the extractor *AB*, the latter made of heavy glass. The upper part, *A*, of the extractor, fits into a groove, *V*, which can be filled with mercury, thus insuring an ether-tight seal. The other joints, *l*, *m*, *n*, *o*, are likewise made ether-tight by means of mercury seals. The material to be extracted is put in a large, hardened filter paper shaped into a bag and placed in *B*, the bottom of the bag resting on a small porcelain filter plate. Vapor from the boiling ether in *F* will pass through the tube *E* and be condensed at *A*, dripping on the substance in *B*. When the ether in *B* has reached the height of the tube *H* it will siphon back into the flask *F*, provided a small constriction be made in the glass tube at *P*. The ether used in the extraction may be recovered by distilling into *B* and draining through the stopcock *S*. It may be of advantage to insert a glass siphon into the flask *F* which will eliminate the trouble of disconnecting the flask to remove the fatty residuum. Action of ether on the corks *l*, *m*, *n* may be prevented by coating them with gelatine or glue.

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## SIMPLE SODIUM LAMP FOR POLARISCOPE

By C. K. FORESMAN

Received December 30, 1915

Special lamps to produce a sodium flame for polariscopes are all expensive and more or less troublesome to adjust and maintain in working order. A simple, cheap and satisfactory substitute is here suggested.

It consists of a piece of fire- and acid-proof asbestos board about 4 in. square and  $\frac{1}{8}$  in. thick, with a slit  $3 \times \frac{1}{4}$  in. and 1 in. from the edge, cut in the asbestos. This is used in connection with an ordinary Bunsen burner with wing-top. The asbestos board is supported about  $\frac{1}{4}$  in. above the wing-top by means of a burette clamp, the burner being directly under the middle of the slit and parallel to it.

The flame burns around the edges of the slit, forming a broad double flame which is easy to locate with the instrument and of greater intensity than the usual flame. Salt is added around the edge of the slit as a saturated solution, by means of a pipette. The sides of the asbestos board may be bound with metal to support it at the ends of the slit. When one slit burns out another may be cut in the same piece of asbestos board, back of the first. The asbestos does not seem to affect the quality of the sodium flame.

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## ADDRESSES

### DYESTUFF SITUATION IN THE UNITED STATES AT THE CLOSE OF 1915<sup>1</sup>

By THOMAS H. NORTON

It is a privilege to meet with the Cincinnati Section of our Society, as it passes the twenty-fifth milestone in its history and celebrates its silver anniversary. We were a small band when we gathered together in my library a quarter of a century ago to-night, some 22 strong, to organize the Cincinnati Chemical Society. Some months passed, and the effort was made to render the American Chemical Society, up to that time largely confined in its membership to New York and the vicinity, a genuine national organization. Our young society promptly recognized its duty and applied for a charter as a Section of the national body. But one other similar organization, that of Providence, preceded us in this patriotic act; so that, to-day and for centuries to come, the Cincinnati Section stands second in the roll of the steadily increasing components of our powerful American Chemical Society.

Since then the Section has steadily increased in numbers, influence and activity, becoming one of the powerful factors in forwarding the interests of American chemical research.

The population of the city has increased by about 35 per cent during the past 25 years. The battalion of her chemists has quintupled. Let me extend my hearty congratulations on this striking evidence to the growth of the chemical interests in Cincinnati.

\* \* \* \* \*

When the great world conflict broke out, August 1, 1914, the status of the artificial dyestuff industry in this country was as follows: Six factories, employing at the utmost 400 operatives, were manufacturing coal-tar colors to the extent of 3,300 short tons annually. Imports from Europe amounted to 25,700 short tons annually. Of this quantity, German manufacturers contributed 22,000 tons. The total annual consumption of synthetic colors in the United States was about 29,000 short tons.

The industries in this country most vitally dependent upon artificial colors are the following:

INDUSTRIES	Establish- ments	Employees	Capital	Value of Product
Textile.....	5,353	915,858	\$1,841,242,131	\$1,634,636,499
Leather.....	5,728	309,766	659,231,312	992,713,322
Paper.....	2,439	145,711	527,537,821	541,736,820
Paint and varnish.....	791	14,240	103,994,908	124,889,422
Ink.....	118	1,626	9,257,817	11,370,918
TOTAL.....	14,429	1,387,201	\$3,141,263,989	\$3,229,346,981

In addition to the above there come a multitude of minor industries—feathers, furs, straw work, woodwork, shoe dressing, etc. It has been estimated that over 2,000,000 working men and working women are occupied in industries which are directly dependent upon the use of artificial colors.

If to these be added the host of industries involving the use of colored wares—the printers, painters, tailors, dressmakers, milliners, etc.—it is easily seen that a large share of the population of the United States, occupied in gainful pursuits, is directly or indirectly dependent upon regular supplies of dyestuffs.

The general public, the ultimate consumers of manufactured articles, are naturally very seriously affected by any crisis which interferes with the normal supply of coloring materials.

The reflex action of the tremendous struggle across the ocean is evident in every phase of our national life, and especially in the field of industrial effort. It can, however, be easily realized from the above statement that in no section of this field

has the influence of trans-Atlantic conditions produced such momentous results as in the manufacture and consumption of artificial colors.

The changes which have occurred since August 1, 1914, may be summarized as follows:

At the outbreak of the war the textile and other allied interests of the United States were threatened by a shortage in the supply of dyestuffs. For some weeks shipments were entirely suspended. Gradually, as the result of the most strenuous efforts on the part of leading representatives of the textile industries and of the firms engaged in importing artificial colors of foreign origin, the movement was restored to nearly normal figures. The possibility of a complete cessation in shipments was, however, constantly present as a menace, hanging like the sword of Damocles over the head of every consumer of synthetic dyes. The threatened danger arrived eight months ago, when an embargo on the shipment of dyes of German origin to neutral countries came into effect. Since March 15th no wares in this category have been received. During nearly all of this period there has been in force a permit issued by the British Government, allowing free passage to the United States of two steamer loads of artificial colors of German origin. Thus far the German Government has steadily refused to allow this supply to pass out of the Empire, unless a *quid pro quo* were accorded in the form of a shipment from the United States to Germany of an equivalent amount of cotton or of nitric acid.

This deadlock still exists. During the last eight months small quantities of coal-tar dyes of Swiss origin have reached the United States. The amount has been very limited, but it has been most welcome.

#### ACTION OF THE DEPARTMENT OF COMMERCE

On February 20, 1915, pursuant to a resolution of the Senate, a full report on every phase of the dyestuff situation was placed by me in the hands of the Secretary of Commerce. Attention was forcibly drawn to the serious risks involved in so complete a national dependence upon foreign sources for a class of products vitally essential to the very existence of our textile and many allied interests. A summary of the report was at once communicated to the Senate (S. Doc. No. 952, 63d Cong., 3d sess.). It appeared also in commerce Reports No. 47, for February 26, 1915. The full report, entitled "Dyestuffs for American Textile and Other Interests," Special Agents' Series, No. 96, was published by the Bureau of Foreign and Domestic Commerce on March 20th.

On May 1st I was instructed to study carefully existing conditions in the dyestuff industry. Visits were paid to all companies engaged in the manufacture of coal-tar derivatives, including several newly organized undertakings. An exhaustive report on this subject appeared in *Commerce Reports*, No. 115, for May 17, 1915. It soon passed into a second edition in the form of a separate reprint.

In the concluding paragraphs of this report it was shown that the available stock of dyes of German origin would probably be exhausted before the close of the summer. Strong emphasis was laid upon the imperative necessity of making timely provision for such a blow on the country's textile and allied industries. The prompt use on an extended scale of natural and mineral dyes was urged, and the pressing need of economy in the employment of coloring materials was fully demonstrated.

#### THE PRESENT SITUATION

As a matter of act, the warning was heeded. Every possible device was called into play to reduce the quantity of dyestuffs used. The average textile mill husbanded its stock of

<sup>1</sup> Author's abstract of address delivered December 20, 1915, before the Cincinnati Section of the American Chemical Society, at the exercises commemorative of the twenty-fifth anniversary of the founding of the Section.

colors so as to make it reach until about October 1st. Since then the shortage has been increasingly felt. One mill after another has been forced to close entirely or in part.

A single instance is typical. The largest full-fashioned hosiery mill in the United States (and in the world) employs 2,500 operatives. Ordinarily it requires 500 pounds of dyestuffs daily to cover the needs of its dyehouses. On October 1st its stock of colors had sunk to half a barrel. Some 160,000 dozen pairs of hose were stacked up awaiting dyes. Over 1,000 operatives were enjoying an unwelcome vacation. With considerable difficulty the manager has secured a ton of aniline oil, to use for aniline black, at a cost per pound of \$1.50. (The price in July, 1914, was 10 cents.)

The files of my correspondence show that similar conditions exist in all the branches of industry depending upon the factor of color. In every sense of the word, American textile and allied interests are facing an acute "dyestuff famine." The occasional arrival of small lots of Swiss colors, or of other artificial colors, secured by various means in out-of-the-way corners of the world, serves only to accentuate the seriousness of the situation. South America and the Far East have been searched for this purpose with exceptional diligence.

The question naturally arises in every quarter, what has the Government done to alleviate the hardships of such a famine, and what is it now doing?

The reply may be briefly formulated. Two departments of the Government only come into consideration in this connection.

The Department of State, for eight months, has exerted every possible effort to secure the free passage of German dyestuffs to our ports. Although, thus far, no results have been obtained, it continues its efforts without relaxation.

The Department of Commerce published in March, 1915, its exhaustive study of the dyestuff situation in the United States, outlining all the factors in the case. In May, it warned all industries concerned of the impending dangers. Since last February it has done all in its power to inform consumers of colors how they can most easily lessen the hardships incident to a shortage in dyes. It has inculcated economy in the use of dyestuffs generally. It has pointed out the desirability of employing natural coloring materials on the most generous scale. It has encouraged and stimulated every undertaking promising to add even the smallest amount to the available supply of dyes. It has done all in its power to prevail upon capital and enterprise to enter the field of coal-tar chemistry, to increase the supply of coal-tar "crudes," to multiply the production of intermediates, to broaden and intensify the output of American-made, finished dyestuffs. It has brought together inventors and capitalists, the producer of colors and the consumer of colors.

It has recognized the fact that all industries dependent upon the factor of color must suffer more or less from the existing conditions, and has urged a mutual spirit of conciliation and compromise between the consumers of colored fabrics and articles and the manufacturers of these wares.

#### ATTITUDE OF THE DEPARTMENT OF COMMERCE

With each added month of the current year it has become increasingly evident that American capital and American enterprise are ready to join in creating a national dyestuff industry, should it be assured of adequate protection against unfair competition on the part of foreign rivals when normal international exchanges are reestablished. The needs of the case were carefully studied by the Federal Trade Commission and by the Department of Commerce.

On September 30th, in a communication from the Secretary of Commerce to the Chief of the Bureau of Foreign and Domestic Commerce, the attitude of the Department in this connection was briefly but clearly formulated.

On October 22nd, in an address before the New York Section of the Society of Chemical Industry, the Chief of this Bureau defined more fully the attitude of the Department, in its conviction that adequate legislation was urgently needed to protect those embarking in a comprehensive coal-tar dyestuff industry against the danger of "dumping" and determined underselling on the part of the foreign competitors, hitherto dominating this branch.

Since then, it has been officially announced that such legislation will be earnestly requested from Congress at the present session.

It is now confidently hoped that American enterprise in the field of synthetic colors will soon be amply protected by a statute making as impossible in foreign trade, as it is in domestic trade, any attempt to crush, stifle, and throttle a new industry on the part of competing rivals beyond the seas.

It remains now to outline what has actually been accomplished toward a material alleviation of the hardships of this period of famine through which we are passing, and to what extent the foundations are being laid for an independent American coal-tar chemical industry.

The present dyestuff famine has made unusual demands upon the adaptability and ingenuity of the American people. It has involved readjustments all along the line, throughout the entire sequence of links connecting the cotton fields of our southern states, the flocks of sheep in distant Australia, the feeders of silkworms in the Far East, with the gayly appareled throngs on our streets. The problem is being attacked from three different angles.

#### INCREASE IN OUTPUT OF AMERICAN DYES

In the first place, the few existing American establishments devoted to the manufacture of artificial dyestuffs have notably increased their production. Prior to the war they made a somewhat limited amount of coal-tar colors. The annual output was about 3,300 short tons. For the purpose of their manufacture, intermediates were imported, chiefly from Germany. These were assembled into finished dyes by the aid of a few American chemicals, and by the labor of not over 400 workmen.

With a nearly total cessation in the importation of intermediates came the necessity for a complete revolution in the organization of the modest American industry. Prompt and resolute decisions were made. Great sums of money were invested in new plants. Before the war was 12 months old the output of American coal-tar colors had doubled. Too much praise cannot be given to the men who accomplished this *tour de force*.

This involved a notable increase in the production of coal-tar crudes. It also called into existence a number of new companies engaged in the manufacture of intermediates, especially of aniline.

The domestic supply of the crudes has now assumed large proportions. The approximate monthly output at present, in short tons, is: Benzol, 7,500; toluol, 1,870; xylo, 950; naphthalene, 12,500; phenol, or carboic acid (largely synthetic), 10,000 tons. Unfortunately, the demand for phenol, benzol, and toluol, to be used in the manufacture of explosives, is now so abnormally high that there has been some difficulty in securing enough for the makers of coal-tar intermediates. The manufacture of these latter, especially of aniline, has suddenly grown to considerable proportions and is constantly increasing. There are over 17 firms engaged in this branch and others are entering the field. There are 14 firms now engaged in making finished coal-tar dyestuffs.

#### LIST OF MANUFACTURERS

A list of the firms now occupied with the manufacture of coal-tar derivatives is here given, in view of the multitude of inquiries regarding American sources of the coal-tar products, formerly secured from European manufacturers:



## MANUFACTURERS OF COAL-TAR CRUDES

The Barrett Manufacturing Co., 17 Battery Place, New York City.

Bayway Chemical Co., Bayway, Elizabeth, N. J.

Baird & McGuire (Inc.), 23 Allerton Street, Roxbury, Boston, Mass.

Samuel Cabot (Inc.), 141 Milk Street, Boston, Mass.

Isaac Winkler & Bro., Cincinnati, Ohio.

Thomas A. Edison, Inc., Orange, N. J. (synthetic carbolic acid; monthly 150 short tons).

American Coal Refining Co., Denver, Col.

A list of the 74 retort coke oven plants in the United States on January 1, 1915, is given on page 411 of the recently issued bulletin on "The Manufacture of Coke in 1914," published by the United States Geological Survey, and forming a part of the report by the Survey on the "Mineral Resources of the United States, 1914." Copies can be obtained by application to the office of the United States Geological Survey, Washington, or to the Superintendent of Documents, Government Printing Office. Practically all of these coke-oven plants are now equipped with benzol-recovery plants and are regular sources of benzol, toluol, and naphthalene.

## MANUFACTURERS OF COAL-TAR INTERMEDIATES

The Benzol Products Co., 25 Broad Street, New York City (aniline, substituted anilines and hydroquinone). The extensive works at Marcus Hook, Pa., has received notable additions. It is now the leading source of supply. This company, organized in 1910, was the first to manufacture aniline on a large scale in this country.

Thomas A. Edison, Inc., Orange, N. J. (aniline, paraphenylenediamine). The monthly production of aniline is 138,000 pounds; of nitrobenzol, 45,000 pounds.

The Midvale Chemical Co., Elizabeth, N. J. (aniline).

The American Synthetic Color Co., Stamford, Conn. (aniline).

The Blackstone Chemical Works, 531 Grosvenor Building, Providence, R. I. (aniline).

Paul Weiler, 326 Front Street, Perth Amboy, N. J.

Middlesex Aniline Co., Lincoln, N. J. (aniline).

May Chemical Co., Perth Amboy, N. J. (aniline).

Upton Brothers, Bristol, Ind. (aniline).

The United States Coal-Tar Products Co., 40 West Thirty-second Street, New York City (aniline).

Seydel Manufacturing Co., 86 Forrest Street, Jersey City, N. J. (aniline).

The Chemical Co. of America (Inc.), Springfield, N. J.; office, 320 Broadway, New York City (aniline).

The Butterworth-Judson Co., Newark, N. J. (aniline).

American Synthetic Dyes (Inc.), Newark, N. J.; office, 60 Wall Street, New York City (aniline).

The Monsanto Chemical Works, St. Louis, Mo. (dinitrochlorbenzol).

The Middlesex Chemical Co., Chester, Conn.

The Manhattan Commercial Co., New York City (aniline).

All of the manufacturers of aniline are, naturally, able to supply nitrobenzol.

## MANUFACTURERS OF ARTIFICIAL DYESTUFFS

Schoellkopf Aniline & Chemical Works (Inc.), Buffalo, N. Y.; office, 100 William Street, New York City. This is the oldest and most important company engaged in this branch. It was organized in 1879. Prior to the war it manufactured over 100 different dyestuffs. Its colors are used very largely by the cotton textile mills, but also by silk, woolen, and other industries.

W. Beckers Aniline & Chemical Works, 105 Underhill Avenue, Brooklyn, N. Y. The works of this company, completed in June, 1915, are very extensive. It manufactures a large variety of dyestuffs and specializes on colors for the woolen industry, more particularly alizarin substitutes. Capital, \$1,000,000.

Heller & Merz, Newark, N. J.; office, 505 Hudson Street, New York City. This company specializes on coal-tar colors used for the manufacture of paper, in connection with its extensive production of mineral pigments.

The Central Dyestuff Co., Newark, N. J. A variety of dyestuffs, for use in all branches, are manufactured.

The Consolidated Color & Chemical Co., Newark, N. J.; office, 122 Hudson Street, New York City. The production is limited to a small group of standard aniline dyes, used chiefly in textile mills.

The Bayer Co. (Inc.), Rensselaer, N. Y.; office, 117 Hudson Street, New York City. This company manufactures some of the colors which are specialties of the Bayer Co., of Leverkusen, Germany.

The Pearsite Co., Clay City, Ky.; office, 346 Broadway, New York City. This company, recently organized with an authorized capital of \$2,000,000, manufactures a group of six colors from the products of the distillation of cannel coal.

The Federal Dyestuff & Chemical Co., Kingsport, Tenn.; office, 30 Pine Street, New York City. This company, organized in October, 1915, with an authorized capital of \$15,000,000, plans for the construction of several plants in different sections of the country. The first plant, at Kingsport, Tenn., is largely devoted to the production on a vast scale of sulfur black.

A. Klipstein & Co., West Charleston, W. Va.; office, 644 Greenwich Street, New York City. The recently constructed factory of an old and well known importing house is chiefly devoted to the manufacture of sulfur dyes—browns, and, especially, sulfur black.

The Dow Chemical Co., Midland, Mich. This company has embarked upon the manufacture of synthetic indigo.

The Stanley Anilin Chemical Works, Lock Haven, Pa.; office, 848 Drexel Building, Philadelphia, Pa. This company is devoting its attention largely at the outset to the manufacture of direct blacks for cottons.

The United Securities Dye and Chemical Co., Wilmington, Del. Incorporated December 11, 1915. Authorized capital, \$5,000,000.

Standard Aniline Products (Inc.), Wappingers Falls, N. Y.; office, 366 Fifth Avenue, New York City (beta-naphthol, paranitraniline, sulfur black).

The Erik H. Green Co., North Attleboro, Mass.; office Grosvenor Building, Providence, R. I. (sulfur black).

## ANILINE AND ANILINE BLACK

Aniline itself, when destined for use in dyeing aniline black, should be classed as a finished dyestuff. A large share of the aniline now being produced is used for this purpose, especially in hosiery mills. When noting that a single firm, such as the Edison Company, is turning out 69 tons of aniline each month, it is possible to grasp what is being done to lay the foundations for a comprehensive American dyestuff industry.

Verbally, and in print, it has seemed necessary to emphasize the eminent desirability of increasing the output of aniline rather than to branch out into the manufacture of a varied list of dyes. Ambitious young chemists are keenly desirous of bringing out at once finished dyestuffs in a greater or less variety. As a rule, they now recognize that they can best serve the textile and other industries dependent upon colors by concentrating their efforts on aniline. The logic of the situation plainly shows that in no other way can they, for the time being, make plant, time, and effort count as effectively in lessening the hardships of the current famine. Four-fifths of our hosiery are dyed black, and the extent to which black is used for both men's and women's apparel is evident to all.

An interesting feature in the evolution of this aniline industry—in the narrower sense of the term—is the introduction of small plants for making the oil, devised more particularly for installation in textile works, consuming relatively limited amounts for the production of aniline black. An enterprising Rhode Island firm, manufacturing itself considerable quantities of the oil, is now installing in various textile mills standard plants capable of producing daily 100 lbs. or more of aniline. Such a

plant, built to produce 100 lbs. daily, costs from \$1,500 to \$2,000. The services of a single operative are needed to carry on the transformation of benzol into aniline, with occasional assistance in the moving of heavy objects. The operations and the application of the requisite tests can be entrusted to a man of ordinary intelligence, without chemical education. The ordinary output is 90 lbs. of aniline for each 100 lbs. of benzol employed. At current rates for this hydrocarbon, it is found possible to make aniline at a net cost of from 30 to 40 cents per lb. This compares favorably with the daily quotations of \$1 to \$1.40 for immediate delivery and of \$.70 to \$.85 for early contract delivery. Within the past month two textile mills have contracted for larger plants, capable of furnishing 500 lbs. of aniline daily.

The policy of all the companies engaged in the direct manufacture of finished dyestuffs has been eminently a wise one. They have resolutely contracted the range of dyes which they attempt to put on the market. There has been a corresponding increase in the quantity of actual dyes manufactured in a given period.

It is evident to all that, under existing circumstances, every possible effort is to be directed toward enlarging the volume of the output; and this can be secured only by severely limiting the number of different dyes produced, and by corresponding simplification in organization and plant. How easily this can be done, without involving any serious hardships to consumers of dyestuffs, can be illustrated from the practice in the silk branch.

#### COLORS NEEDED IN SILK DYEING

Ordinarily silk dyers in the vicinity of New York are accustomed to use a very large variety of colors. Recently one of the leading dyers was requested by me to make out a list of what dyes were absolutely necessary. For purposes of comparison he added also the quantities of each color required annually in his large establishment, in which 3,000 dyers are employed. The following is the list:

YELLOW	LBS.	PURPLE	LBS.
Auramine.....	1,200	Hofmann's Violet N	600
Azo Yellow.....	14,000	Methyl Violet 5B	1,000
Quinoline Yellow.....	1,200	Fast Acid Violet 10B	5,000
Chrysoidine.....	3,600	GRAY AND BLACK	
Crysophenin.....	1,000	Induline	2,500
Orange IV.....	3,000	Developed Black:	
		Diaz Black BHN	10,000
		Diaz Brilliant Black B	
		Sulfur Black	15,000
		Various Direct Blacks	1,000
GREEN		BLUE	
Brilliant Green.....	1,000	Alkali Blue 2B	4,000
Diamine Green G (Direct Green).....	1,000	Charge Blue OB (Opal Blue)	2,500
RED		Methylene Blue	10,000
Alizarin Granat or Claret.....	1,500	Patent Blue	1,000
Rocellin (Fast Red).....	7,000	Victoria Blue	12,000
Rhodamine B.....	2,000	Sky Blue	1,000
Alizarin Red SX.....	2,500		

He added that the following colors were very helpful:

YELLOW	LBS.	GREEN	LBS.
Chrysamine G (Direct Yellow).....	1,000	Malachite Green	1,000
		Wool Green S	1,500
BLUE		PURPLE	
Pure Blue.....	1,000	Brilliant Violet 6B	1,000
		Various Alizarin, Algal, Ciba, Helindon, and Indanthrene Colors	
RED			
Fraise.....	1,200		
Direct Red.....	1,000		

As is seen, the actual needs of a leading silk dyer narrow down to 25 different colors. With an adequate supply of these 25 dyes, he claimed that his business would suffer no material hardship. Similar statements regarding the variety of dyes needed would hold good in cotton and woolen branches.

It is a welcome fact in this connection that four well-equipped works are now about to manufacture sulfur black on a large scale, as shown in the list above. Two other works engaged in the production of intermediates have perfected their arrangements to make ample supplies of the dinitrochlorbenzol required in this special branch.

The most interesting feature to note in this development is the establishment recently on our soil of the commercial production of synthetic indigo. This manufacture has been taken up by one of the older chemical companies and with success. The daily output will soon reach 5,000 lbs of 20 per cent paste. Naturally all that can be made is sold for months ahead. Three other powerful firms are carefully studying the possibilities of manufacturing this most important dyestuff.

When one reflects that the great "Badische" company on the Rhine expended \$5,000,000 on its indigo plant and on the necessary research, before a single pound was placed upon the market, and when we further consider that indigo is upon the free list, the pluck and enterprise now manifested in this field cannot but excite admiration.

#### EXTENDED USE OF NATURAL DYES

While the output of artificial dyes of domestic origin was thus increasing at a rapid rate, it was necessarily far removed from meeting the bulk of the country's demand under normal conditions. Here, the existing equipment in half a dozen large American works, organized for the production on a large scale of natural dyes, has proved to be a national asset of pronounced value.

The methods for using natural dyestuffs, such as logwood, fustic, cutch, etc., have been notably perfected of late. In nearly all branches of textile manufacture it has been found practicable to introduce their use. The current output of dyewood extracts is now about three times as great as it was before the war, and it is constantly increasing. Logwood blue is now in wide-spread use, instead of indigo, for dyeing denims and similar cotton fabrics.

The silk industry is already accustomed to the use of large amounts of logwood. Dyers of silk fabrics are now attentively studying the availability of other dyewood extracts under existing circumstances. A welcome addition to the domestic supply of natural dyestuffs is the handsome yellow, obtained from the Osage orange of the Mississippi Valley. The dye is the same as that present in fustic. It is, however, a pure compound, free from the varying admixture of a reddish coloring matter, which renders the use of tropical fustic somewhat uncertain. The Forest Products Laboratory, at Madison, Wis., maintained by the Forestry Service of the Department of Agriculture, furnishes full information regarding the application of this new dyestuff and the sources from which it can be obtained. It was in this laboratory that the value of the new color was first demonstrated.

#### COÖPERATION OF MANUFACTURERS AND CONSUMERS

Even with the aid of a vastly increased employment of natural dyestuffs, we meet little over one-half of our customary requirements of organic colors. It has become evident that a serious dislocation in the whole organized system of retailing and using such textile fabrics as involve the factor of color, can be avoided only by a genuine spirit of sympathy and coöperation between the two final links in the chain joining the producers of raw material and the consumers of finished products.

Manufacturers, for example, are practicing a most rigid economy in the use of color compounds. This is exemplified in the use of pencil lines for heavy stripes, in the substitution of outline designs for conventional patterns requiring extravagant quantities of color, and in analogous directions. There is also a decided tendency to urge the wearing of white articles of apparel.

In order, however, to limit to the utmost the hardships incident to such a pronounced shortage of dyes, the conditions must be met in a brave and common-sense manner. Unless the American public is willing to see our textile interests thrown completely out of gear, there must be a most pronounced spirit of compromise and adaptation on the part of the ultimate con-



sumer. Whims, fancies, fads, habitudes of the past, rivalries of the future, all must disappear before actual conditions.

Consumers must recognize and accept these existing conditions in a considerate manner, adjusting themselves to limitations in variety of shade as well as in fastness. This will take a vast burden of anxiety from the shoulders of tailors, milliners, and dressmakers. They, in turn, can make more easily their contracts with the retailer. He can deal with greater certainty and assurance with the jobber. The relations of the latter with the manufacturer will be vastly simplified, and he can with increased confidence order supplies to be handled six months or a year hence. It is a long chain. A spirit of generous compromise on the part of the ultimate consumer will give to it the needed strength. A finical, critical, fault-finding attitude will, on the contrary, cause the chain to snap and break.

#### THE PROMISE OF THE FUTURE

What is being done to lay the foundations of a genuine, comprehensive, self-contained, American coal-tar chemical industry, one which will free the country ere long from all economic dependence on foreign sources for the element of color, as needed by our vast textile and allied interests?

In reply it may be stated that amid all the great haste to meet pressing and insistent demands, with the enlargement of existing plants and the erection of new plants there is every evidence of thrift and economy. This augurs well for a complete absence of unnecessary overhead charges, as the scope of the industry broadens.

As a rule, the firms now engaged in the production of intermediates contemplate the manufacture later on of finished dyes. Mr. Edison, who has done such magnificent work in this field by his rapid organization of the production on an extensive scale of synthetic carbolic acid and of aniline, does not intend to continue the output of the latter after the close of the current war. With this exception, all of the numerous firms now occupied with the manufacture of coal-tar compounds are planning to continue their production along the lines already taken up, and to enlarge such production or enter upon the manufacture of additional intermediates or finished dyes, as circumstances dictate.

The extent to which capital has been enlisted in the development of the dyestuff industry is indicated in the list of companies now in full operation. Several other smaller companies, lately incorporated for active work in this field, reveal a widespread tendency among investors to enter vigorously upon a campaign to build up a coal-tar chemical industry.

There is quite noticeable an evident effort on the part of some ardent chemists to further the movement by attempting the introduction of hitherto unknown organic dyes, produced apparently by relatively simple chemical reactions, some from coal products, others from petroleum waste. Such attempts are regarded with a benevolent eye, as are all other efforts made intelligently and earnestly to limit the strain of the dyestuff shortage. Time must elapse before careful and exhaustive testing shows the permanent value of these new dyes, as regards cost of production and actual tinctorial properties.

Possibly some of the new colors, of entirely unknown composition, may possess enough tinctorial value to warrant their use during the period of a distinct color famine. No prophecies can be made as to the permanent value, when brought, under normal conditions, into keen competition with highly perfected coal-tar dyes of standard qualities.

It is distinctly to be regretted that in the daily press statements have occasionally appeared tending to convey the impression that these attempts to produce new dyes—for they cannot be regarded as more than attempts—were destined to revolutionize the whole color industry and immediately solve the problem of a dyestuff shortage. The entire lack of basis or any such optimistic claims I have promptly and repeatedly

shown in printed statements and in public utterances. While no intelligent chemist was misled by press announcements of this character, they unfortunately did cause more than one manufacturer, dependent upon the color factor, to feel as if all danger of a "dyestuff famine" would soon be removed.

#### FAVORING CONDITIONS

The conditions favoring the establishment of a permanent, comprehensive, American coal-tar chemical industry are as follows:

The United States possesses all the needed raw materials in abundance, in such amount that it could meet the demands of the world's dyestuff industry. It offers the largest existing market for the consumption of dyestuffs.

Enterprise, inventive talent, and technical ability are present to an almost unlimited extent.

The time is eminently propitious for the establishment of a national industry. All indications point to the continuance for a year or two of conditions—most deplorable in themselves—which favor a period of construction, free from the disturbing element of foreign competition. Capital is ready to enter the new field in ample amount and is daily being invested.

It demands simply an adequate measure of statutory protection against unfair competition on the part of foreign rivals. This, we now have every reason to hope, will soon be accorded.

It is most refreshing to note the indifference to minor side issues manifested by the men who are determined to build up this new industry. But a few years ago discussion would have centered about the tariff. To-day the men who are ready to finance a color industry or to throw into it the best of brain and nerve are asking simply for a fair show—laws to prevent a competitor from hitting below the belt.

This marked readiness of capital to now enlist generously in the new effort, this willingness even to establish upon our soil the manufacture of a coal-tar derivative, such as synthetic indigo, without a cent of tariff protection, do they not tell the whole story?

#### POSSIBLE SWISS COÖPERATION

There is possibly one factor lacking to bring rapidly into existence a comprehensive American coal-tar dyestuff industry; that is, the coöperation of a few men possessing highly developed capacity for organization, combined with a perfect experimental command of the exceedingly complex and intricate field of color chemistry in all its ramifications—men such as created in the past the great works on and near the Rhine, or those now directing them. It might be possible to secure such needed coöperation from the large and well-equipped staffs of the four color works at Basel, in Switzerland.

These highly specialized staffs include scores of men of broad experience in the manufacture of the whole range of coal-tar dyes. Most of them have enjoyed in earlier days the advantages of the "Polytechnic" of Zürich, one of the best-equipped institutions in Europe for the training of color chemists. Many have served a more or less extended apprenticeship in the gigantic German chemical works.

It is not difficult to imagine a union of forces in this field—a consolidation of interests between the Swiss companies and the American firms now striving to expand, but forced, as it were, to grope in the dark at times. The transfer of a sufficient corps of Swiss expert color chemists to the United States, at this critical moment, would be of untold value in furthering the rapid evolution of the American industry.

It would be possible, by their aid and direction, to attain, as regards time and money, the maximum of economy, in constructing new plants, in adopting the most practical and effective mechanical devices, in applying the most economical methods, in coördinating the diversified features of a complicated branch of manufacture, so as to avoid loss of material and restrict the dependence upon highly skilled and expensive labor.

At every step in the organization of a new plant, and in the initial months of its operation, directive coöperation of practical experts would insure the establishment of a self-contained coal-tar color industry on American soil, with a minimum of outlay and a maximum of efficiency in the shortest possible period of time. It would probably enable the industry, in its broader phases, to become so thoroughly rooted in the economic life of the country that, upon the return of normal international exchanges, legitimate competition of foreign rivals could be easy and effectually met.

#### SWISS CHEMISTS AND THE RUSSIAN PROBLEM

A striking example of how the dyestuff problem of a great nation can be solved by the coöperation of Swiss intelligence and experience is now seen in Russia. The textile and allied interests of the Russian Empire formerly depended chiefly upon Germany for color materials. The largest dyestuff company of Germany conducted a branch factory in Russia prior to the war. Dependence upon Germany for semi-manufactured material and for finished dyes was quite as pronounced as in our own country or in Great Britain.

The sudden interruption in current supplies of dyes, consequent upon the outbreak of hostilities, was a heavy blow to Russian textile works. A way out has been found by the organization of a strong company, of which the leading dyestuff house of Basel is a constituent member. This latter furnishes an administrative and technical staff—in other words, the “brains” of the undertaking. Capital is supplied by a group of prominent Russian textile manufacturers who at the same time are the chief consumers of the dyes produced.

The arrangement is eminently practical. As in the recent British organization, the consumers of dyestuffs are the owners and controllers of the undertaking, and a continued market for the output is assured. An abundant source of crude material is furnished by the Russian coke works. The requisite factories have been erected at a considerable distance from the present line of military operations.

What has been done so easily and simply in Russia to meet present emergencies and lay the foundation for a future national dyestuff industry can serve admirably as an object lesson to the United States, ordinarily so much more prompt in recognizing and improving industrial opportunities.

The creation of a comprehensive manufacturing plant by an alliance between Swiss experience, enterprise and skill on one side, and the large financial resources under the control of our great textile interests on the other, is a solution by no means difficult of realization. It would assure capital, management, and market, the three essential factors to success.

A less complex, and perhaps more feasible, method of accomplishing the end in view would be found in establishing a comparatively close organic connection between individual Swiss companies and individual American companies already engaged in the active manufacture of dyestuffs, but limited hitherto to a very narrow range of products.

It is well to note in this connection the relations of the Swiss color industry to both the American and the international markets.

The average annual value of the Swiss exports of artificial colors to the United States during the five years ending June 30, 1914, was \$815,911, as follows: Alizarin and alizarin colors, \$1,777; synthetic indigo, \$48,904; other coal-tar colors, \$765,230; total, \$815,911.

In 1913-14, Switzerland supplied 7 per cent of our imports of indigo and 10.6 per cent of the imports of aniline dyes. The import of alizarin was insignificant. Since the outbreak of the war, and the resultant scarcity of artificial colors, the Swiss import has been of great assistance to American textile interests.

The normal production of the Swiss dyestuff works available for export purposes has an annual value of about \$5,500,000.

It is equivalent to nearly one-ninth of the German export and could cover alone nearly 60 per cent of the average annual imports of artificial colors into the United States.

Few realize the rôle which Switzerland has played in the evolution of the artificial dyestuff industry, despite the entire absence in the land of coal and of raw material for the manufacture of chemicals, with the exception of salt. Immediately prior to the war, Switzerland, on the basis of population, was supplying twice as much as Germany relatively, to the world's market for synthetic colors.

Correspondence is now under way which may lead to a more or less close coöperation between the dyestuff interests of the two Republics.

#### PROBLEMS TO BE MET

There are several other phases in the evolution of an American color industry which deserve careful attention at the present time.

The first is connected with the somewhat rapid entrance into this field of a number of separate interests, imperfectly acquainted with the complexity of the problem.

It is well known to every one who has studied the fundamental basis of the past dominance of German color chemistry in the world's markets, that the chief cause of this marvelous control lies in the solidarity of the German industry as a whole. It is so organized that all the correlated parts act in unison. They form practically a unit when, in any land, a serious effort is exerted to secure freedom from dependence upon foreign sources of color.

The question now arises, Is it not eminently desirable that a comprehensive American coal-tar industry, striving to supply nearly all American tinctorial needs, with products made from American raw materials, should possess a higher degree of unity—financial, technical, commercial—than is now the case? Is it not of prime importance that all unnecessary overlapping and duplicating of effort be excluded, at least in the formative stage?

The problem is more easily stated than solved. It is economically important, during the initial period, that the industry should be characterized by that unity and solidarity which contribute so largely to the might and effectiveness of the German rival; and yet it must be free from any tendency toward monopolistic power.

For the moment it suffices to express an aspiration, a hope, for economic conditions which may powerfully aid a young industry in bravely holding its own.

#### STANDARDIZATION OF DYESTUFFS AND METHODS OF APPLICATION

A very distinct element of strength to a growing domestic color industry would undoubtedly result, from the establishment of a “Bureau of Standards for Dyestuffs,” possibly by the combined action of the great textile organizations of the country. Such a bureau could be modeled after the admirable Division of Chemistry in the well-organized Bureau of Standards of the Department of Commerce. Its function would be to formulate the physical and chemical criteria of purity for all dyestuffs, exactly as is now done for the drugs listed in our pharmacopeia. In the laboratories of such a bureau—and they would necessarily be vast—it would be as easy and simple to check and control the tinctorial dyestuffs as is now the case for our medicinals.

Such principles of standardization could likewise be applied to the varied methods of the application of colors on the different fibers and on other wares. A single finely equipped bureau could advantageously replace the multitude of laboratories now maintained by rival dyestuff firms or in textile works. Such an institution could effectively protect a half-grown American industry against attempts to depreciate the quality and value of American-made dyes, and could insure a far greater degree of economy in cost of production than otherwise would be possible.

Every one familiar at all with the employment of colors in



dyeing can easily picture to himself the enormous advantages resulting from the impartial and exact classification and standardization of all coloring materials encountered in commerce, or the simplification, economy, and certainty attendant upon their use in connection with the different fibers and fabrics, as well as with leather, feathers, ink, varnish, paper, etc.

Instead of hundreds and thousands of isolated, blundering attempts to obtain the best dye for securing certain color results, the desired data could be requested by return mail from a national laboratory. If a dyer wished to know exactly under what conditions, and in what quantities, a given dye should be employed to produce certain tinctorial effects upon a specific fiber, with a minimum expenditure of color, the full directions could be obtained, free of cost, with but little loss of time.

#### THE COMING NATIONAL INDUSTRY

A genuine American coal-tar dyestuff industry this country is bound to have, unless all indications prove false. Our textile and other allied interests resolutely demand that they shall never again be exposed to the disasters accompanying such a dyestuff famine as we now face. Such a powerful national organization as the Association of Hosiery Manufacturers, at a recent session, unanimously resolved that it would willingly bear the burden of increased tariff duties on dyes of foreign origin, if such be necessary, to insure the establishment upon American soil of a domestic, self-contained color industry.

American chemists insist that the one great branch of color chemistry, now wanting in the cycle of our national industries, shall be created in all its ramifications upon our soil; and that American chemical technology shall no longer be so conspicuously lacking in the most brilliant feature of applied science.

Before the advent of this deplorable war we imported annually about 2,500 short tons of aniline oil and aniline salts. In 1916 over 11,000 tons will be manufactured on American soil, from American coal-tar crudes.

In 1913 our American color works produced 3,300 short tons of coal-tar colors, made chiefly from German intermediates. We imported 25,700 tons of artificial dyes, 22,000 tons coming from Germany.

To-day we are making over 15,000 tons of these colors, all from American coal tar. Are the Nation's color chemists too optimistic in confidently looking forward to the year 1917 as a date when the great bulk of artificial dyes consumed in this country will be made in American works, from American raw material, by American labor?

When this Section, in December, 1920, celebrates the completion of the third decade of its existence, I am confident that it will witness, firmly established in our land, a comprehensive, self-contained, American coal-tar chemical industry, furnishing from the by-products of our magnificent array of coke plants, the nation's needs, not only for artificial colors, but also for high explosives, photographic chemicals, synthetic perfumes and synthetic medicinals.

BUREAU OF FOREIGN AND DOMESTIC COMMERCE  
WASHINGTON

#### THE DEVELOPMENT IN THE UNITED STATES OF THE MANUFACTURE OF PRODUCTS DERIVED FROM COAL<sup>1</sup>

By H. W. JORDAN

During 1915 we read statements in the press almost daily, which gave the impression that our American chemical industry was wholly unable to manufacture synthetic coal products, and that the only relief in sight was from the wonderful discoveries of a small group of chemical amateurs, who, having patriotically hurled themselves into the situation since the war began, were on the verge of evolving the entire 900 synthetic coal-tar dyes and the whole list of pharmaceuticals from palmetto

and other sources, hitherto unsuspected as being fundamental to organic chemical products. These statements, by implication, and by omitting mention of the extensive plants erected and put into operation by the old, established chemical companies in 1915, tended to create the public belief that these companies were doing nothing to supply the American market.

Some of the most important products which were widely heralded as having produced for the first time in America in 1915, were manufactured by these companies 15 to 30 years ago. Benzol and its homologues have been regular American products, with shipment in car-load lots or tank cars, and with occasional exportation to Europe, since 1900. Salicylic acid was manufactured at Jersey City by Zinsser & Company from 1880 until 1897, when foreign competition closed the plant.

SYNTHETIC CARBOLIC ACID was manufactured by the Smet-Solvay Company from benzol at Syracuse in 1900 and the following years, in quantities up to 2500 lbs. daily. This carboic acid was synthesized into trinitrophenol, commonly known as picric acid, which was bought by the United States Government for use in national defense. The United States had several well-equipped plants, prior to 1885, for manufacturing the principal coal dyes of that day. The industry grew, and produced an increasing number of synthetics, from which all those survive which could surmount the natural and artificial barriers in the road to a complete American coal products industry. The principal ones of these manufacturers have continued without interruption, and constitute the main body of our present organic chemical industry.

The failure to give credit in the daily press for the large amount of capital invested, and for the extensive work accomplished during the past year, is not fair to these American companies which built up our great American chemical industry during the past 30 years, and who are now the prime movers in expanding our American coal products industry to meet the new conditions.

THE BENZOL PRODUCTS COMPANY is an example of this growth. Organized in 1910 by men long associated with the acid, alkali and coal products industry, it began the manufacture of aniline and aniline salt at Frankford, Pa., in the aniline plant operated several years before by the late Dr. Jayne. Although the Company's output of aniline in 1910 was but a small percentage of the American consumption, the English and German producers immediately dropped the price from 10c or 11c per lb., where they had held it for several years, to 9c or 8c per lb.

Most of the American consumers of aniline refused to buy this American aniline at the fair price of 9c to 10c at which it was offered. Instead they followed their usual custom and sacrificed the American producer by supporting the cut-rate foreign producers.

These American consumers were the very ones who rushed to Washington when the war began, and frantically implored the Department of the Interior to dig up right away, quick, through the Division of Mines, some unfailing source of supply to provide the two thousand or more synthetic coal-tar dyes and pharmaceuticals which had required 45 years of German science and organization to develop. The trip to Washington was easy for them. They had been there repeatedly since 1880, whenever a tariff bill was under consideration, to advocate no tariff on dyes.

The Benzol Products Company received the support of a few of the most far-sighted American consumers, who realized that the permanent establishment of aniline manufacture in the United States was of far greater value than the profit for a few years on their purchase of aniline, at 2c per pound below its former price. With their support the manufacture of American aniline was continued.

Since the war, a new plant was built at Marcus Hook, Pa., and put into operation in August, 1915, with ultimate capacity

<sup>1</sup> Read at the 8th Annual Meeting of the American Institute of Chemical Engineers, Baltimore, January 12 to 15, 1916.

equal to the former United States consumption of aniline. Notwithstanding war conditions, which multiplied the price of raw materials, benzol, sulfuric acid and nitric acid, the company sold its aniline at a price less than half the prevailing market price of aniline during 1915.

This production of aniline, supplemented by that of a few other plants, has supplied the American market to a fairly comfortable extent.

The Benzol Products Company's aniline has been distributed, by preference, to those consumers who employ directly or indirectly the greatest number of people. The important fact that in 1916 a supply of aniline equal to the former American consumption will be available at fair prices, and that this supply not coming from mysterious nor untried sources.

**BENZOL SUPPLY**—Since 1900 the production of benzol has readily increased in the United States, so that there was enough benzol at all times for the manufacture of dyes, if the industry had been established by the assistance of the Federal Government and by the sustained support of the American textile manufacturers. Not only were both these lacking, but the textile manufacturers persistently favored the English and German producers in preference to any American manufacturers.

Benzol supply is only one factor, and alone it is not sufficient to justify the very heavy investments required to establish an American coal products industry.

In 1915, several steel companies operating by-product coke ovens, installed benzol recovery plants, so that a heavy production of American benzol is assured. When the war ends the output from these plants will be so abundant that it may become available as motor fuel for automobiles. In this service, one gallon of motor benzol gives 15 per cent greater mileage than does the gallon of gasoline.

#### ACIDS AND ALKALIES THE FOUNDATION OF COAL PRODUCTS INDUSTRY

Under the abnormal conditions and inflated prices caused by the war, many small plants sprung up and have produced products derived from coal, at a profit. At the end of the war, these plants will fall like autumn leaves. A few will struggle on and consume their war profits in hopeless endeavor to establish permanent business. Only those built on a firm economic basis will survive.

The manufacture of products derived from coal is not an industry by itself. It is founded upon, and is an extension of, the manufacture of mineral acids and alkalies, and was created as a means of making a wider market for those acids—sulfuric, nitric, hydrochloric, acetic, for chlorine and the like, and a market for the alkali products, soda ash and caustic soda. For this reason a permanent coal products chemical industry cannot be created in America except by cooperation with, or extension of, the American acid and alkali manufacturing companies.

**THE VALUE OF EXPERIENCE**—In 1915, with prices ten to fifteen times normal, it was possible to manufacture some coal products with large profit in the United States. With the return to normal conditions, we must conduct our processes with the closest attention to the most scientific methods, because losses of 1 or 2 per cent in the steps of manufacture mean bankruptcy. Proof that Americans sadly lack this scientific detail was given in 1915 by the many serious accidents, fires and explosions in plants manufacturing these products, the cause of which was faulty engineering design, inexperienced superintendence, untrained plant housekeeping and careless workmen. With unconscious humor, we have done homage to German efficiency by ascribing these accidents to the German diplomatic service.

To illustrate the necessity of attention to detail, take synthetic manufacture of carboic acid. This process, starting from benzol, involves five chemical reactions and from ten to fifteen chemical operations, if all by-products be recovered.

If an avoidable loss so small as 1 or 2 per cent be permitted in each of these steps, the final yield of carboic acid would be so low that the process might be a commercial failure. Yet carboic acid is one of the most simple products to manufacture.

Many others involve more steps, or steps in which the lack of technical skill produces larger loss. For example, a certain product with a normal price of 30c per pound has a possible maximum yield of 100 units attainable by extreme care in manufacture. With moderate care the yield is 88 per cent, and with only ordinary care the yield drops to 75 per cent. Expressed in dollars and cents the result per ton is:

Possible yield	100%, 2000 lbs. at 30c	\$600 per ton
Usual yield	88%, 1760 lbs. at 30c	\$528 per ton
Common yield	75%, 1500 lbs. at 30c	\$450 per ton
Loss at 88% yield		72 per ton
Loss at 75% yield		150 per ton

**NATIONALIZATION OF THE INDUSTRY**—Approach to 100 per cent technical efficiency is not the only requisite for commercial success. The intricate processes yield numerous by-products. Some are acids and alkalies which must be recovered and returned for use in the process. Others are salts or coal products which must be refined and sold. For many of these no market exists in the United States.

A network of markets must be created for every one of these by-products, either in the United States, in South America, Asia or Europe, if our American coal products industry is to grow with the world and pay reasonable dividends on the investment.

It is not sufficient that American consumers acquire the habit of buying chemicals "Made in the United States." Our chemical industry, to endure, must cover the world's market; indeed, its ultimate success may depend upon an American merchant marine.

The German system of nationalized industry handles this multitude of by-products with military precision, by fitting each one into the particular technical and commercial sink best suited to it, so that all by-products are marketed at or above cost. This permits the main product to be sold at a profit large enough to sustain the normal growth of the plant and to develop new products, without adding new capital, and in addition, to pay 10 to 25 per cent dividends.

In complete contrast it has been, and is, the policy of our Federal Government to forbid any such interlocking national cooperation.

**NATIONAL DEFENSE**—The coal products chemical industry is vital to national defense. One source of the extraordinary military strength of Germany is her ability to manufacture ammunition, literally from the air and earth, in unlimited quantity. This ability was created by the chemical industry, which built huge works and trained an industrial army of men with the scientific knowledge and technical skill necessary to transform the nitrogen of the air, and certain ones of the coal products, into ammunition. The fundamental reason for the support which the Imperial Government gave to the coal products industry was that Germany should develop a supply of ammunition adequate for national defense and world conquest.

While developing home resources, the German industry bought benzol, carboic acid and other crude coal products from England, thus absorbing England's commercial and military strength. Meanwhile we were more backward than England, for we were so quick to grasp the red-hot opportunity presented by German dyes and pharmaceuticals at low prices that we did not even take the trouble to produce enough crude coal products to export.

Ammunition cannot be manufactured in sufficient quantity during the exchange of diplomatic notes prior to war; it must be manufactured and stored long in advance of hostilities. One main national defense is that great coal products chemical plants be established and operated steadily at commercial profit



during peace, so that they will be instantly available to produce unlimited ammunition during war.

In 1915 we built many ammunition plants in the United States, every one on an artificial basis; few of them can make a profit at peace prices. Unless the United States establishes a complete and profitable national coal products industry on a basis to keep abreast of all scientific progress, our program of "National Preparedness" will descend to the plane of comic opera.

NITRIC ACID FROM THE AIR is one step in such scientific progress. Our supply of nitric acid comes now from nitrate of soda imparted from Chili. After the war, if the importations are not obstructed, we will receive nitrates and nitrogenous products manufactured in Norway and Germany by fixation of atmospheric nitrogen. Part of these products will be for fertilizer, part for explosives.

Exhaustion of the nitrate of soda mines in Chili will ultimately make the United States wholly dependent upon this European supply, unless we manufacture our own nitrates and nitric acid from the air.

The potash situation is a parallel condition. With German potash cut off, we have no potash. Various American sources will be brought into operation, but several years must elapse before we produce all the potash we consume.

Fixation of atmospheric nitrogen as nitric acid will also require several years, even though the Federal Government give the manufacture its strongest support.

Nitric acid is the effective end of every explosive and is the first chemical reagent used in the manufacture of aniline, and thence of indigo and others of the most important coal products and dyes. Without nitric acid, our entire navy, army and coast defense becomes helpless the instant the stock of ammunition is exhausted.

Our entire investment in National Preparedness will be wasted money, if it does not include the manufacture of nitric acid from the air on a scale to render us absolutely independent of foreign nitrates.

TARIFF—A reasonable tariff, if formulated upon rational lines, will be of much value in supporting our coal products manufacture. Such a tariff would divide these products into three classes according to their degree of advancement in manufacture, and would levy duties proportionate to this degree. The classes would be: 1st, Crude Products. 2nd, Intermediates. 3rd, Dyes, pharmaceuticals and highly refined products. The duties should be: on crudes 10 per cent *ad valorem*; intermediates 20 per cent *ad valorem*; and dyes 30 per cent *ad valorem*.

If a specific duty be included it should be at the rate of  $3\frac{3}{4}$  cents per lb. on the intermediate class and  $7\frac{1}{2}$  cents per lb. upon dyes and pharmaceuticals. There should be no specific duty on crude products.

The free list should include coal tar, coal-tar pitch, creosote oil and mineral acids. Natural indigo and other natural dyes of vegetable or animal origin should be placed with synthetic dyes, in Class 3.

Class 1, crude products, should comprise a small list. It should be described as: All crude products of coal produced through destructive distillation of coal, or otherwise, and not refined by more than one distillation, nor refined by any process other than distillation, nor refined nor produced by synthesis, such products being crude light oils, benzol, toluol, xylo, cumol and naphthalene, crude tar acids containing less than 80 per cent pure tar acids, and all other products from coal not otherwise specially provided for, and not medicinal and not colors or dyes, the duty to be 10 per cent *ad valorem*.

The second, or intermediate class, should include all products manufactured from those of the crude products class, and all so-called intermediates, not colors nor dyes nor pharmaceuticals

nor medicinal products, such products being phenol, cresol, aniline, anthracene, etc.—duty 20 per cent *ad valorem* and  $3\frac{3}{4}$  cents per lb. specific.

The third class should include all colors or dyes derived from coal, including indigo, natural and synthetic, and alizarine—dry or suspended in water—and dyes obtained from indigo or alizarine, and all products derived from coal, which are used for pharmaceutical or medicinal purposes, or other purposes—duty 30 per cent *ad valorem* and  $7\frac{1}{2}$  cents per lb. specific.

Natural indigo and all dyes, pharmaceuticals and medicines, and all other products derived from natural sources of vegetable or animal origin, and which are used interchangeably with similar products derived from coal, should be included in Class 3.

ANTI-DUMPING CLAUSE—There should be an anti-dumping clause to prevent unfair competition instituted for the purpose of destroying American industry. A dumping clause must be drafted with utmost care and its working tactfully handled. If it be too drastic, or if handled without good judgment, it will become worthless, or worse, because foreign countries, in retaliation, will inflict the anti-dumping penalty upon any American manufacturers who may sell their goods in those countries at lower prices than in the United States. We cannot afford to take any chances with American industry now that our export trade in manufactures is becoming better established than ever before in our commercial history.

COMPULSORY WORKING OF PATENTS in theory looks attractive. In practice there has been nothing in the history of the coal products industry which could have been changed or improved by it to the slightest degree. Compulsory working of patents has been tried in England, France and Russia as recently as 1907, and proven a total failure in those countries.

As stated by the German authority, Prof. Otto N. Witt, "the success of a coal-tar dye factory is no longer dependent upon the careful guarding of factory secrets as in the past, but upon a systematically arranged plant and the proper distribution therein of the work to be performed, and above all upon skillful commercial management, both within and without the factory."

LACK OF TECHNICAL COMMON SCHOOL EDUCATION is a further disadvantage from which we suffer. Our system of early 19th century education includes no technical or trade schools, by which in Germany, the entire population is perfected in 20th century methods for earning their living in 20th century industries. In consequence American labor does not give effective attention to its job, and it is extremely difficult to secure labor in the United States which will give competent attention to the delicate chemical manufacturing operations of the coal products industry.

#### SUMMARY

The essentials for creation in the United States of a complete industry in the manufacture of products derived from coal are: coöperation of the American acid and alkali manufacturers with the coal products industry; coöperation of the American consumers with American producers through long-term contracts to assure us the American market; establishment of the industry on a peace scale big enough to make it a fundamental factor in national defense; establishment on a profitable commercial basis of the manufacture of nitric acid, by fixation of atmospheric nitrogen; nationalization, or rather internationalization, of the industry to insure a balanced world market for all by-products; development of a system of 20th century common school and technical school education; finally, maintenance of a rational tariff.

That a larger coal products industry will be established in the United States is certain. The degree to which it attains perfection will be in proportion to the extent with which these requirements for its profitable operation are provided.

SYRACUSE, NEW YORK

## THE CHEMICAL EVIDENCE OF SMELTER SMOKE INJURY TO VEGETATION<sup>1</sup>

By J. P. MITCHELL

The injurious effect of smelter smoke on vegetation presents a problem which is serious in that it concerns the profitable development of one of the most important of the western industries, namely, the smelting of sulfide ores. It is not a new problem, but one which has become acute in recent years as a result of the development of very large smelting establishments. In fact, it is an old problem which was recognized some fifty years ago in Germany, and which still remains unsolved.

This problem of smelter smoke injury is a special case of the larger subject of smoke injury in general, using the word "smoke" in its most general sense to cover all the materials which reach the atmosphere from smokestacks. Much work has been done in the broad field of city smoke, and while the realization of the deleterious effects produced by many of the solid constituents of smoke—especially soot—has resulted in both legal and technical measures being taken for their control, much less recognition has been accorded to the less conspicuous and more insidious gaseous constituents. Smelter smoke is a peculiarly obnoxious smoke in that among its common, solid constituents the lead and arsenic are poisonous substances, and, where sulfide ores are smelted, the gaseous constituents, sulfur trioxide and sulfur dioxide, may be present in large amounts.

### PROBLEMS OF GREAT SMELTING DISTRICTS

There are three great smelting districts in the western states: the Anaconda in Montana, the Salt Lake in Utah, and the Shasta in California. In all of these very large amounts of capital have been invested in smelting plants, and each of them has a long history of litigation over the injury inflicted upon the surrounding vegetation by the smelter smoke. These histories differ widely in detail and are too intricate for recitation on this occasion, but all have certain points in common. At first the smelters were small, the injury apparently well localized, and results negligible. With the growth of the industry came larger tonnage, higher stacks, greater volumes of smoke, and as a result far more wide-spread injury in adjacent, as well as distant, forest and agricultural districts. Then followed in turn complaints of injury, damage suits, and finally injunction suits, which in some cases now threaten a complete shutting down of the smelters and serious loss of capital to investors. That the seriousness of the possible outcome of this litigation has not been exaggerated is indicated by a recent decision in a similar industry, by which a cement company which, in spite of the fact that at least 95 per cent of its relatively innocuous dust was being recovered, was enjoined from operation as long as it discharged any dust whatsoever from its stacks.

The constituent of smelter smoke most injurious to vegetation is sulfur dioxide. This was well established by the work of Wieler in Germany, Haywood and other experimenters in the United States. The speaker, in collaboration with Profs. G. J. Peirce and R. E. Swain, conducted experiments lasting three years on a variety of different plants, using low concentrations of sulfur dioxide, and obtained positive results in every case. The smelting industry in this country was slow to realize the injurious effect of sulfur dioxide. As recently as 1913 the belief was expressed that such injury as has been inflicted was due to other causes, but the great amount of experimental work which has been undertaken by the smelters themselves during the past two years has necessarily altered this belief. In fact the most hopeful aspect of the whole situation lies in the realization on the part of the smelters that the control of their sulfur dioxide output is one of their great problems, and that some means, other than through litigation, must be found for the adjustment

of the conflicting interests of the smelting and agricultural industries. The character of this experimental work has undergone great changes. At the outset potted plants in small cabinets were used, then plants in larger pots or boxes in relatively large houses, and finally field conditions have been obtained by the use of portable chambers which may be set over plants growing naturally in the open. The latter is doubtless the best method, but requires much space and equipment, and involves an expense which may often be prohibitive.

### EFFECT OF SULFUR DIOXIDE ON VEGETATION

The effect of sulfur dioxide on vegetation is that of a poison, and its action is quite distinct from that of sulfur trioxide or sulfuric acid. The latter destroys the plant tissue, turning it brown or black and giving rise to the appearance usually known as "burn." Sulfur dioxide on the other hand is less immediately destructive. It is absorbed by living plant tissue, combines chemically with some constituent of the plant, remains fixed in the tissue, and, when present in sufficient amounts, results in a complete disturbance of the physiological processes normally taking place in the plant cells. Analyses show that the sulfur content of plants which have been exposed to sulfur dioxide is always increased thereby. The visible effects produced vary in character with the conditions which existed at the time the sulfur dioxide came into contact with the plant. In a general way the symptoms may be described as those typical of the effect of any slow poison on a living system. The natural color of the plant fades, portions die slowly and become brown in color, normal growth is inhibited, completely bleached areas may appear, and finally the whole plant may succumb. In the case of trees the leaves or needles fall, the tree then develops another crop which in turn dies and falls; the process repeats itself as often as the tree recovers and the exposure is repeated; later the twigs and small branches lose their life completely, and the last surviving foliage is found along the trunk and main stems in a manner peculiar to this sort of injury. Eventually the tree dies, and is not reproduced by seedlings or saplings. The complete absence of young growth is one of the serious characteristics of "smelter smoke" forest regions. Different species of plants vary widely in their power of resistance to sulfur dioxide, and even among the same species certain individuals show greater resistance than others. The whole effect is therefore gradual and insidious; the destruction wrought is not abrupt and complete.

The details of the chemical reactions taking place between sulfur dioxide and plant tissue are not known. Since a change in color is the first visible result it is possible that chlorophyll enters into the reaction. It is possible that the unsaturated substances which normally combine with carbon dioxide in the process of photosynthesis combine with sulfur dioxide instead, and that the whole process is thus disturbed. The one well established fact is that the sulfur dioxide is fixed, and the sulfur content of the plant is thus increased. This is true without exception. It has been repeatedly proven by various German investigators, by Haywood in this country, and by the speaker, working first in collaboration with Prof. R. E. Swain, and later independently. I have analyzed approximately 100 samples of various plants which had been exposed to sulfur dioxide experimentally, 600 samples from "smelter smoke" districts, and in every case have found this increase in sulfur content. As ashes record the presence of a fire, as high chloride content records the pollution of a water supply, so high sulfur content records the exposure of plants to sulfur dioxide.

The chemical evidence of smelter smoke injury is of two kinds: that dealing with the deposition of poisonous substances such as arsenic or lead on the surface of the plants, and that concerning the effect of sulfur dioxide. The first is relatively simple and easily obtainable. The analysis of a sample of hay or grass will disclose the presence of significant amounts of

<sup>1</sup> Read at the San Francisco Meeting of the American Institute of Chemical Engineers, August 27, 1915.



arsenic or lead. A study of the results as regards their distribution in a district, correlated with records of the prevailing wind directions and the relative amounts at increasing distances from the smelter, will usually give satisfactory evidence as to the source of the poisonous ingredients.

The second class of evidence—that concerning sulfur dioxide—is more difficult to obtain. While it is true that an increase in sulfur content results from exposure to sulfur dioxide, it does not necessarily follow that such increase, when observed in the field, is due to sulfur dioxide. It has been shown that plants absorb sulfur compounds from the soil, and that they do so to an abnormal extent when growing in soils in which large amounts of sulfates are present. It is necessary, therefore, to prove in any given smelter district that the increase in sulfur content of the plant does not come from the soil. This can be done only by analyzing samples of the soil in question and determining their sulfate content. In practice this apparent difficulty is not so serious as it might appear to be. Several hundred determinations have shown that the sulfur content of the soil in a district is very uniform, rarely varying more than 0.02 per cent, and such small variations as do occur are quite independent of the variations in the sulfur content of the corresponding samples of plant tissue. When all the results from a given district are considered, I have never found it possible to discover any relation between the sulfur content of the plants and that of the soil.

#### DETECTION OF EXPOSURE TO SULFUR DIOXIDE

The method used for determining whether or not the vegetation of a district has been exposed to sulfur dioxide depends, therefore, on three steps: (1) the determination of the sulfur content of the vegetation in question; (2) the comparison of the results obtained with the sulfur content of similar plants growing under similar conditions, except for the possible exposure to sulfur dioxide; and (3) the determination of the sulfur content of the soil in which each sample of vegetation grew, in order to eliminate the soil as a source of any abnormally large amount of sulfur found in any of the vegetation. This method was first used on a large scale in this country by Haywood in a study of the forests in certain smelter districts, later by the speaker, in collaboration with Prof. R. E. Swain, and recently by the speaker alone, in a study of the grains in four widely separated smelter districts. The results obtained have been uniformly satisfactory, and have been in complete accordance with the results of botanical studies in the same districts.

**SAMPLES**—The method of collecting samples of vegetation for analysis is of some importance. In case of trees the leaves or needles, in grains the blades, should be taken, and care should be exercised to secure specimens of every age obtainable. Thus on a pine tree all the needles should be taken from one side of a branch, beginning with the youngest growth on the tip, down to the oldest needles remaining on the tree. With grain all the blades on a stalk should be gathered. Furthermore, since the normal sulfur content of different species varies widely, and that of different individuals of the same species varies slightly, a large number of samples of each species under examination should be secured. The same precautions are necessary in the collection of the control samples of normal vegetation, to be used as standards for comparison, and these should be obtained from the same species, growing under similar climatic and physical conditions, and far removed from any possible source of sulfur dioxide.

**ANALYTICAL METHODS**—The methods of analysis which have been used in this work are those commonly employed for sulfur determinations. Thus the vegetation is fused with sodium peroxide and sodium carbonate<sup>1</sup> and the sulfur precipitated, after dehydration and removal of the silica, under the conditions outlined by Folin.<sup>2</sup> The soil samples are extracted with

hydrochloric acid and the sulfur precipitated after thorough dehydration and removal of the silica. These methods require care and attention to many details, but give accurate results. Some examples of duplicate, and entirely independent, analyses are given in Table I, which show the accuracy obtainable.

TABLE I—DEGREE OF ACCURACY OBTAINED IN ANALYSES OF SOIL  
Results in Percentages of Sulfur

Results in Percentages of Sunlight												
	DUPLICATE SAMPLES OF VEGETATION									SOIL		
A.....	2.06	0.35	1.66	0.36	0.81	0.58	0.80	0.39	0.35	0.025	0.025	0.103
B.....	2.07	0.32	1.66	0.34	0.80	0.57	0.84	0.39	0.39	0.022	0.027	0.098

Tables II and III give some results obtained in the field, and illustrate the manner in which the method works out in practice. The figures given under the heading "Sulfur Factor" indicate the number of times the normal amount of sulfur is contained in that found in the sample in question. The sulfur content of the samples of soil taken from the districts in which the data given in Tables II and III were gathered varies between 0.01 and 0.02 per cent. These tables might be extended to include several hundred analyses, without, however, increasing their value for the purpose of illustration.

TABLE II—SULFUR CONTENT OF VEGETATION NOT EXPOSED TO SULFUR DIOXIDE

SUBSTANCE	PERCENTAGE OF SULFUR								AV.
Barley.....	0.38	0.36	0.30	0.42	0.41	0.28	0.36	0.36	0.36
Wheat.....	0.27	0.28	0.38	..	..	..	..	..	0.31
Alfalfa.....	0.43	0.33	0.29	0.46	..	..	..	..	0.38

TABLE III—SULFUR CONTENT OF VEGETATION EXPOSED TO SULFUR DIOXIDE

BARLEY		WHEAT		ALFALFA	
Per cent sulfur	Sulfur factor	Per cent sulfur	Sulfur factor	Per cent sulfur	Sulfur factor
1.27	3.5	0.62	1.7	0.99	2.7
0.97	2.7	1.27	3.5	1.10	3.0
1.36	3.8	1.22	3.4	1.02	2.8
0.85	2.4	0.82	2.3	0.87	2.4
0.67	1.9	0.68	1.9	0.91	2.5
0.58	1.6	0.91	2.5	0.79	2.2
..	..	1.01	2.8	0.84	2.3

If results such as those given in Tables II and III are obtained in a smelter district, and are studied with regard to the relation of the points of collection to the smelter, it will be found that in general the sulfur content of the vegetation increases from all directions towards the smelter. The rate of increase is not uniform from all directions, but is affected by such general factors as the topography of the district and the directions of the prevailing winds, and such local factors as windbreaks, buildings, and other sheltering agencies. It is very much as if the smelter were surrounded with a great pile of sulfur, highest near the plant and decreasing with increasing distance from the smelter, only in this case the sulfur is invisible to the eye, since it is held in combination within the tissue of the vegetation.

#### INTERPRETATION OF RESULTS

The interpretation of such results as have been presented requires some caution. This chemical evidence is evidence of injury only in the sense that it shows that the vegetation in question has been exposed to sulfur dioxide, which is known to be a substance highly injurious to vegetation. Taken by itself it does not prove that the plants died, or that the crops failed. There is no quantitative relationship known between the increase in the sulfur content and the degree of injury to the plant. The possibility of subsequent recovery by the plants is not eliminated. Taken together with evidence as to the appearance of the vegetation, the time and manner in which the injury was inflicted, the yield of grain or growth of tree, with botanical evidence as to the character of injury and absence of other possible agencies, this method does give evidence, with the definiteness of chemical analyses, that the vegetation in question has been exposed to sulfur dioxide, and that to this exposure may be ascribed the losses which have actually taken place.

DEPARTMENT OF CHEMISTRY  
LELAND STANFORD JUNIOR UNIVERSITY  
STANFORD UNIVERSITY, CALIFORNIA

<sup>1</sup> Bull. 107, Bureau of Chem., U. S. Dept. of Agriculture.

<sup>2</sup> Otto Folin, "Sulfate and Sulfur Determination," *J. Biol. Chem.*, 1 (1906), 137.

## PERKIN MEDAL AWARD

The Perkin Medal for 1916 was conferred on Leo Hendrik Baekeland, B.S. and Sc.D., for his distinguished services in the fields of photography, electro-chemistry and plastics, at the regular meeting of the New York Section of the Society of Chemical Industry held at the Chemists' Club, January 21, 1916.

The meeting was opened with an introductory address by Dr. W. M. Grosvenor, Chairman of the Section; the presentation address was made by Prof. C. F. Chandler, Senior American Past President of the Society of Chemical Industry. The acceptance of the medal by Dr. Baekeland was followed with informal talks by Mr. Richard A. Anthony and Mr. Elon Huntington Hooker. The program was concluded with the Medal Address by Dr. Baekeland. All of these addresses are printed in full below.

Rumford Hall, where the exercises were held, presented an unusually attractive appearance, since it had been lavishly decorated with American flags and flowers, together with exhibits of Bakelite and its applications, as well as photographs made by the use of Velox paper.—[EDITOR.]

### INTRODUCTORY ADDRESS

By W. M. GROSVENOR

LADIES AND GENTLEMEN:

We are as much surprised and pleased as you can be to find ourselves in such a bower of beauty. These beautiful decorations are not a precedent but a present, for which we have to thank the same generosity that accounts in no small measure for much of Dr. Baekeland's genial success—Mrs. Baekeland.

Nine years ago, Sir William H. Perkin, one of the unique figures in the chemical world, visited our shores as the invited guest of our branch of the Society. He came from England after having been heralded the world over as "the founder of the coal-tar dye industry." It is not the mere magnitude of this industry that appeals most to the imagination. So far as this country's requirements are concerned, the coal-tar dye industry represents only a few millions a year, but with its hundreds of typical reactions, its thousands of substances, and its pro-

found study of the actual spacial relation of atoms in the molecule, scientifically its development represents one of the greatest intellectual achievements of the race. Therefore, in 1906, the scientific world was celebrating the fiftieth anniversary of Perkin's discovery of the first coal-tar dye—Mauve.

It is interesting to remember to-night that almost ten years ago the recipient of this tenth Perkin Medal represented the chemists of these United States at the international celebration of the golden jubilee of the coal-tar color industry, in London, where representa-

tives of six great nations did honor to the founder of this industry.

At the time of Perkin's visit to these United States in 1906, this Section of the Society of Chemical Industry planned in numerous ways to recognize the peculiar achievements of the man rather than his intimate connection with the Society as its first Vice-President and fourth President, twenty years before. Among other tokens of appreciation, he was presented with the first Perkin Medal not so much in recognition of his scientific discovery of Mauve while trying to make camphor, as in recognition of his foundation of an industry, his quick appreciation of the industrial value of the discovery when made and his practical energy in joining with congenial business associates and in beginning the successful manufacture in which he continued to be a leader for 17 years (until '73). To perpetuate this recognition the Perkin Medal Fund was established for the purpose of offering each year a similar medal in recognition



LEO HENDRIK BAEKELAND, PERKIN MEDALIST, 1916

of similar service. The industrial history of this color and its successors, as well as the part taken personally by Perkin in this development, illustrate well the ideal underlying the Perkin Medal Foundation—the scientific creation of new industries. The founders of this fund were Americans. In offering the medal to chemists residing in America and considering the requirements of candidates for this honor they had in mind the lesson taught by the specific work and personality the medal serves to commemorate.

Not mere scholarship or research, not even originality or profundity of conception, command the acknowledgment



and encouragement of the honor to be conferred to-night by the 15,000 members of ten different scientific societies. It is conferred for work that has been proven of commercial value to society by the importance of industrial results—"the most valuable work in applied chemistry."

Witness the roll of honor and some of the achievements:

SIR W. H. PERKIN	(1907)	FOUNDER OF THE COAL-TAR COLOR INDUSTRY
J. B. F. HERRENHOFF	(1908)	CONTRIBUTIONS TO HEAVY CHEMICAL INDUSTRY
ARNO BEHR	(1909)	CORN PRODUCTS INDUSTRY
E. G. ACHESON	(1910)	CARBORUNDUM AND ARTIFICIAL GRAPHITE
CHAS. M. HALL	(1911)	ALUMINUM
HERMAN FRASCH	(1912)	DESULFURIZED PETROLEUM AND LOUISIANA SULFUR
JAMES GAYLEY	(1913)	DRY BLAST IRON SMELTING
JOHN W. HYATT	(1914)	CELLULOID AND FLEXIBLE ROLLER BEARINGS
EDWARD WESTON	(1915)	CONTRIBUTIONS TO THE ELECTRO-CHEMICAL INDUSTRY

We are to hear of other achievements from one whose pellucid statements have carried conviction to so many judicial minds in the last forty years that other experts seem like tyros.

It is our great good fortune to have with us to-night, hale in body and brilliant in mind, the beloved dean of our profession. Born in 1836, two years before Perkin himself, Dr. Chandler presided at the first of these meetings when the initial cast of the medal was presented to him whom it commemorates. He will preside to-night. May he do so for many years to come!

#### PRESENTATION ADDRESS

By C. F. CHANDLER

MR. CHAIRMAN AND BROTHER CHEMISTS:

It is my privilege and very pleasant duty, as Senior Past-President of the Society of Chemical Industry, residing in this country, to present to Leo Hendrik Baekeland, B.S. and Sc.D., the tenth impression of the Perkin Medal, in recognition of his most original and valuable work in Applied Chemistry.

Dr. Baekeland was born in 1863 at the old Flemish City of Ghent, where he received his early education. He passed through the elementary schools, the Atheneum (a Government High School), where he prepared for the University, and the Ghent Municipal Technical School, which resembles our Cooper Institute.

In 1880 he entered the University, where he studied various natural sciences, specializing in chemistry. Although the youngest student in his class, seventeen on entering, he promptly won his degree of B.S. and later, when 21 years old, the youngest graduate, he received his degree of Doctor of Science, passing his examinations with the highest honors.

Dr. Baekeland must have been as industrious while a student as he has been since he graduated, for from the age of 17 he supported himself entirely by tutoring and as lecture assistant.

Later he was appointed Assistant Professor, and in 1889 Associate Professor at the University of Ghent. In the meantime, in 1887, he had been appointed Professor of Chemistry and Physics at the Government Normal School, then existing in the City of Bruges.

In a competition among the Alumni who had graduated from the four Belgian universities during a preceding period of three years, he was awarded the first prize in chemistry, by a jury of the Senior Professors of Chemistry of the four universities: Theodore Swarts and W. Spring for the Government Universities of Ghent and Liege; P. DeWilde and Louis Henry for the Universities of Brussels and Louvain; the president of the jury was Jean-Servais Stas, best known by his classical researches on the Atomic Weights. This prize, besides a gold medal and other awards, entitled him to a traveling scholarship,

by which he was enabled to visit some of the universities in England, Germany, and Scotland, and to make a trip to the United States in 1889.

I have given you these details of Dr. Baekeland's early life, because I believed few, if any, of you were familiar with them; because they are most creditable to him, and show his personal character; and because I knew he would not disclose them himself.

Before leaving Ghent, he had become deeply interested in photography. Since the early eighties Ghent had become a center of the new industry of dry-plate manufacturing, started there by Dr. Van Monckhoven. Dr. Baekeland was an enthusiastic amateur photographer, and had followed every step of the new processes, with the result that he acquired some reputation in this new branch of chemical industry.

On his arrival in New York, he became acquainted with Richard A. Anthony, of E. and H. T. Anthony & Co., with whom I had been associated for some time as editor of their *Photographic Bulletin*. Richard Anthony brought us together, and I think it was a case of love at first sight, for we have been the very best of friends ever since.

The Anthony firm, which later joined the Scoville Co. in establishing the Ansco Co., had engaged in the manufacture of photographic films and bromide paper, and they offered Dr. Baekeland an excellent position as chemist in their factory, an offer which he promptly accepted, deciding to remain in the United States.

The Minister of Education of Belgium, in accepting his resignation, paid him the unusual compliment of authorizing him to retain the honorary title of "Associate Professor at the University of Ghent."

After two years, he left the Anthony firm and established himself as a consulting research chemist, and devoted himself to developing several chemical processes which he had devised.

In 1893, in partnership with Mr. Leonard Jacobi, he founded in Yonkers the Nepera Chemical Co., where he started very modestly the manufacture of various kinds of photographic papers. One of these papers, which was called "Velox," has since earned a great reputation as a photo printing paper. Dr. Baekeland had worked to perfect this paper as far back as 1883, while he was still a student in Ghent, but its importance as a possible subject for a commercial enterprise did not become apparent to him till much later.

Silver chloride emulsions had been proposed and described in 1881 by Eder and Pizzighelli, but their process was carried out along the same general lines as silver bromide emulsions, namely, precipitation and ripening, followed by washing to remove the soluble salts resulting from the reaction.

Baekeland had found that as far as chloride of silver emulsion is concerned, the last two operations, although they increased the sensitiveness of the emulsion, had a disastrous influence on the tone and general gradation of the image, specially in the shadows. He had discovered that in order to keep these desirable qualities, it was necessary to produce chloride of silver in a special colloidal condition, which is easily disturbed by any after-treatment of the emulsion, as, for instance, "ripening" or "washing." By committing an act of "photographic heresy," in omitting the washing entirely, Baekeland found he could make a variety of colloidal silver chloride which was relatively insensitive to the yellow rays of the spectrum, and therefore could be manipulated by candle- or gas-light, if not brought too near. This made the paper incomparably inferior to bromide paper, or ordinary chloride of silver paper, as far as speed is concerned.

But Baekeland realized the important fact that by exposing quite close to the artificial light, and developing the image at a safe distance (a few feet) the apparent defect could be turned to a great practical advantage. But the process had to be

studied in all its endless details of manufacture, before it could be carried out on a large scale, so that it could be standardized for use by the photographic public; this was no easy task.

The paper was put out in the trade under the name of "Velox," and met with very scant favor at first; in fact, it took years of education and hard work before the value of the process was fully recognized. Then as soon as the first indications of success were apparent, several competitors started in the same field.

But after the value of the process was clearly recognized, it gained rapidly in popularity, and in 1899 the Eastman Kodak Company offered to buy out the entire business enterprise on very liberal terms, which were promptly accepted.

This relieved Dr. Baekeland from all further commercial worries, and placed him in a position in which he was free to live the life he had always ardently desired; in which he would be able to devote his time and energy to study and research, free from school, university, and business cares.

Dr. Baekeland next turned his attention to Electro-Chemistry. It was a new branch of Chemical Industry scarcely known in his early student days. Its field was limited then to the electro-deposition of a few metals from aqueous solutions, such as copper, nickel, silver, and gold. He was very much impressed by the wonderful expansion of the applications of electricity for chemical purposes, in recent years, especially in the United States.

Charles M. Hall, a Perkin medalist, had brought out his beautiful and simple process for extracting aluminum from alumina, in 1886, and had given a practically new metal to the world to replace copper, tin, and zinc in many arts.

Hamilton Y. Castner, a Columbia boy, had invented in 1890 his simple process for making sodium a commercial metal, and simplifying the preparation of some of its most valuable compounds, *vis.*, cyanide and peroxide; and in 1892 his ingenious process for making pure caustic soda and chlorine from salt.

Edward Goodrich Acheson, a Perkin medalist, in 1892, had discovered carborundum, and devised a simple process for producing it in unlimited quantities, and in 1895 had devised his process for the manufacture of artificial graphite, which he followed later, in 1906, with the invention of that remarkable and useful substance, "deflocculated graphite."

Thomas L. Willson had, in 1899, devised a process for producing, in unlimited quantities, crystalline calcium carbide, which by the action of water creates acetylene gas, and by the action of nitrogen from the atmosphere, produces the new and most valuable atmospheric fertilizer, "calcium cyanamide."

There are two facts which make me linger here with pleasure; every one of these inventions was made by an American chemist, and every one of them resulted in the establishing at Niagara Falls one or more large works, where the inventions are utilized by the use of electricity developed by the waters of Niagara.

These industries are financed and most successfully worked by:

THE ALUMINUM CO. OF AMERICA, Hall's Aluminum.  
THE NIAGARA ELECTRO-CHEMICAL CO., Castner's Sodium and Cyanides.

THE CASTNER ELECTROLYTIC ALKALI CO., Castner's Caustic Soda and Chlorine.

THE CARBORUNDUM CO., Acheson's Carborundum.

THE INTERNATIONAL ACHESON GRAPHITE CO., Acheson's Graphite and Deflocculated Graphite.

THE UNION CARBIDE CO., Willson's Calcium Carbide.

Who can question the ability of American chemists to make original researches and devise new and useful processes? And these are not all by any means; they are merely examples which I have selected because I am most familiar with them.

Dr. Baekeland was very much impressed by these developments, and decided to enter the electrochemical field. So he spent a winter at the Technological Institute at Charlotten-

burg, near Berlin, in the electrochemical laboratory, to freshen up his knowledge of the subject. On his return to America, he equipped a modest private laboratory, on his grounds at Yonkers, and provided it with a few electrochemical appliances for further study.

His work drifted in many other directions, but about that time Mr. Clinton P. Townsend had just invented his now famous electrolytic cell, for producing caustic soda and chlorine from salt. Baekeland was requested by Mr. Elon H. Hooker to take the direction of the work preliminary to the industrial development of this invention. This he did in company with the inventor and several other skilled experts.

The work finally resulted in the formation of the Hooker Electrochemical Co., and the erection at Niagara Falls of one of the largest and best equipped electrochemical plants in the world, with which he is still connected in an advisory capacity.

In this connection he took out his first two patents, "Apparatus for Regenerating Electrolytes," and "An Electrolytic Diaphragm and Method of Making Same."

#### BAKELITE

Dr. Baekeland's crowning work is the solving of the mysteries involved in the action of formaldehyde upon phenols, and giving to the world the new material "*Bakelite*."

Bakelite is a so-called condensation product of phenol—or carbolic acid—and formaldehyde. Instead of phenol, its homologues (cresols or other phenolic bodies) can be used. Instead of formaldehyde, other substances which have the same functions may be utilized, as for instance, methylal, paraform, and hexamethylentetramine.

It should be well understood that formaldehyde in reacting upon phenol does not necessarily give bakelite. Quite to the contrary, it is only under very special conditions, now well established by the published research work of Baekeland, that this substance can be obtained.

In fact, when formaldehyde is let to react on phenol under ordinary conditions, almost anything may happen but the formation of bakelite.

There are very few examples where the same two substances, reacting upon each other, can give such a variety of products. For instance, a nicely crystalline substance, called saligenin, or oxybenzylalcohol, found in the willow-tree (*Salix*), may be the result. This substance has been used in medicine, and is known also as diethesin.

In other cases, a resinous material is formed, but it has no specially new properties and is very similar to cheap, natural resins. For instance, it can be melted and dissolved rapidly just like any other natural resin, and neither its hardness nor other general properties give it any special claim above the natural resins. This is the substance which has been called "Novolak," and which has been prepared by Blumer and others; it has never found any serious applications as such, although at one time it was expected that it would be useful as a shellac substitute, when the price of shellac was unusually high.

It is generally known that as far back as 1872, Adolf Bayer and his pupils<sup>1</sup> showed that it was possible to obtain condensation products of *aldehydes* and *phenols*. These experiments, at that time, were not conducted with formaldehyde, because formaldehyde, as such, was not obtainable, so the reactions were mostly conducted either with the methylene representatives of formaldehyde or with the then available acetaldehyde.

The substances studied at that time varied considerably in character and embraced more particularly certain crystalline, well-defined products. Now and then some uncrystallizable substances were obtained, but no special attention was paid to them, nor had they much in common with the present product, except that they had a resinous appearance.

<sup>1</sup> *Ber.*, 5, 1095; 19, 3004; 25, 3477; 27, 2411.



About 1891, formaldehyde was put on the market as an article of commerce, and Kleeberg tried to repeat some of the work of Bayer by using formaldehyde, in presence of strong hydrochloric acid. He thus obtained a worthless, irregular mass, which he attempted to purify by the usual methods and bring to a constant composition, but he did not succeed, so he dismissed the whole subject and continued his studies of phenolic condensation products along other lines which enabled him to prepare well-defined crystalline substances which are in no way related to the present subject, except as to the origin of the raw materials.

Others, like Smith, Luft and Story, took up the same subject, using formaldehyde, endeavoring to master this reaction either by the presence of solvents, which were partially eliminated afterwards, or by the introduction of foreign substances like camphor. But none of these processes developed into anything on which an industrial enterprise could be founded with any chance of success.

In the meantime, Blumer and DeLaire had described methods by which formaldehyde and phenol could be made to produce, with certainty, special resinous substances which were entirely analogous to the natural resins, like shellac, copal, etc., of which they had practically all the general properties; that is to say, they were fusible, they could be melted, they could be dissolved in suitable solvents. These processes were calculated carefully to avoid the formation of anything but these fusible and soluble products, on which they built great hopes as possible substitutes for shellac.

If the methods of preparation described by these inventors are not carefully followed, then it happens frequently that disturbing side products are produced. The latter, instead of being easily fusible and soluble, are irregular masses of the Kleeberg type containing variable amounts of infusible and insoluble substances which are of no value for further purposes, because you cannot do anything with them after they are once formed. These are exactly the substances which Kleeberg had rejected on account of their negative properties.

This was the state of the art until Baekeland made the disclosure of his own work. He was particularly attracted by the failure of Kleeberg and hoped to find a suitable solvent for his worthless product. It occurred to him that if he could find a solvent for this material, he would be able to make a varnish superior to all existing varnishes. The difficulty was to find the solvent.

His assistant, Mr. Nathaniel Thurlow, felt very skeptical about it and pointed to the unsuccessful attempts of others, after trying most of the available solvents. The fusible, soluble resins of the Blumer and DeLaire type seemed considerably more attractive.

But Baekeland took the point of view that their qualities were not better than those of the natural resins. In fact, in practical tests on a large scale, he had found that in many respects their qualities were inferior to those of shellac, which, furthermore, could be purchased at a more advantageous price than the cost of production of these synthetic resins.

So he concluded to purchase or prepare further solvents of every kind so as to determine whether he could not do something with the substance of Kleeberg, and finally, after many renewed attempts, he had to give it up as a hopeless task.

Then he changed his tactics. He reasoned that if nothing could be done with the substance after it was once produced in a flask or any other vessel, he should attempt to carry out the reaction so as to generate the substance right on the spot where he wanted it. For example, he thought that if he could make the synthesis inside of the fibers of wood by injecting first the two reacting raw materials, and then start the reaction, he might be able to incrust the fibers of the wood with an un-

usually hard and inert substance, and give to the wood new properties.

This was easier said than done. He encountered endless difficulties. Certain classes of wood, especially the higher grades, instead of becoming harder, became softer. He also noticed that chemical reactions in these capillary conditions proceed in a very different way than in a flask or other container, for the reason that the chemical dynamics in capillary spaces are considerably disturbed, so that the reaction which may terminate rapidly and completely in a wide vessel, will be considerably hampered when the mobility of the reacting molecules is disturbed by capillary conditions.

He also perceived that, just on this account, the carboic acid, before it had time to react upon the formaldehyde, had every opportunity for destroying the fiber. He concluded that in order to have any success, he should either be able to speed up the reaction by some special means, or he should find a way whereby he could partially start the reaction outside of the fiber of the wood in a flask, and finish it afterwards within the tissue of the wood, after injection.

This led him to a long systematic investigation, when he tried to study all the different factors of the reaction. When he was through with this line of research, he had established practically all the important facts on which is based the foundation of the present industrial processes of bakelite.

He found that under certain conditions he could dissect the reaction in different succeeding steps, where one of the first steps was the production of a certain intermediary substance which, although it had the general appearance of a resin on account of its brittleness, its solubility and its fusibility differed radically from the natural resins by the fact that as soon as he heated it at a certain temperature above its melting point, it changed into an entirely different body, incomparably harder and stronger than the original resinous material, and which, furthermore, looked like natural amber although it was much stronger than amber, and had another advantage over amber or similar resins in the fact that it did no longer melt if heated, and that it was insoluble in all known solvents.

He also established the fact that in the different reactions which engendered this substance, there is one phase where polymerization occurs and that this phase is accompanied by self-heating, which brings about a considerable rise of the temperature of the mass, so that whenever any attempt is made to hasten this part of the process which produces hardening, the self-heating becomes so exaggerated that gaseous products are evolved, which blow up the mass and cause porosity, which makes it worthless. In order to offset this, he introduced, besides other means, the use of a very strong counter-pressure during the period of polymerization.

He discovered also the important fact that the presence of ammonia, or another base, in suitable proportions, will surely make the reaction go the right way towards the production of the infusible product, while with the presence of an acid, the formation of permanently fusible resins will be favored in case the amounts of carboic acid are preponderant; that, furthermore, the use of a suitable base in proper quantities gives an easy means of controlling the reaction at whatever phase is desirable. From then on, it became possible for him to avail himself of practical means for preparing, as a starting point, an initial condensation product which was still fusible and plastic, and do with it whatever he pleased while it was still in that initial condition. For instance, he could mold or form it or dissolve it, and then afterwards, under the action of heat, polymerize and harden it to the final condition of maximum hardness and strength, where it is no longer fusible or soluble after it had acquired its permanent shape.

The initial bakelite is designed usually as Bakelite A; before it is polymerized, it dissolves and melts to a liquid; but this

liquid has the strange property of "freezing" when sufficiently cooled and then afterwards can never again melt or dissolve; it has been "polymerized" into Bakelite C.

It should be pointed out here that ammonia, in conjunction with formaldehyde, gives a chemical which is called hexamethyltetramine, and that the action of ammonia in presence of formaldehyde in this process is entirely similar to that of the use of hexamethylenetetramine.

It was found also by him that the mechanical properties of these infusible condensation products were enormously improved by the introduction of fibrous substances, as, for instance, wood or asbestos. All pulverulent fillers which are successfully used in conjunction with other plastics, instead of improving bakelite, injure it. This is due probably to the fact that bakelite, although it has an unusually high tensile strength, has a relatively low degree of elasticity which makes it sensitive to impact and shock. The introduction of fibrous materials into bakelite makes it enormously more resistant to shock than the pure article.

Many other facts were established by his work. For instance,

#### I—BAEKELAND'S PUBLICATIONS ON BAKELITE AND RELATED SUBJECTS

"The Synthesis, Constitution and Uses of Bakelite," *Journal of Industrial and Engineering Chemistry*, Vol. 1 (No. 3, March, 1909),

"On Soluble, Fusible, Resinous Condensation Products of Phenols and Formaldehyde," *Journal of Industrial and Engineering Chemistry*, Vol. 1 (No. 8, August, 1909),

"The Use of Bakelite for Electrical and Electrochemical Purposes," *Transactions of the American Electrochemical Society*, Vol. XV (1909), 593.

between the crystalline product saligenin (oxybenzylalcohol) contained in the willow tree and how it is possible ultimately to convert it, at will, either into the fusible resin of the Blumer type, or into bakelite, by submitting it to further chemical reactions.

To sum up: Before he had published the results of his work, there existed not a single industry, nor a single application of any importance based on these condensation products. Since he has published his patents and read his papers before the American Chemical Society, there have been started here and in Europe numerous factories where these processes are used for the most varied purposes, ranging from the manufacture of a billiard ball to that of a wireless telegraphic apparatus; from the manufacture of a self-starter for automobiles to that of transparent fountain pens, this range of varieties embracing such articles as switchboards for battleships, moldings for kodaks, phonograph records, casings for instruments of precision, armatures and commutators for dynamos and motors, telephone receivers, railroad signals, grinding wheels, umbrella handles, buttons, cigar holders and pipe stems, articles of ornament, etc.

"Recent Developments in Bakelite," *Journal of Industrial and Engineering Chemistry*, Vol. 3 (No. 12, December, 1911),

"Phenol-Formaldehyde Condensation Products," *Journal of Industrial and Engineering Chemistry*, Vol. 4 (No. 10, October, 1912),

"The Chemical Constitution of Resinous Phenolic Condensation Products," *Journal of Industrial and Engineering Chemistry*, Vol. 5 (No. 6, June, 1913),

#### II—BAEKELAND'S PATENTS—ARRANGED IN THE ORDER OF APPLICATION

DATE OF APPLICATION	DATE OF ISSUE	NUMBER	TITLE
1906 Feb. 16	1907 Feb. 19	844,314	Apparatus for Regenerating Electrolytes.
1906 Mar. 10	1907 May 28	855,221	Electrolytic Diaphragm and Method of Making Same.
1907 Feb. 18	1910 Feb. 15	949,671	Method of Indurating Fibrous and Cellular Material.
1907 July 13	1909 Dec. 7	942,699	Method of Making Insoluble Products of Phenol and Formaldehyde.
1907 July 13	1909 Dec. 7	942,852	Indurated Product and Method of Preparing Same.
1907 Oct. 15	1910 Apr. 12	954,666	Varnish.
1907 Oct. 15	1909 Dec. 7	942,809	Condensation Product and Method of Making Same.
1907 Oct. 26	1909 Dec. 7	942,808	Abrasive Composition and Method of Making Same.
1907 Nov. 21	1913 Mar. 25	1,057,211	Method of Impregnated Wood and Products Thereof.
1907 Nov. 21	1913 Mar. 25	1,057,319	Impregnated Wood and Method of Preparing Same.
1907 Dec. 4	1909 Dec. 7	942,700	Condensation Product of Phenol and Formaldehyde and Method of Making the Same.
1909 Jan. 28	1909 Nov. 16	939,966	Method of Molding Articles.
1909 Jan. 28	1913 Feb. 25	1,054,265	Antifriction Device.
1909 Feb. 1	1909 Nov. 30	941,605	Packing Material.
1909 Apr. 30	1912 Mar. 5	1,019,408	Wood-Finishing.
1909 Oct. 2	1915 Nov. 16	1,160,362	Method of Making a Plastic Body.
1909 Oct. 2	1915 Nov. 16	1,160,365	Paper-Like Product and Method of Making the Same.
1909 Oct. 4	1912 Sept. 10	1,038,475	Process of Making Insoluble Bodies Derived from Phenol Alcohols.
1909 Oct. 4	1915 July 13	1,146,045	Process for Making Insoluble Bodies Derived from Phenol Alcohols.
1909 Oct. 8	1910 May 3	957,137	Container for Food-Products.
1909 Nov. 22	1911 Jan. 24	982,230	Coated Object and Method of Making the Same.
1909 Dec. 2	1915 Mar. 23	1,133,083	Phenolic Condensation Product.
1910 Mar. 14	1914 Mar. 3	1,088,677	Infusible Condensation Product of Meta-cresol and Formaldehyde.
1910 Mar. 14	1914 Mar. 3	1,088,678	Infusible Condensation Product.
1910 June 11	1913 Dec. 30	1,083,264	Sound-Record.
1910 Nov. 30	1912 Mar. 5	1,019,406	Composite Cardboard.
1910 Nov. 30	1915 Nov. 16	1,160,363	Waterproof Object or Article.
1910 Dec. 16	1912 Mar. 5	1,019,407	Method of Uniting Objects.
1910 Dec. 16	1915 Nov. 16	1,160,364	Machine Element.
1911 Mar. 14	1912 Feb. 20	1,018,385	Varnish.
1911 Mar. 14	1912 Sept. 3	1,037,719	Varnish.
1911 Oct. 24	1915 Oct. 12	1,156,452	Insulating Composition.
1912 Feb. 29	1914 Jan. 27	1,085,100	Protective Coating Composition.

was demonstrated that among the homologues of phenol, was not indifferent what kind of homologue is used. It so happens that ortho-cresol tends towards the formation of fusible products of low strength. Para-cresol also gives condensation products of very inferior qualities, while meta-cresol, or mixtures of meta-cresol and para-cresol, give the best product. This enables the use of some of the more available cresols, instead of expensive phenol.

He not only pointed out unmistakable methods for procuring every time, at will, either a fusible or an infusible resin, but he gave the explanation why in one case one substance and in another case, a different one was obtained, when starting from the same raw materials. He established the theoretical relations and parentage of those different substances, all derived from the same raw materials and yet so different in their properties and technical uses. In this way he established the relation

The General Bakelite Co. has a very complete plant at Perth Amboy, where the raw materials are made; there are a large number of licensees in the United States; bakelite plants in Germany, France, and England; and several factories in Europe where bakelite goods are manufactured under license, for example, two bakelite button factories in Germany and one in Russia.

It is absolutely impossible to tell the story of "Bakelite" with any completeness in the time allotted to me, and I must refer you to Dr. Baeckeland's articles and patents, where you will find everything fully set forth.

I have prepared a complete list of both the articles published in this country, and the United States patents arranged in the order in which they were applied for, as that order will enable you to follow chronologically this stupendous investigation. There are many additional patents which have been allowed



but not yet published, and many more which are now before the Patent Office.

It was at first thought, by some persons, that some of the early investigators, beginning with Adolf Bayer, whose names I have already mentioned, must have anticipated Dr. Baekeland in his discoveries and inventions. This is not the case; Dr. Baekeland's inventions, as described in his patents, are not anticipated. The subject was most thoroughly tried out in the U. S. District Court, Eastern District of New York, before Judge Chatfield, who rendered his decision in Dr. Baekeland's favor, in a most elaborate and lucid opinion, covering 20 pages of "The Federal Reporter."

His Honor clearly pointed out step by step the radical differences between the work of Baekeland and each one of the prior writers and patentees.

In closing I will call attention to the distinctions which Dr. Baekeland has had showered upon him, in recognition of his scientific standing and achievements in the domain of Industrial Chemistry.

#### DISTINCTIONS

PRESIDENT CHEMISTS' CLUB, 1904  
VICE-PRESIDENT SOCIETY CHEMICAL INDUSTRY, 1905  
CHAIRMAN NEW YORK SECTION AMERICAN CHEMICAL SOCIETY, 1908  
PRESIDENT AMERICAN ELECTROCHEMICAL SOCIETY, 1909  
PRESIDENT AMERICAN INSTITUTE CHEMICAL ENGINEERS, 1912  
PRESIDENT INVENTORS' GUILD, 1914  
OFFICIAL U. S. DELEGATE TO INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY, LONDON, 1909  
PRESIDENT SECTION OF PLASTICS, INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY, New York, 1912  
FIRST CHANDLER LECTURESHIP—COLUMBIA SCHOOL OF MINES, 1914  
MEMBER NAVAL CONSULTING BOARD OF UNITED STATES, 1915  
NICHOLS MEDAL, 1909  
JOHN SCOTT MEDAL, 1910  
WILLARD GIBBS MEDAL, 1913  
CHANDLER MEDAL, COLUMBIA UNIVERSITY, FIFTIETH ANNIVERSARY SCHOOL OF MINES, 1914

#### CONFERRING THE MEDAL

LEO HENDRIK BAEKELAND, DOCTOR OF SCIENCE, MY DEAR FRIEND:

It gives me the greatest pleasure, as the representative of the Affiliated Chemical and Electrochemical Societies of America, to place in your hands this beautiful Perkin Medal, as a token of the appreciation and affection of your fellow chemists.

#### ADDRESS OF ACCEPTANCE

By L. H. BAEKELAND

MR. CHAIRMAN, LADIES AND GENTLEMEN:

In accepting the great honor you are willing to bestow upon me, I realize at the same time how many of my fellow chemists have achieved much better work than anything I ever attempted.

On this account, my feeling of gratitude towards you changes entirely into a sentiment of profound humility and arouses in me the ardent desire of endeavoring to do better in the future. Should I not live up to this resolution, then every time I shall look upon this medal, it will appear to me as a symbol of reproach instead of a token of merit.

And now, what shall I say further on this occasion? So much has already been told about me this evening, that if I could drop the whole subject right at this point and go quietly home, I should feel intensely glad and relieved.

But the Perkin Medal Committee urges me to take this opportunity for explaining some of my experience as far as it relates to the handling of problems connected with new chemical enterprises.

Therefore, I can spare you a repetition of technical details about my work, which you have heard abundantly on other

occasions, and which are now available in the chemical literature. I shall thus try to make this occasion serve a better purpose by presenting my point of view in relation to the chemical development of this country, and I hope that by the time I am through, I may have convinced some of my younger fellow-chemists that a reasonable measure of success in their chosen career is not such a difficult matter after all.

#### THE DISCOVERY OF DR. BAEKELAND

By RICHARD A. ANTHONY

Having been the discoverer of Dr. Baekeland, I presume that I am here as Exhibit A for that reason, but I think I am really Exhibit A for Dr. Chandler who taught me how to appreciate men of brains. All that I know about chemistry was learned at Dr. Chandler's lectures during my senior year at Columbia in the School of Arts. He did not pretend to teach us chemistry, but to teach us how much there was to learn in chemistry. When I graduated I felt that I knew much less than I thought I did when I entered, because when I entered I thought I knew it all, and Dr. Chandler taught me how little I really did know.

So when Dr. Baekeland came to me with a letter of introduction in 1888, and with his first patent—for in spite of what Dr. Chandler has just said, Dr. Baekeland's first patent had been applied for, at least, before he came to this country—I remember, as if it were but yesterday, what this was for: it was for a method of mixing photographic developer with gum arabic and smearing that on the back of a photographic plate, then putting it in water; the water would dissolve the developer and there you were. We were not manufacturing photographic dry plates, but I was not going to let go of Dr. Baekeland, so I kept talking to him and luring him on, realizing that the man was the greatest photographic chemist that I had ever met. I never knew before to-night that the reason he had succeeded was because he did not do as much washing as others had done.

But Dr. Baekeland did not get along very well with us. He came in one day and said good-bye. I could not find a reason for his going, but we didn't have any quarrel. He knew he could paddle his own canoe and went off and paddled it, and always after that when I wanted any chemical problems solved I used to go to Dr. Baekeland.

I remember, that once a paper company wanted us to start a paper factory at Rumford Falls. They knew nothing about the manufacture of photographic paper, and of course supposed that we could make the paper from wood pulp, and I thought if they wanted to give us some land and put up buildings for us that we could take our rags up there and make the paper. So I proposed that we go up and look the ground over and I asked Dr. Baekeland to go with me. On our arrival there, Dr. Baekeland sniffed the air and said: "You might just as well try to make your photographic paper in hell as to try to make it here." "Why, what's the matter with this place," I asked him. "Do you not smell the sulfur in the air? Your paper would be blackened before you got it made. What's the first train back?" There was no train until the next morning, so as we had a letter of introduction to the superintendent we decided to go and look him up. We found him and he showed us through the works. We saw logs coming in at one end and paper bags and postal cards going out of the other. In the pulp room there were great large tanks some 50 or 60 ft. high and 20 ft. in diameter. Dr. Baekeland asked questions about particular forms of digesters, and went into the many details of the manufacture of paper. The superintendent said, "Are you a manufacturer of paper?" "No," replied Dr. Baekeland. "Then how do you know so much about it?" asked the superintendent. "Oh, I've just been reading it up in a general way for my own information;" and he actually knew more about it than the superintendent of the factory.

On another occasion I had invited Dr. Baekeland to take dinner at the University Club with me, and there we met one of my friends who said that he was terribly troubled over a cargo of barrel staves that he had just sent to Argentine. These had been shipped in a vessel that had been used for carrying creosote. They could not be sold because of the creosote, which it was impossible to remove; what to do he did not know. I said, "Ask Dr. Baekeland." Dr. Baekeland knew all about that too; he had just been making a study of that. He pulled out a piece of wood soaked with creosote. He told all the different methods of getting the creosote out. My friend said that they had tried every one of these methods and none of them were practical because they were too expensive. Then, said Dr. Baekeland, "Out in Michigan they put creosote into wood because they want it there. The proper thing for you to do is to bring all the barrel staves back here and send them to Michigan, where they prefer to have them soaked in creosote. You will get more money for them that way," and my friend did just that thing and made a profit instead of a loss.

I remember Dr. Baekeland went to a man connected with the Pittsburgh Reduction Company and wanted some apparatus made of aluminum. "What do you want it for?" "I want to use it for separating brine into chlorine and caustic soda." "But you can't do that in aluminum. It won't stand it." Dr. Baekeland replied, "That does not make any difference. What is your price?" "But you cannot use it for that." "I do not care whether I can use it or not, just give me a price." It was finally settled that Dr. Baekeland should pay in advance and furnish the company with a release from all claims for damages. A price was named and the apparatus furnished. It is working to-day at Niagara Falls.

Dr. Baekeland's ability has always appealed to me as that of a practical chemist of great business ability, not merely that of a theoretical chemist.

Once I was interested in a rubber reclaiming factory. They consulted various chemists about troubles they had. I said to the president, "If you take my advice, you will get Dr. Baekeland to go into this thing, and then follow his advice. Do exactly as he says. If he says you cannot improve the process, then shut up shop." He finally said, "Go ahead and see what he will do." So I went. As usual, Dr. Baekeland was just reading up the literature of the rubber reclaiming business. He went over all the details of our process and made a great many experiments, covering a period of three months. Finally he said, "There is nothing inherently wrong with your process in general, but there are a number of minor details, governed entirely by economical conditions, that makes it practically impossible to make a success of your method. There are ways of making the process perfect, but they would be too expensive." Accordingly, he advised us to "shut up shop," and we shut up shop, thereby saving ourselves a great deal of money.

#### AN APPRECIATION OF DR. BAEKELAND

By E. H. HOOKER

In this Republic, when offering the highest laurels, we delight to place back the connection with humble associations, of him we honor. So it is characteristic to wish to link this occasion with the amusing, but, none the less, highly dramatic and serious incidents of Dr. Baekeland's intervention in the original testing of the Townsend Process in commercial units.

Imagine, if you can, a wing of the Edison Power Station in an altogether disreputable section of Brooklyn, and two ill-sized Townsend cells erected with necessary supply tanks, exhaust chimney, etc., producing chlorine in juxtaposition to the valuable generating units of the Edison Company. Upon these the lighting and transportation conveniences of the City where we sleep are dependent. Picture further, three young men who did not know chlorine gas from attar of roses

or caustic from lemon ice, but of undoubted bravery, assisted by negroes whose only aim was Saturday night's pay and the hope of a possible bleaching, guided sporadically by Townsend and Sperry, but presided over, their drooping spirits revived, and their hope of heaven determined, by the genius of Baekeland.

He, you understand, had just been rescued from the depths of photographic invention, with its spirit-dulling, materialistic opulence, and uplifted to the rare delights of electrolytic research—that shadowy borderland between pure science and commercialized industry where mathematics and chemistry join hands in the Great Unknown.

Here our friend held forth long hours in shirt-sleeved efficiency, while his social reputation became tainted, his domestic status strained, and his short nights of peace in Yonkers, even in Harmony Park, were rent with agonized appeals for help from Brooklyn at 3 o'clock in the morning:

"Cell No. 1 has broken down; the place is full of chlorine gas; we are all out in the street; the Edison boss says his \$100,000 generators are being eaten up by a green substance. What shall we do?" *Answer* (punctuated with picturesque speech): "Start it up, of course. It will be over before breakfast." Or, again: "Cover of Cell No. 2 has blown off from hydrogen pressure. What would you do?" *Answer* (in a voice choked with sleep, or deep emotion): "Put on a new cover and have the dorky sit on it until I can get over in the morning."

That Brooklyn equipment had been timed with all the nicety of shrapnel. Exhaust fan and stovepipe chimney resisted the chlorine until a mere shell, and then like the "wonderful one-hoss shay" crumbled into a mass of iron dust the last day of the test. The Edison janitor, like a true homeopath, shoveled us into the street and disinfected the place from garret to cellar with drums of *chloride of lime*.

But sunshine came after the clouds; tests were successful, and through these unhappy days and nights the Niagara enterprise came into being.

The design of the works proceeded apace until a mooted question arose between Emil Kuichling, the civil engineer consulted, and Baekeland, the consulting chemist. Ventilating air under the cell house floor was the impalpable rock on which these two eminent scientists split. Kuichling was clear that the air should be pushed through, while to Baekeland it was obvious that it should be pulled. In the interest of Peace through Preparedness, Marsh, the designer, arranged a fan on his drawings so it would run the one way or the other, according to which happened to be criticizing his plans. This famous controversy was never settled, so we abandoned the ventilating ducts altogether.

To touch on Dr. Baekeland's important connection with the inception of this project, and his unselfish and loyal coöperation through the various stages of its development, in the presence of some who have shared its burden, and all who are his friends, brings to each a picture typical of one aspect of the many-sided man. You all know his multifarious activities: a helping hand here, a word of inspiration there, a cheery hand-grasp, with wisdom dissolving away technical difficulties, speech clean, from a heart that thinks no ill of others, the standard of professional ethics carried high where all can approve, and a breadth of scientific grasp and knowledge which illumines whatever his swift mind plays upon.

We, his friends, lack the proper perspective to do him and his work justice. Time alone can furnish that.

His associates, who have fought through the struggles of founding a business enterprise side by side with him, honor his indomitable spirit and energy, his loyalty, his unflinching courtesy, and a mental alertness and keen vision, amounting, yes! to that rare gift called genius.

Coming to this country, a young scientist, fired by the native ideals of the Belgian race, the pure gold of whose patriotism



has this last year thrilled the world, he has put his faith and his life into American institutions, until he stands, known of all men, as one of the best Americans; one whose enthusiasm, patriotism, and love of his adopted country takes us back to the Americans of an elder day. It is thus I like, best of all, to think of him.

#### PRACTICAL LIFE AS A COMPLEMENT TO UNIVERSITY EDUCATION—MEDAL ADDRESS

By L. H. BAEKELAND

Reference has been made by Professor Chandler to my early training. I feel very grateful for the excellent opportunities of education I had at the University of Ghent. I should state, however, that my real intense education began only after I had left the University, as soon as I became confronted with the big problems and responsibilities of practical life; this education I received mainly in the United States, where for twenty-seven years I was thrown in contact with so many varied subjects. I hope to remain until I die, a post-graduate student at that greater school of practical life, which has no fixed curriculum and where no academic degrees are conferred, but where wrong petty theories are best cured by hard knocks. There was a time in my life when, as a young teacher of chemistry, I was just as cock-sure as some of my older colleagues that everything was as simple as it appears in the text-books. This lasted until I tried to make bromide of silver for commercial purposes in the preparation of photographic emulsions. Stas had already published the fact that there were three or four different varieties of bromide of silver, all of exactly the same chemical composition, yet differing in their physical properties. By the time I got fully engaged in the manufacture of silver-salt products for photographic purposes, I had come to the conclusion that instead of three or four varieties of bromide of silver, there existed, perhaps, a hundred varieties, but that of those hundred varieties, there was only one which might probably keep me from the poor-house, and assure me success as a manufacturer. And yet, until then, that unexciting chemical reaction which produces bromide of silver and which in our text-books is expressed by such a simple chemical equation, always had appeared to me as hardly worth while of further investigation. By and by, I began to look at chemical phenomena from quite a different standpoint, and I well remember the day when I reasoned to myself as follows:

"Here is one of the very simplest of all chemical reactions, so simple that any chemist hardly wastes any time over it, and yet it involves phenomena so intricate, so varied in scope and effect, that we have not yet found the proper means to fathom them. Here is bromide of silver, freshly precipitated in the dark; it has the property of not darkening if brought in contact with a reducing agent—a developer—and yet the mere action of light, even for only an infinitesimal fraction of a second, brings about such a profound alteration in its constitution that henceforth it will blacken and set silver free if treated with a reducing agent, and thus produce a photographic image. Furthermore, this bromide of silver, before and after it has seen the light, is exactly the same, as far as we can decide by chemical analysis, or any of our other clumsy means of observation. Suppose now that the human race were not provided with the sense of eyesight—just as we probably are missing several other senses—we would forever remain unaware of that peculiar effect of light on silver bromide or on chemical reactions in general."

This gave me one of my first warnings not to accept any chemical explanation in too simple terms, and engendered in me the ever-growing belief that the very plainest chemical reactions are incomparably more complicated than our hasty generalizations in text-books lead us to believe.

It thus became my good luck that my early struggles with

photographic problems cured me of too much confidence in easy explanations of chemical phenomena and made me lose somewhat that youthful overabundant faith in classroom theories. I suppose my experience is very similar to that of many an industrial chemist who has had to learn by sheer experience, that after he may think he knows everything on a certain subject, he is constantly confronted with endless matters of detail which at first seemed so trifling, alongside the broad lines of the subject, as to be unworthy of the attention of the theoretical chemist. And yet these details frequently determine whether the practical solution of a problem is possible or not—whether the ruin or success of a chemical enterprise is in sight.

#### TOO MANY IRONS IN THE FIRE

Nor was it all plain sailing in my early days here in this country. Like so many others, I committed the mistake of scattering my attention on too many subjects at the same time. After I left the Anthony firm, I tried to work out, without sufficient financial means, several half-baked inventions, the development of each of which would have required a small fortune. Fortunately for me, I was taken out of this muddle and shaken to my senses by a very severe illness which nailed me to bed for several months. While I was hovering twixt life and death, with all my cash gone and the uncomfortable sentiment of rapidly increasing debts, I had abundant time for sober reflection. It then dawned upon me that instead of keeping too many irons in the fire, I should concentrate my attention upon one single thing which would give me the best chance for the quickest possible results.

Among many other matters, I had an electrolytic process for extracting tin, a safety explosive, and a new photographic paper. The tin process had lost all its charms since the swampy meadows of New Jersey, where I was carrying out my experiments, had brought me almost within close acquaintance of the undertaker. Nor did the manufacture of explosives appeal much to me after I had been for so many months in the hands of surgeons and physicians; so I turned to my old love, photography, ready to manufacture some new kinds of photographic paper.

#### THE HISTORY OF VELOX

I was lucky enough to make the acquaintance of Mr. Leonard Jacobi, of San Francisco, who was willing to risk some of his cash in my venture. He knew nothing of chemistry, nor of any technical matters, but he was a generous-minded, cheerful and very industrious man, who furthermore honored me with his implicit confidence. Although much of an idealist, he was in business matters very sober-headed and very careful and conscientious towards all the immediate problems before him, and I owe it to the excellent example of his common sense that I learned some of the practical rules of business life which afterwards came in good stead in my future career.

Do not imagine that from the beginning of this enterprise everything went smoothly—quite to the contrary. As luck would have it, we started this venture just at the very worst time, in 1893, during the famous business panic, when so many of the industries of the United States went under. In this instance, our salvation was that we had started on a modest scale and that whatever disadvantageous conditions we encountered, or whatever mistakes were committed, we could straighten up matters without too fatal a loss of capital. We had more than our share of the usual technical troubles which accompany the starting of any new enterprise. It was found, for instance, that while we could make excellent paper in temperate weather, it became practically a hopeless task to do so in the hot summer days. Our sales were small and when we had any sales, we were confronted with the problems of the climate; hence our manufacturing methods were more or less like a gamble. This caused us considerable losses. The remedy seemed easy enough, so we

ied to rectify the conditions of temperature by artificial cooling, as others had done. But this had not the required effect and new disappointments confronted us. After awhile, special scientific investigation disclosed the fact that the troubles were not due so much to the factor of temperature as the moisture in the air. This led us to install a refrigerating system over which the air could be drawn first so as to extract its moisture by precipitating it as ice, after which the dried air could be sent over heated pipes so as to raise its temperature to the proper degree before it entered in the paper coating machine. At that time, this seemed a rather paradoxical method of operating, but to-day it has been adopted by several large manufacturers of photographic papers and films. It was only many years later that I heard of the Gayley process for blast furnaces where similar method is used for insuring the steady dryness of the air in the smelting of iron.

Manufacturers in Europe, where the amount of moisture in the air does not vary to such an extraordinary extent between seasons, have scarcely any conception of what difficult manufacturing problems are encountered here in the United States where in winter the air is so dry as to cause electric sparks and abundant static electricity by friction, while in the summer months the air is often so saturated with moisture that many objects and machinery condense humidity on their surfaces at temperatures as high as 76° F. But I believe that it is just this account that in some industries, American manufacturers have been compelled to solve with more thoroughness and with more effective means, the greater difficulties they encounter in the varying climatic conditions; this also is the reason why some of our industries have reached a higher degree of development and perfection than the corresponding European enterprises. The humidity in the air during our hot summer season, aside of the manufacturing problems, is very hard on photographic prints. Photographs made with inferior processes may give prints which last many years if kept in Europe, but frequently happens that the same prints deteriorate here in a few weeks in summer time.

In the early nineties and the following years, this country was using more and more photographic printing methods which consisted of the so-called combined-bath processes, and by which toning and fixing of the image was produced at the same time.

At that time, practically all manufacturers of new sensitized paper advocated this rather easy process. Few, if any, hesitated to promise permanency of these prints, and this on the strength that such prints had been preserved successfully in Europe. A rather simple test gave me a method of distinguishing which kind of photographic prints were most likely to fade. This test consisted in cutting a photograph in two and exposing one-half in a jar to the fumes of ammonium hydroxide. This treatment, in a few hours, showed the same amount of fading as would have been produced under ordinary conditions after months or years. Upon the result of these experiments, I had based the manufacture of several sensitized papers which I could unhesitatingly recommend as giving permanent prints. One of those papers we called "Velox," on account of the speed with which the prints could be made independently of weather conditions. In this process, prints were exposed for a short time to artificial light and developed in the same light. I was firmly convinced that this process had a great future. Unfortunately, the public did not think so. In fact, it was very disappointing to notice how every photographer, amateur or professional, was wedded to the older processes and wanted to have nothing to do with the method out of which I felt so enthusiastic. To make matters worse, my very best friends did not hesitate to tell me that there was no chance whatsoever for this new method of printing, because they thought that it was so much simpler and easier to print

in the sun, to which everybody was accustomed. I never was more impressed with the fact of how routine holds sway over this world; but I was rather stubborn in my point of view. I kept on trying to convince others how much simpler it is to be independent of sunshine. I shall never forget the endless correspondence I had with many people all over the country. I remember too well the kind of letters I used to receive and of which the following are some examples:

"I have tried every photographic paper in existence and I have been more or less successful with all of them until I tried yours, but it is hopelessly no good. You cannot blame my insuccess on faulty manipulation, because I am professor of chemistry at \_\_\_\_\_ College."

Or another: "I am a professional photographer of twenty-five years' experience. Your paper is the greatest photographic swindle of the age. You claim your method of printing is several hundred times faster than albumen paper, and here I have kept a print in the printing frame for several hours in the sun and I can hardly see a faint image."

It was only later on that I realized that most of those people *knew too much* about photography and, on this account, never gave themselves the trouble of even glancing at the printed directions which were sent to them; they were, like so many other people, past the age where they are willing to learn anything new.

Finally, our success came from the most unexpected quarters. A new generation of modestly beginning amateur photographers came up and began to give themselves the trouble of reading and following our printed directions. To the disgust of their more experienced friends, "who knew it all," they began to show them excellent prints made on the new paper, better in several respects than experienced men in the profession had been able to produce with older processes. Nevertheless, it took considerable time before so many converts had taken up the new process that the grumblers and faultfinders were finally in the minority; it required four years of strenuous introduction before the business began to show some slight profit, notwithstanding the fact that all unnecessary expenses were carefully avoided. Two years more and the business enterprise began to prosper rapidly and then I was offered good cash for my interest in the business, by the Eastman Kodak Company, and I retired entirely from this field.

I should mention right here that if I had tried to sell my processes at the beginning and before they had been developed into a commercial, paying enterprise, I could hardly have expected anything, because at that stage, my inventions would have been of little or no value beyond a mere gamble. It required the careful nursing of a business enterprise and it was indispensable to establish the process firmly on a practical commercial scale, before we were in a position to dictate our own price; even at that rate, the buyers took less risk than if they had obtained the process as a gift, before it had been worked out for several years and during several seasons. If I go into all these details, it is merely as a hint to some of my friends who are apt to build castles in the air on processes which are not yet beyond their laboratory stage, and who are not willing to incur all the hard work and risk connected with their full development and yet expect to obtain a large sum of money for their mere patent rights.

#### UNCERTAINTIES OF CHEMICAL PATENTS

Professor Chandler has already explained to you the underlying principles of the Velox process. I should mention that Velox was never patented, except that its name is a trade-mark. At that time, I was already aware how difficult and expensive it is to carry on patent litigation and I realized too well that we could neither afford the money nor the time connected with patent fights; so I preferred to take some chances and to keep the process secret long enough to permit us to build up a solid



business by the time our competitors would have been able to devise the same methods.

Although I have had to change somewhat my views on the subjects of patents, I still believe that the man who takes out a patent for chemical processes and does not have at his disposal abundant means to defend his patent rights before the courts, is at a considerable disadvantage against unscrupulous infringers. Chemical process patents which can be followed out in secrecy can be too easily infringed with impunity because it is too difficult and expensive to establish these infringements before our courts of law.

"Product patents" for chemical substances protect somewhat better; but, even there, litigation is considerably more difficult and intricate than for purely mechanical patents which are easier to understand by intelligent judges even if they have no scientific training; this important point of difference has too often been lost sight of in any proposed changes of our patent laws.

But whether you patent a chemical process or not, it appears to me of the highest importance to try it as soon as possible on a small commercial scale, and thus test its essential practical details before risking too large a commercial enterprise on it.

#### ELECTROLYTIC SODA

I was fully imbued with these facts when, about twelve years ago, I was entrusted by my friend, Elon Huntington Hooker, with the examination of the Townsend Cell. The inventor of this cell, Clinton Paul Townsend, one of the most clear-minded and careful men I have ever known, had already studied the details of his invention with a thoroughness which is rather uncommon; he furthermore, in its construction, had the benefit of the engineering experience of Elmer A. Sperry, of Gyroscope fame. Together they had practically tested out in the laboratory everything which seemed of importance about the design and operation of the cell. At that time, there existed much skepticism as to whether a diaphragm cell for the manufacture of caustic soda and chlorine would ever rival the mercury cell, brought to such a remarkable state of perfection by that distinguished American inventor, Castner, a pupil of Professor Chandler.

Here, then, was a distinct advance in the art, an invention which for its commercial use required a plant costing millions of dollars. I felt it was dangerous to take any such large risk until there was an absolute certainty about the smooth working of the cell. I reasoned that we all knew *how good* the cell was under laboratory conditions where it was supervised by unusually able and skillful men, but it was just as necessary to establish *how bad* the cell would be if put under actual factory conditions where it would be operated by average labor. To investigate this was very expensive and took considerable time. Two full-sized model cells were built and operated under varying conditions, day and night, uninterruptedly, for months. This gave us all an opportunity of improving details of construction. With the additional experience thus gained, we could now make more correct estimates and specifications for a full-sized plant. But even this plant was not built in full at once, but only to the extent of the smallest section which could be operated. We had thus further opportunities for detecting weak points and introducing further improvements or simplifications. After this period, however, there was no further risk in the construction of the full-sized plant. Moreover, the experience which had been gained by the preliminary expenditure of about \$300,000, prevented blunders which might have cost several millions; through carefully planned development like this, the Hooker Electrochemical Company has to-day become one of the leading electrochemical concerns of the world.

In as far as my name has been connected with this enterprise, I take this opportunity of disclaiming any further credit

for the success of its technical development, and more specially for the Townsend Cell, beyond the fact that it was my good fortune to work in collaboration with a group of unusually able men. Aside from the men already mentioned, there were Albert H. Hooker, H. Willard Hooker, Clarence W. Marsh, Jasper M. Rowland, T. B. Lyster, C. N. Lansing, George W. Stone, and others, all of whom did their full share in introducing a number of improvements.

I mention this example of successful team work in opposition to other instances where similar problems were entered into recklessly and where, either through impatience or through false economy, a large-sized plant was put up at an enormous cost before all doubtful details of the process had been eliminated, with the result that the irregularities in manufacturing became so overwhelming and money losses became so heavy that the enterprise failed before it was possible to overcome them.

The principle: "Commit your blunders on a small scale and make your profits on a large scale," should guide everybody who enters into a new chemical enterprise, even if it taxes the patience of some men who cannot conceive that one single apparently minor detail in a chemical process may upset all the good points and lead to ruin.

#### SYNTHETIC RESINS AND BAKELITE

When I undertook the intricate study of synthetic resins, which led to bakelite, I did not rest until I had mastered the details of the subject as far as my laboratory methods allowed me to do so. Then immediately afterwards, I installed a small working unit where I could prepare the material in ton lots under various conditions, so that it could be tested right and left for practical purposes. Experience has taught me that many inventions may look very good to an inventor, but some way or another, do not suit the demands of the public. On this account, before embarking on a regular wholesale manufacture, I wanted to make absolutely sure that the new substance could be used permanently for the many different industrial purposes I had in view. I reasoned as follows: "Here is a new material which might develop disagreeable surprises either in its process of manufacture or in its uses. Therefore, the best way is to manufacture it repeatedly on a small commercial scale for a limited number of users selected in such a way that I can watch easily the progress of their work." As usual, I found that I had much to learn and had to change my views several times. At the beginning, I had the erroneous idea that almost anybody would be able to make the new material easily, himself, and that it would simplify matters if I issued licenses on a royalty plan for the use of my patents without going myself to the trouble of any manufacturing work. I soon found I was greatly mistaken in this, and that it would have caused no end of disappointment to teach to others chemical details which, to me, seemed rather simple, but which are easily overlooked by men who cannot afford to concentrate their full attention on the subject. I concluded that a simpler way would be to sell them a partly finished product and to teach them how to use it. But I noticed, before long, that I had to go again all through the same old experience as the introduction of Velox. I found, to my astonishment, that people who were proficient in the manipulation of rubber, celluloid or other plastics, were the least disposed to master the new methods which I tried to teach them, or to appreciate their advantages. This was principally due to the fact that these methods and the properties of the new material were so different in their very essence from any of the older processes in which these people had become skilled. This rather unexpected drawback is so true that even to-day the most successful users of bakelite are just those who were not engaged in plastics before, this simply for the reason that they did not have to divorce themselves from the routine of older methods, and were willing to listen patiently to suggestions from new-comers in the field.

At the beginning, I committed another mistake by trying to make the processes and the material as inexpensive as possible, using mostly the cheaper cresols, being guided by the idea that cheapness is a paramount consideration in the manufacture of plastics. It took me some time to find out that the best chances for bakelite were where special technical effects are more important than mere cheapness, and that there was no use of wasting time and money in trying to introduce the new process in those cases where about the same results could be obtained with the older plastics. In other words, the process had to be reduced on its own merits, where, for instance, unusual strength or great resistance to heat or chemicals are essential, and not as a competitor to hard rubber, celluloid or natural resins.

The most important part of the problem we had before us was to give technical instruction to those who were willing to learn, and this technical instruction ranged from the first principles of how to use the product to all the engineering details of the equipment of their plant. It took me some time to realize that, contrary to my first intentions, it would create no end of appointments and irregular results, and it would certainly not the reputation of the process, if every licensee were allowed to carry out, according to his own fancy, the different operations from the beginning to the end. I concluded that the best way of avoiding such a failure was to conduct the manufacture of the raw materials to beyond the stage where chemical knowledge or too much experience is required. At first, I intended to sell the raw material unmixed with fillers, so as to let the individual user make his own molding compositions. This idea, too, had to be abandoned after I found that the proper preparation of these molding compositions in itself involved a great amount of skill, knowledge and minutious care, which could hardly be expected from average workmen. Unless we followed this rule, we were disposed to clash all the time with conflicting opinions or attitudes as to what was advisable and what was not, and to mention the prejudices and petty notions of foremen and superintendents. Only after all these details had been well established and taken into consideration, could I proceed to organize a complete factory, and similar establishments were started in Europe. Each of these factories was supplemented by a research laboratory and experimental department in which could be investigated the different applications of bakelite as well as the refinements in its processes of manufacture, and a further general scientific study of the subject.

But even then we were soon confronted with the paradoxical situation that the greatest drawback of bakelite was its multiplicity of applications, which threatened the squandering of our efforts in too many directions at the same time. On this point, we had to adopt the policy of concentrating our attention along the lines of least resistance, and to be guided somewhat by opportunism and learn when and where it was best to direct our efforts, leaving it to future opportunities for developing some of the applications which at first appeared rather attractive, but which were found to involve a disproportionate amount of attention or money for their successful introduction.

#### PROBLEMS CONNECTED WITH NEW CHEMICAL INVENTIONS

Most people do not realize that many new chemical enterprises present problems totally different from those connected with the running or the development of a purely mechanical industry. Indeed, some chemical processes involve factors and details which are not always easy to ascertain beforehand. I embark upon such enterprises without testing out beforehand these factors is very much like plunging into a gambling proposition; therefore, it is better to spend the necessary money on preliminary research work and preparation, then start tentatively on a modest scale, even if it tries your patience and your pocketbook. Then after you have every right to feel sure

about your proposition, there is no longer any reason for further hesitation in extending your plant to the required size.

#### THE IMPORTANCE OF SELECTING THE RIGHT BUSINESS ASSOCIATES

In my latter enterprise, I was able, not only to carry out all my preliminary work by my private resources, but I felt that if necessary, I could run the whole commercial enterprise without the financial assistance of others. This undoubtedly put me at a great advantage, as I was not hampered by any interference with my plans. If I had looked at the narrow money side of the proposition, I might have concluded that in as far as I was practically sure of the ultimate success of this enterprise, there was no reason to divide profits by accepting financial support from others. But I had learned by former experience how very valuable it is to have the cooperation of competent men for advice or influence. Therefore, in selecting business associates for my new industry, I took less in consideration any money they were willing to introduce as stockholders, than their exceptional personal qualifications and business experience. This point of view, on which I put great stress, is too often overlooked by chemists who start in a new enterprise where they are primarily confronted with the problem of finding the necessary funds. Frequently they make reckless connections with almost anybody who can furnish them the first money, regardless of whether they are the proper persons to help or advise or inspire them in their work, or whether they are men utterly uncongenial or who do not see in an enterprise anything but getting quickly as much cash as possible out of it, regardless of any other consideration.

If in the enterprises with which I have been connected, I managed to get along pretty well, I can attribute it, to a large extent, to the fact that in each instance I had the good fortune of being surrounded with congenial partners or collaborators, who, instead of causing friction and irritation, aroused my highest enthusiasm.

Nor do I think the grouping of business associates simply a matter of luck. It is worth some deliberation in picking out the right men. If in some instances I made a mistake, I did not hesitate to rectify it even at considerable trouble and pecuniary sacrifice. To put my opinion in a short formula, I would say: "Better not attempt much if you have as business associates only men whom you cannot trust, or who do not trust you, or who irritate or depress you, or who are dangerous by their greed, their recklessness, their superficiality, their weak character, or their general unreliability."

#### CONCENTRATION OF EFFORTS

Whatever task I undertook, I found it necessary to concentrate my full attention and my full enthusiasm on it, sometimes during several years in succession, until I felt I had overcome all the main difficulties connected with that line of work. During these periods of intense concentration, I hardly had the time or the desire to take interest in anything else; so much did I become enwrapped in my subject that even a vacation was irksome to me, because it took me away from my favorite problem. It was only in those periods of interval between each succeeding enterprise that I made up abundantly for all this and relaxed and was open to any other matters which might strike my fancy. Then, during such intervals, I lost almost entirely my interest in problems which I had successfully solved, but was ready to take up a new thing. This explains perhaps why the different subjects with which I have been connected are so little connected among themselves, and are situated in almost opposite corners of chemistry. The very difference of the succeeding subjects contained in itself that element of novelty which fed my interest and enthusiasm. It was every time like turning a new leaf, and this prevented me from becoming too one-sided. I should state, however, that the older I became, the more cautious I was not to spend



my enthusiasm on subjects which I considered unworthy of my best efforts. Several of my friends asked me, "How did you happen to strike such an interesting subject as that of the synthetic resins?" I can readily answer that I did not strike it haphazardly; I looked for just such a subject for a number of years until I found it among the many lines of research which I undertook in my laboratory. More than once, it has happened that at the end of years of work on some particular subject or another, I had to come to the conclusion that what I had found was not worth while following up further, although it might appear attractive enough to other chemists. So, more than once, I abruptly closed my work on some subject or another, and took up another line, until finally I succeeded in finding a subject on which I could feel thoroughly enthusiastic. In this way, my work became a real pleasure, regardless of the fact whether at the end it was going to bring the results I expected or not.

There is no doubt that I had a decided advantage over most of my fellow-chemists, who cannot dispose of their time the way they please, but who are bound to certain subjects whether they like them or not. If I had remained bound to my first successful enterprise, or if I had tied myself to others in some way or another, in the desire of making money, or for other reasons, I would not have possessed, at the age of 35 years, that absolute freedom of my time which gave me such excellent opportunities for further study and work along more congenial lines.

#### DANGER OF STARTING CHEMICAL ENTERPRISES WITH INSUFFICIENT CAPITAL

A great mistake has frequently been made by chemists of starting into a new business with just enough money to get along, provided everything goes well. Starting a chemical manufacturing enterprise with insufficient capital is one of the surest ways of getting caught in failure. I can say that I know of few chemical enterprises, if any, where the initial expenses were not decidedly higher than what was estimated at first. This is usually the most critical period through which every enterprise has to pass. It happens too often that there is not enough reserve capital at hand for weathering safely the first storms through which the newly launched ship has to navigate. It is easy enough to find all the capital when things go smoothly, but it is hard work to induce anybody to advance funds for a business enterprise which encounters troubles, except at an entirely disproportionate sacrifice. More failures in chemical enterprises have resulted from this than from almost all other causes.

#### PRESENT OPPORTUNITIES FOR CHEMICAL INDUSTRY IN U. S POSSIBLE SOURCES OF FAILURE

If I have risked trying your patience by going into all these details of a rather personal nature, or by giving my opinion as to the causes of success or failure of chemical enterprises, I beg to assure you that in doing so my object lies higher than merely to pose as some kind of an example to any of you. I want the men of this country who are desirous of joining in your chemical enterprises to realize that it is not enough to have good chemists at their disposal. I want to try to convince them that there are numerous conditions under which even the best chemists can not possibly make a success. I would like to impress this fact upon all those who have the welfare of our Nation at heart at a time when no country in the world has ever had such extraordinary opportunities for becoming foremost in all branches of chemical industry. I ask myself: Will our present magnificent opportunities lead us to efficient development of an unprecedented advantageous position, or shall we stumble and fall through sheer blundering in the way we conduct our new chemical enterprises; will these unparalleled chances of success only result in some kind of

a "flash-in-the-pan?" If we turn our present opportunities into a gigantic fiasco, then let me tell beforehand to the public at large, that we should not put the whole blame on our chemists. This country has enough able chemists, all eager to do their full share of good work. Our principal universities and engineering schools are now at least as good, for all practical purposes, as the very best European institutions of the kind. If some special branches of chemical industry, as, for instance, synthetic dye manufacturing, have not attained here, in the past, the same development as in Germany, this was mostly a matter of different opportunities. On the other hand, we can point to some of our other chemical industries, where conditions were more favorable, and where this country has become a leader in quantity, in quality and in pioneerism.

Shall we now strengthen our position of economic independence from foreign countries, by adding new chemical industries for which heretofore there was scant inducement for the man of enterprise, alongside of much better opportunities in other directions? Shall we become what we ought to be with the abundant opportunities just now at our disposal—the greatest center of chemical enterprise of the world?

The answer to this question will depend at least as much on the kind of men who are at the business end of those new chemical enterprises as on the chemical part of the problem. In this respect, I look with considerable apprehension on the future of some of the ventures which are being started now by men who are merely trying to make quick money and who, in a chemical enterprise, see only a pretext for realizing their greedy ambitions; men who look upon their chemists merely as temporary tools, ready to sacrifice their enterprise and everything connected with it, as soon as they can quickly cash in their profits, instead of trying to build up a permanent establishment run along steady business lines with a good underlying financial foundation, with the purpose of insuring, for years to come, regular and lasting profits, even if they may seem more modest.

It will certainly do no harm to many of our new chemical enterprises, if, among their directors, they have at least some chemists as well as purely business men, or bankers and lawyers. I know that such a statement will go against the belief of some of my friends who imagine that a chemist or a technical man is essentially unfit to treat a business proposition in a business-like way. If the average chemist makes a poor business man, it is simply due to the fact that he seldom, if ever, has an opportunity of obtaining business experience by being allowed to participate in discussing important business propositions in the councils of the concern that employs him. I would like to ask some of our business men, how they ever would have acquired business sense and business methods if they never had been allowed to learn to exercise their judgment in the handling of business problems? It is really a sad thing to see in this and some other countries, so many chemical companies where the board of directors does not comprise any chemists, except in a subordinate capacity. Why should a chemist, if he is intelligent enough to master the most intricate problems of chemistry, not be able also to learn how to exercise enough common sense and good judgment to help to discuss and devise successful business policies. Those of the large chemical enterprises of the world, which are counted as models in their line, have always had prominent chemists among their directors, and the policy of these enterprises has not been left entirely in the hands of a set of purely business men who remained willfully ignorant of the essential technical facts upon which their enterprise was based. I have known too many instances where serious technical difficulties were not estimated at their proper value by ignorant directors and where serious losses, disappointments and even failure arose from that source. Of course, it would be out of the question to expect that every director in

chemical enterprise should be a full-fledged chemist, but he ought at least, to some extent, be able to follow the difficulties, the vicissitudes and progress of the technical problems with which the enterprise is confronted. It has been my experience at intelligent business men, even if they have no technical or scientific training, can easily be made to follow with intense interest the technical questions of a chemical enterprise, provided there be among them, as fellow-directors, some chemists who can keep them informed, without going into unnecessary details, and who in doing so, can speak with some authority, instead of the directors obtaining their information from subaltern employees who are often so dependent on their position that they are too timid to speak without hesitation, or to present their views with some insistence.

#### OUR BANKS ILL-PREPARED FOR NEW CHEMICAL ENTERPRISES

The matter of financial support for new chemical enterprises, another subject which might be considerably improved in this country. The most successful chemical enterprises of the world have been started in a small way. At first sight, this would seem an unequivocal advantage; in reality, it is often a serious disadvantage from the banking standpoint. Our big banks are unwilling enough to back vast enterprises, but look with contempt at beginning industries. Nor have our banks the organization to enable them to investigate promptly or inexpensively the prospective merits of such small scientific enterprises. The result is that when a chemist has a good idea, he has to look for private financial backers. If he could do this directly, this might be well enough, but most of the time he has to go through the intermediary of a promoter, who complicates matters considerably by interposing himself as a self-constituted middleman, and who usually begins by diluting in advance the prospective profits of the concern, even if he does not attempt foremost to insure his own immediate benefits to the detriment of the healthy future development of the enterprise.

Before the convulsions which are now shaking Europe, our ardent sympathies may lie with one or the other side of the fighting nations. But your personal likes or dislikes do not diminish the fact that Germany has set us an example in industrial preparedness and that her large banks, long ago, have mastered the art of nursing new chemical industries. These large German banks have their staff of scientific experts, whom they freely consult about any new chemical enterprise which requests their financial support. To these scientific representatives of the bank, the chemist or inventor can talk in his own scientific language and explain clearly what he has proposed, without being barred in his appeals by the hopeless ignorance in technical or scientific matters of the bank directors, or without having to resort to the trick of playing on their imagination or hypnotizing them with fairy stories and winning them with exaggerated promises.

Just imagine what it would mean here in this country for a chemist to know that he could be backed by respectable banks, in any legitimate enterprise, however small, provided he could obtain to their experts, in his own way, that he has reasonable probability of success. The prestige of the bank alone would give him confidence in his work, and make him immune against the usual tactics of crushing and violent competition to which our powerfully established competitors might try to subject him. Our large American banks know how to float railroad projects, loans, real-estate transactions, or to consolidate established enterprises, or issue bonds or carry out similar whole financial operations; but they have not yet begun to learn how to support beginning enterprises, based on new scientific discoveries and which on this account can best thrive and grow to powerful maturity if allowed to be started tentatively on a small scale, provided they can reckon on adequate financial support when they need it.

#### THE HIGHER EDUCATIONAL EFFECT OF CHEMICAL ENTERPRISES

I would certainly not take such an intense interest in the future development of the chemical industries of this country if I looked into this matter merely from the standpoint of a so-called "prosperity" of dollars and cents. I know too well that there are easier means of making money. But I am convinced that a Nation, the prosperity of which is based on the development of scientific industries, is bound to furnish citizens of more worthy aims than a community where people get rich by slaughtering hogs and cattle, or by speculation in the fluctuating prices of real estate, or stocks and bonds, or merchandise, or by any other occupation where gain is the exclusive purpose.

A successful industry built upon sound scientific knowledge does not mean merely dividends for its stockholders or wages for its workmen. It consists in putting in practice principles of efficiency and introducing knowledge where formerly existed ignorance, and its usual accompaniments of waste, slovenliness, misery, want, vice and sorrow. It means surrounding our life with increasing and better opportunities by using the laws of nature to the greater help of man.

Progress, in general, is very slow to grow and is still more slow to assimilate. But, strange to say, our reactionary attitude has, in some cases, been cured through sheer greed. To state it brutally, science only began to make rapid progress as soon as it found applications which led to the payment of cash dividends. Chemical and electrical companies, for instance, spend more money for research and scientific investigation than all the universities combined. The result has been that it is just those two fields of science which have shown by far the greatest development, as compared to all others. By a sort of hyperinduction, science, after helping industry, got stimulated itself by the growing exigencies of industrial enterprises. But some of you will ask me: "Where does all this lead us to; will the world at large be better for it? Are not our scientists, our chemists and engineers just those who have helped to make the present war so atrocious?" To this, I can answer, without hesitation, that those who are responsible for what is happening now are not the scientists themselves, even if their work has been impressed into service for means of destruction and sorrow. War is many ages older than science. Greed, iniquity, lust for power, the main inheritance of the aims and thoughts of the past, rendered respectable by a rather large share of our so-called classical literature, together with our awe for tradition, are the main influences which keep us in the cold, relentless grip of the wrong ethics of bygone ages. Even our men of science have not been able to shake off entirely so many superstitious beliefs, so many erroneous traditions, rendered respectable through pedagogic smugness and—shall I say it—with which the minds of the children of each succeeding generation have been mummified in prejudice of certain points of view. This accounts for the fact that the average man is still more easily swayed by elegant phrases than by scientific truths. True science, on the contrary, has no more respect for the most brilliant rhetoric of classical literature, if this latter promulgates ideals which are contrary to facts, than it has any patience with the utterances of a politician whose passion or interest makes him overlook or distort facts.

As far as the ethical side is concerned, has it ever occurred to you, that notwithstanding the fact that chemistry and electricity have enriched an enormous number of people, there are few, if any, instances where scientific men, engaged in applied science, have become as absurdly rich as some of the big money hoarders of this world? Why? Because their work is too interesting to induce them to get into a life of mere money-getting; for the chemist, the financial consideration is a necessity for his existence, but that is not the chief end, as it is for those whose conception of success does not go much beyond the desire of



money or power. To him whose imagination is so rudimentary that he can perceive nothing else in the cultivation of science than dry knowledge, the shrivelling up of all sentiment, I should say with Jacques Loeb<sup>1</sup> that there is a sufficiently wide play for our emotions in our generous response to all that is beautiful and just and in our sympathy with all those who suffer or are treated unjustly, and that the active participation in the improvement of the masses, economically, physically, socially, intellectually, and aesthetically, will offer for a long time to come, a sufficient outlet for all human desire for emotion. What progress the world has made, not only in physical welfare but also in the conquest of superstition and hatred, and in the formation of a correct view of life, it owes directly or indirectly to exact science.

It is infinitely more costly if a mistake is made in arousing nations or social groups to hatred or fear than if a mistake is made in some special problem of physics or biology; but by an irony of fate, the denunciation by society in the latter case is apt to be much more severe than in the former. This is the result of the fact that the rigid consideration of truth and the feeling of responsibility for truthfulness which exact science has established, have not yet reached the masses. And this situation

will last until the influence of the metaphysical romanticist has been replaced by that of the scientist.

To you, then, and all those who are willing to build up chemical industries, let these thoughts be the guiding inspiration of your work.

MY FRIENDS, CHEMISTS OF AMERICA:

How can I let pass an occasion like this without reminding you of what you did for me?

Twenty-seven years ago, I came here as a stranger among you and now I feel so much as one of you that sometimes I wonder that there was ever a time when we did not work and play together.

When I was young and poor and unknown, you never hesitated to extend to me the cordial hand of welcome, you never missed an opportunity to show me your friendliness, to help me by advice or otherwise. Much of what I have used in my work, I learned from you, at the meetings of our chemical societies, or in the brotherly surroundings of our Chemists' Club.

You—your friendship, your generosity, your good-natured modesty, your example, inspired me in my work.

I wish I could better express my thanks.

YONKERS, NEW YORK

## CURRENT INDUSTRIAL NEWS

### BLEACHING MECHANICAL PULP

According to an article in a recent edition of the *Paper-Maker*, the bleaching of mechanical wood pulp not only increases the whiteness of the pulp but prevents the formation of fungi during storage. Sodium bisulfite has been found a most satisfactory bleaching agent. The pulp, saturated with it, becomes whiter for about a fortnight and retains its whiteness for some time. Afterwards, it assumes a grayer tint but only slowly. When the demand is small, it suffices to brush each board uniformly with the bisulfite solution and then to tie them together and pile them into heaps. The quantity of bisulfite used is  $2\frac{1}{2}$  gallons per ton of pulp. When the demand for bleached pulp is large, a wooden box lined with sheet lead is arranged on the board machine, the lead lining hanging over on one side. A strip of felt is placed in the channel, then the longitudinal side of the strip of felt is cut notched and this side is allowed to hang about four inches over the top of the lead. If bisulfite solution diluted in the ratio 1 : 3 is poured into the tank the solution drips uniformly onto the wood pulp. The size rolls of the board machine should not be of iron but of wood or of copper. If it is desirable to increase the quantity of the bisulfite, the strip of felt may be allowed to hang farther out of the tank or a second or even third strip of felt may be employed, or a bisulfite solution of greater concentration may be used. To accelerate the bleaching, a second tank which allows dilute sulfuric acid to drop onto the pulp, is arranged behind the tank above described. The flow of sulfuric acid must be so regulated that 48 to 64 oz. of concentrated acid are used per ton wet mechanical wood pulp. Bleached pulp may be thus obtained in two days. The above method, however, has the disadvantages that a somewhat irritating odor of sulfurous acid is produced, that the process is expensive and that the manipulation of the sulfuric acid requires care. Sulfuric acid, however, is only used when the bleached pulp has to be obtained quickly.—A. MACMILLAN.

### NICKEL-PLATING ALUMINUM

A process of nickel-plating aluminum, invented by M. J. Carnac, which is claimed to produce a firmly adhering coating, is described in *Ind. e. Inv.* (Barcelona). The aluminum is first

<sup>1</sup> See *Yale Review*, July, 1915, "Mechanistic Science and Metaphysical Romance."

cleaned in a bath of boiling potash, next washed with milk of lime and then immersed in a bath of potassium cyanide for several minutes; finally it is subjected to the action of a bath of ferrous chloride composed of 500 g. hydrochloric acid, 500 g. of water and 1 g. of iron. After each operation the object is washed with clean water.

Good results are obtained from a plating bath composed of 1000 cc. water, 50 grains nickel chloride and 20 grains boric acid with a current of 1 ampere per square decimeter at 2.5 volts. The good results of the process appear to depend upon perfect cleaning and a suitable deposition on the aluminum of a coating of iron from the iron bath. The existence of this thin coating of iron is verified by comparing with a magnetic balance a treated and untreated specimen of aluminum. Under these conditions the nickel deposit infiltrates through the surface of the aluminum, and adheres to it so thoroughly that however heavy the deposit, it is impossible to detach the nickel without removing particles of aluminum.—M.

### BRITISH ALUMINUM REGULATIONS

By a British regulation of December 7th, aluminum and alumina are included among the materials to deal in which a special permit from the government is required. This new regulation simply means that all supplies of aluminum which can be obtained from abroad will, in future, be held at the disposal of the state, as the production of British works has, for some time past, been in the hands of the Government. It is reported from the United States that, in consequence of the high price of aluminum, which at present is about three times that of copper, transmission lines in which aluminum wire has been used are being replaced by copper wire. The present boom tends to show that aluminum is not a competitor of copper at such times, whatever it may be in times of depression, as its price always rises much more rapidly than that of copper.—M.

### BRITISH METALS AND MUNITIONS

Brass, copper, zinc, aluminum, nickel and other non-ferrous metals being of such enormous value in the production of munitions, it is not surprising to learn from the *Chemical News* that the Institute of Metals, which takes cognizance of all other metals except iron and steel, should be especially interested in the pro-

tion of the numerous metal articles required for the prosecution of the war. The Institute is in daily touch with munition factories throughout the kingdom and also with certain Government departments requiring metallurgical information.

The publications of the Institute have proved of great value, as these contain the very latest scientific methods dealing with non-ferrous metals and large shipments of the journal have been despatched to Japan and the United States to be used for works producing munitions for the allies. In addition, copies are being sent to various public and university libraries situated in United States munition centers. Copies of the Journal can be purchased by non-members from the office of the Institute of Metals, Westminster, London.—M.

### NICKEL ANODES

Some interesting experiments recorded in *Metal Industry* describe the welding of nickel anodes by the oxyacetylene process, means of which worn nickel anodes, which have been previously scrapped and sold at less than half price, are now being reclaimed. The anodes were castings of 90 per cent nickel, 5 per cent carbon, 2 per cent iron and were in the form of elliptical bars approximately  $1\frac{1}{2}$  in. by  $3\frac{1}{2}$  in. cross section and 30 in. long, weighing 30 lbs. By welding up old anodes which have been in the solutions, the former scrap nickel was converted into anodes which acted like new ones at a comparatively trifling cost.—M.

### TRADE OPENING IN SIBERIA

The weekly bulletin (Ottawa) of the Canadian Department of Trade and Commerce contains a report which deals with the development of trade in Siberia. It has seemingly been the aim for foreign firms to place their representation in the hands of a single firm in European Russia and to pay little attention to the Siberian market. German firms, however, seeing the disadvantages of this system, some years ago began to send out travellers with a full range of samples of their wares, and have, in this way, been able to set up a substantial business. Among the items of machinery for which there is an increasing demand in Western Siberia may be mentioned oil engines of the Diesel type, of from 50 to 80 H. P., for operating saw mills.

There might also be a good market open for the supply of agricultural machinery, especially engines. Oil tractors find preference on account of the prevalence of alkaline water in Western Siberia. Lightness is a desirable feature, as the heavy engines tend to pack the soil and prevent the growth of vegetation. Tractors of the "caterpillar" type might also find a ready market.—M.

### BRITISH DRUG TRADE

Of late, considerable publicity has been given to statements dealing with the present scarcity of certain drugs, the dearth of belladonna, which is obtained from Central Europe, being of account for the shortage and high price of atropine. It is most desirable, says the *Chemical Trade Journal*, that this common misconception as to the sole source of atropine should be dispelled. Belladonna is certainly one source, but a more valuable one is, as has been proved by investigations of the Imperial Institute, London, the Egyptian hyoscyamus henbane. This plant is found wild in the Egyptian desert and in the Sudan and these countries are the sole source of the commercial supply. Prior to the war, Egyptian henbane was shipped to Germany for manufacture, but large supplies of the plant can be readily obtained and a considerable quantity is ready for manufacture into the drug.

Eserine, also much used in ophthalmic surgery, the scarcity of which has been lately commented on, is produced from the Calabar bean of West Africa, and, if there is a dearth of the drug, it is more probably due to extreme pressure on the manufacturing resources of the British drug trade than to any scarcity of the raw material.

As to cod-liver oil, the present high price—five times more than that of last winter—is due to Germany's demand for Norwegian supplies. The increased demand should, however, have an ultimate beneficial effect on Newfoundland which has been for some years producing, according to the Norwegian process, the highest grade of medicinal cod-liver oil. Supplies of this oil are available in the home market.—M.

### GOLD DISCOVERIES IN WINNIPEG

It is reported from Winnipeg that samples have been produced by prospectors in the Rice Lake district, 100 miles north of Winnipeg, which seem to indicate that the locality is rich in minerals. Claims are also being staked in the Gold Lake district, about 50 miles north of Lake Rice. The strata extend from Cumberland Lake northwest of La Pas, southeasterly in the direction of the Rainy River. The formation is gneissic with seams of about 1 to 6 in. wide, which show tracings of gold, iron, barytes with some copper and silver. Nearly all the claims staked in this district are for speculative purposes and have been visited by prospectors and mining engineers. No definite information, however, has been given as to the prospects. The provincial government is to make an effort to obtain mineral rights from the Dominion Government which owns all the minerals in the Province of Manitoba.—M.

### NEW SHAFT COUPLING

According to *Engineer*, Mr. J. W. Boulton, of Cheadle, Manchester, has introduced a simple form of shaft coupling. The external appearance is exactly the same as that of an ordinary flange coupling except that there are no bolts. In the face of one flange a circular recess eccentric to the center is bored; on the face of the other flange a corresponding spigot projects. This eccentric forms the driving member. The two parts are kept in line by the shaft end projecting into the recess entering a hole in the spigot. Owing to the absence of bolts the coupling has a certain amount of flexibility. The whole thing is easily produced in the lathe.—M.

### JAPANESE MINING IN 1914

According to the *Mining Journal*, the outbreak of the war seems to have exerted a serious influence on the mining industry of Japan. The output of copper has advanced steadily in recent years and reached the high-water mark in 1914 with a total of 67,909 tons, with an export tonnage of 45,556, which exceeded by a few tons the total yield for the year 1910. The Japanese market suffered disorganization with the closing of the metal exchange but as soon as the London metal exchange reopened, large sales in Japanese copper were made and the situation relieved. Thus, it will be seen that Japan was one of the few countries where copper production last year showed an increase.

The production of coal, next in importance to copper, does not appear to have been much affected. The output was 20,602,000 tons compared with 20,425,000 tons for the previous year. Owing, however, to a restriction of output due to declining prices, the prospects for the current year are for lower production.

The sulfur industry showed expansion, the production being estimated to have increased some 10,000 tons. Most of this is exported to the United States and Australia.



The gold production of Japan proper is small and amounted last year to 164,987 ozs., while that of Formosa gave an addition of 3,700 ozs. more. A further source is that derived for foreign companies in Korea. Taking altogether the total output of gold for the year was about 303,000 ozs.

The amount of SILVER produced for the past year is returned at 4,615,422 ozs.

The ANTIMONY output of Japan shows increased activity and the export for the year was valued at \$570,000. The general demand for sulfuric acid and iodide of potassium is leading to an increase in the production of these commodities.—M.

### WOLFRAM

The British *Mining Journal* reports a shortage of wolfram ore which is thought to be due to the interruption of existing sources of supply caused by recent Government measures. There is, however, good reason to suppose that this shortage is only temporary and is mainly attributed to the difficulty in getting new machinery into order. The Indian Government has taken more active steps in Burma, and the Lieutenant-Governor has paid a visit to Tavoy and Mergui in connection with the wolfram industry. He has solicited the support of large firms in Rangoon and has intimated that unworked claims may be cancelled. From the producer's point of view, the most important question is the financial assistance to be forthcoming. There can be no doubt that the production of wolfram is increasing in Burma and elsewhere. The Mawchi mines are producing close on 30 tons per month and anticipate a much increased output in the future. The Wolfram Mining and Smelting Company gives the November output as 27 tons. The price remains unchanged at \$13.20 per unit.—M.

### THE BRITISH MOLYBDENITE MARKET

The *Mining Journal* reports the question of supply and demand of molybdenite as one of the recent problems of the British. The price was exceedingly high in the six months preceding the war, but, since the Government took the control of the market, the price has lowered considerably and may be further reduced, though it is noted that the Australian Government has fixed it at \$25.20 per ton for twelve months. What makes the position a very difficult one for decision is that the offers made by producers in Canada of supplies of concentrates are on a hitherto unheard-of scale. A British Columbia firm has offered to supply the British market with 100 tons a month or probably more than six months' supply on the rate of the world's production before the war. The remarkable feature about the offer is that previous to 1914 no one was aware of any molybdenite having been produced from British Columbia. In that year about 50 tons of ore, of about 14 per cent, were shipped to the United States.

Offers of concentrates are not confined to British Columbia, and, consequently, the expectation of mine owners in the aggregate must amount to a very large figure indeed. It is certainly very curious that so alert a community as the Canadians should have been content to forego such large profits as molybdenite has offered for something more than two years past, and while, of course, those who fix the price in the British Empire cannot ignore such positive assurances as definite offers of material convey, the fact cannot be ignored that molybdenite is a new product for Canada, so that the estimates are, at any rate, not based on experience. As matters stand to-day, statistics for the Canadian production are not available, but, so far as can be learned, Canadian molybdenite has not made its appearance in Great Britain as yet in any appreciable quantity.

Whether it is due to the fact that British Columbia dealers have been assuring the miners that there was little or no market for the mineral, and that, if it were mined in any quantity, it would not be sold, is a question. Putting aside British requirements altogether, the United States Mining Bureau has published a list of buyers in the United States, and there is a regular demand for molybdenite from France and also to some extent from Russia.—M.

### BRITISH BOARD OF TRADE

During the month of December the British Board of Trade has received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles:

Anatto, dry, for food coloring	Paper fasteners
Basic slag	Perfumes for soaps
Bottles, square with metal caps	Pumice stone, powder
Boot polish	Rubber bellows
Brace bits, gimlet pattern	Rubber friction-pads
Brushes, goat hair	Soap boxes, aluminum
Cat gut, as used for drums	Steel, high-speed
Celloloid, thin transparent sheets	Thermometers, veterinary, 6 in
Celloid substitutes	in length
Colors, dried lithographic	Thermometers, food, in nickel or
Cerium stones for automatic lighters	card-board boxes
Drumskins	Typewriting machines
Films for bioscopes	Vacuum flasks
Glass, bulbs and tubes for making	CHEMICALS
incandescent lamps	Blue stone (copper sulfate)
Glass jars	Caustic soda
Licorice	Iceland spar, crystals
Lithophone	Marble dust
Litmus powder, commercial	Methylated spirit, commercial
Marbles, glass and other	Silica, ground
Milk, natural sterilized, in tins	Sodium bromide
Magnets, telephone receiver	Toluidines
Nails, wire, cheap	Vanillin (crystals)

—M.

### VENEZUELAN PAPER FACTORY

The paper factory at Maracay, Venezuela, is approaching completion and is expected to be in operation towards the end of 1915. The building is of Venezuelan cement, the roof of Belgian galvanized iron, and all the paper-making machinery from Silesia. Only the motive power is American. This consists of a hydro-electric installation at Cheroni which will develop 300 horse power in the wet and 200 in the dry season. The raw material consists of an aquatic plant which grows in great quantity on the margins of Lake Tacarigua, near the shore of which the factory is situated. Wrapping paper and straw board will be produced at first, the capacity of the plant being 10 tons in 24 hours.—M.

### POTTERY SUPPLIES FROM INDIA

Pottery exporters report that samples of clay and feldspar sent from Mysore, India, are suitable for the manufacture of porcelain. The quartz can be most conveniently used for porcelain and earthenware glasses, also as fluxing material for porcelain.—M.

### DISINFECTION OF HOSPITAL SHIPS

The use of electrolyzed sea-water containing hypochlorites has recently been tried for the disinfection of hospital ships carrying infectious cases. The test seems to have proved highly satisfactory.—M.

### BRITISH REGULATION OF EXPORTS

An order has been published in Council prohibiting the export from Britain of magnesite, magnesite and its alloys. Beeswax is prohibited to all destinations except British possessions. Silica bricks and all articles wholly or partly made from copper are prohibited to all foreign countries of Europe other than France, Russia, Spain and Portugal.—M.

# SCIENTIFIC SOCIETIES

## CHEMICAL EXPOSITION AT URBANA

The Chemistry Department of the University of Illinois is organizing an Exhibition of Chemical Industries to be held in conjunction with the Spring Meeting of the AMERICAN CHEMICAL SOCIETY and the dedication of the new Chemistry Building at the University of Illinois, April 17-21, 1916.

The Committee propose to emphasize especially the importance of American chemicals and apparatus, and at this critical time cooperation in making them better known will be of real service both to the profession and to the chemical public. A large attendance of chemists is expected at the meeting, in addition to the 2000 students registered for courses in chemistry. The conditions governing the exhibition are as follows:

1—No charge is made to exhibitors for floor space; a nominal charge to cover the cost of printing a catalog will be made.  
2—Necessary gas, water, electricity and drayage will be furnished free.

3—There will be no admission fee.

Correspondence should be addressed to the chairman of the Exhibits Committee. Applications for floor space, together with specifications with regard to water, gas, and electricity needed, will be filled in the order of their receipt.

W. A. NOYES, *Director of the Laboratory*

EDWARD BARTOW, *Chairman of Executive Committee*

H. L. OLIN, *Chairman of Exhibits Committee*

## CHEMICAL ABSTRACTS

### PROGRESS OF THE DECENNIAL INDEX PROJECT

Although the members of the American Chemical Society have responded well to the request for advance subscriptions to the proposed collective index to *Chemical Abstracts*, considerably more support is needed to insure publication. On January 15th subscriptions had been received for a little over one thousand copies; at least as many more are needed to make the index pay for itself.

It is difficult to make an accurate cost estimate for the index. The cost will, of course, depend on the size of the edition, the number of pages occupied by the index and the amount of extra assistance that will be required for its preparation. Because of a lack of uniformity in the methods of indexing subjects used in all but the last few volumes the number of pages needed for the collective index cannot be accurately predicted. For this reason the collective subject index will have to be prepared directly from the abstracts if it is to reach its highest degree of usefulness. This is going to add considerably to the cost of preparation. It seems probable that an edition of 2,000 copies would cost at least \$20,000. It would cost over \$18,500 just to print 2,000 copies of 6,000 pages each; probably a little less than 6,000 pages will be required.

Among the many opinions regarding the project that have come to the attention of the editor there is perfect agreement at it is a highly important undertaking. Especially noteworthy is the large number of statements that the index is considered a good investment, one that will pay back many times the original expenditure. One man has said: "Aside from the fact that it will save me, I cannot afford not to buy an index because I have invested in the journal and the value to me of the accumulated volumes will be great only in case I add the collective index. The latter is the keystone that will make the arch of the ten volumes complete and useful."

In the belief that there are many more who will want an index and who may have mislaid their subscription blanks, there is being published on the first page of *Chemical Abstracts*, 10, No.

3 (February 10th) a blank which can be used for subscription. Since the possibility of publishing the index may depend on immediate action, subscriptions should be sent in at once.

E. J. CRANE

## AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

### EIGHTH ANNUAL MEETING

BALTIMORE, JANUARY 12-15, 1916

The meeting was called to order at the Emerson Hotel on Wednesday, June 12th. As Dr. Rosengarten was not present, on account of illness, Dr. Samuel P. Sadtler, the first Vice-President of the Institute, presided. After an address of welcome, a committee was appointed to canvass the ballots for officers. This resulted in the reelection of Dr. Geo. D. Rosengarten as *President*, and the present *Vice-Presidents*, G. W. Thompson, A. C. Langmuir and J. M. Stillman; the present *Secretary*, J. C. Olsen; *Treasurer*, F. W. Frerichs, and the election of H. O. Chute as *Auditor*, and Dr. Chas. F. McKenna, A. D. Little and Richard K. Meade, as *Directors*.

The REPORT OF THE SECRETARY showed a total membership of 226, with several applications unacted upon. The sale of Transactions has very materially increased during recent years. The death of Mr. H. C. Humphrey, of the Corn Products Refining Company, was reported by the Secretary.

The adoption of an Amendment to the Constitution, permitting reelection of the President for a second term, was reported. When the President is reelected, the terms of the Vice-Presidents are automatically extended for another year.

The REPORT OF THE TREASURER showed a balance on hand of about \$1500.

Professor James R. Withrow, *Chairman of the Committee on Chemical Engineering Education*, reported the results of the responses received to a Questionnaire sent out by the Carnegie Foundation, which indicated that, in the opinion of engineers, the theory of engineering is well taught in the universities, but applied engineering is not well taken care of.

The Committee on Chemical Engineering Catalogue reported substantial progress in cooperation with the Chemical Catalogue Company, who have already secured a large list of manufacturers of chemicals and chemical apparatus who will cooperate in making this catalogue a success. Mr. Francis M. Turner, Jr., having been engaged to take charge of the Information Bureau, in which will be listed, indexed and filed data concerning the products of these firms. The Institute Committee, of which Dr. Chas. F. McKenna is Chairman, is cooperating in preparing specifications for the catalogue. The most important paragraph in the specification refers to the matter to be published and is as follows: "There shall be no display advertising. Copy is to be under the editorial supervision of the Committee. The Committee suggests that manufacturers confine themselves to simple statements of design, capacity, etc., and include only such claims as are readily demonstrable."

The Committee on Public Policy reported a resolution offering the services of the members of the Institute to the United States Government in the present organization of chemical industries in the campaign for preparedness. The resolution was referred to the Council for action.

The following papers were then read and discussed: "The Development of the Manufacture in the United States of Products Derived from Coal," by H. W. Jordan (see elsewhere in this issue); "The Cracking of Petroleum and Other Hydrocarbons as a Chemical Engineering Problem," by W. F. Rittman, who reported substantial progress in the installation of methods for cracking petroleum and the production of considerable



quantities of gasoline and other products from this process. (This paper will appear in full in an early issue of *THIS JOURNAL*.)

On Wednesday afternoon a visit was made to the Sewage Disposal Plant of the City of Baltimore, where the sedimentation and Imhoff tanks were inspected. The effluent from these tanks was further purified by sprinkling filters, the effluent from which operated a small dynamo by which the plant is lighted.

The Ozone Water Purification Plant of the Baltimore County Water Co. was also inspected with great interest. Several million gallons of water are purified by ozone in this plant. Mr. Powell, the engineer in charge, conducted the party and also presented a paper on Friday morning, giving a description of the installation and the results obtained.

The plant of the Maryland Steel Co., at Sparrows Point, was also visited on Wednesday afternoon.

On Wednesday evening a meeting was held at the Johns Hopkins University. Mr. A. D. Little presented a paper on the "Utilization of Wood Waste." (This paper appears in full in this issue.)

Dr. W. S. Landis presented a paper on "The Production of Ammonia from Cyanamid." Detailed drawings of the plant were given and yields stated. (This paper is printed in full in this issue.)

Mr. Maximilian Toch read a paper on the barium industry, showing by means of slides the Tennessee plant where the barium sulfate is mined, ground, and finally worked into various barium salts.

On Thursday morning, the plant of the Emerson Drug Co. was visited and the process of making Bromo Seltzer inspected.

The members and their guests then proceeded by a special car to the Naval Academy at Annapolis. The Naval Experiment Station was first visited and the methods and apparatus in use for testing steel and other products examined with great interest. After lunch at Carvell Hall, the grounds, buildings and laboratories of the Academy were visited. Special interest was shown in the sarcophagus of John Paul Jones and also a large number of flags and other trophies.

On Thursday evening the subscription dinner was held at Emerson Hotel. Dr. Ira Remsen, of Johns Hopkins University, addressed the members and emphasized the great necessity of scientific research in connection with the chemical industries of the United States. Addresses were also made by A. D. Little, Richard K. Meade, Mr. C. P. Van Gundy, Chairman of the Local Section of the American Chemical Society, Ex-President Samuel P. Sadtler, and Secretary J. C. Olsen.

On Friday morning the following papers were read: "A New Process of Bleaching," by S. F. Peckham. (Printed in full in this issue.) "Lutes and Cements for Chemical Purposes," by S. S. Sadtler. "Ozone Purification of Water," by Mr. Powell, of the Baltimore County Water Company.

On Friday afternoon the plant of the Standard Fertilizer Co. and the Davidson Chemical Co. were visited. Members were especially interested in the very large pyrite burners at the latter plant and also the use of silica dishes for the concentration of the sulfuric acid.

The plant of the Maryland Glass Company was visited as well as the new engineering buildings at Homewood, the new site of the Johns Hopkins University. Special interest was shown in the arrangements which have been made for complete boiler tests in the power house, including arrangements for taking samples of the flue gas and making other tests on the chimney at various points.

On Friday evening a joint meeting with the Maryland Section of the American Chemical Society was held at the Johns Hopkins University. Mr. G. W. Thompson presented a paper on "Changes in the Volume and Specific Gravity of Linseed Oil Films on Drying." Very marked changes in the specific

gravity were shown to occur in the linseed oil films. Dr. H. E. Ives, of the Illuminating Engineering Society, presented a paper on "Artificial Daylight," which was very fully illustrated. The theory was demonstrated by which artificial daylight could be produced both from gas and electric light, and demonstration given of changes in color by artificial daylight and the ordinary illumination.

The smoker at the Johns Hopkins Club, given by the Maryland Section of the American Chemical Society, was enjoyed by all. On Saturday morning the plant of the Tidewater Portland Cement Company was visited at Union Bridge and also the Holtwood Power Plant.

The attendance at the meeting was excellent.

COOPER UNION, N. Y.  
January 17, 1916

JOHN C. OLSEN, Secretary

## SECOND PAN-AMERICAN SCIENTIFIC CONGRESS DECEMBER 27, 1915 TO JANUARY 8, 1916

Among the abstracts of papers presented before Section VII of the Pan-American Scientific Congress, the following appear to be of especial interest:

**Area, Distribution, and Present Working of the Petroleum Deposits of Argentina,** by ENRIQUE M. HERMITTE—The petroleum deposits of Argentina are found in four different regions: (1) In Cacheuta, which lies at the southern end of the Mendoza precordillera; (2) in the Province of Mendoza and the Territory of Neuquen; (3) in Comodoro Rivadavia, on the Patagonian coast; and (4) in the subandine zone that runs from Bolivia into the Provinces of Salta and Jujuy. Of these (1), (2) and (4) are of great geological interest, owing to several peculiarities, which the author studies in detail; but the only one that so far has acquired practical importance is District 3, to which he devotes nearly one-half of his paper. This region is characterized by the fact that, unlike the other oil regions, it exhibits no signs of dislocations or slides in the geological formations. Except for slight creases on the surface, the sedimentary beds are practically horizontal.

Of the oil region of Comodoro Rivadavia, the Government has reserved 5,000 hectares, in which 20 wells have been bored, distributed over an area of 300 hectares. Bores have been made by private persons and companies over an area of 6,000 hectares to the south of the Government's reservation, but the operations have not been conducted with sufficient thoroughness to afford many data of practical value.

It appears from the borings and investigations conducted by the Government that the first aqueous layers occur at depths of between 300 and 350 meters below sea level; that the oil begins between 50 and 80 meters farther down, and that the intervening strata are of such nature as to prevent infiltration from the water to the oil deposits. The latter have been found in one of the wells to extend as far as 620 meters below sea level, which is as far as the boring has been carried, and there seems no reason to believe that they do not extend farther. The soil as far down as 400 or 450 meters is mainly clay of various kinds; between 450 and 520 meters, sandstones consisting of quartz granite cemented by clay; farther down, sand and gravel, sandstone, and sandy clay containing petroleum. The proportion of petroleum in the beds containing it is about 41.2 per cent, of which about 70 per cent can be extracted. Assuming the average workable thickness of these beds as 5 meters, it is estimated that the possible yield is 1.443 cubic meters of petroleum per square meter of surface. As a matter of fact, however, there are data that permit an assumed productive thickness of as much as 20 meters.

In some places high-pressure gas has been found before reaching the oil; in others only at the depth of the oil, the pumping of which has been accompanied with violent eruptions.

Systematic working of the wells began only in 1913. During

at year 21,000 cubic meters were drawn from four wells. In 1914 the production was 44,000 cubic meters, and up to August of this year (1915) it has amounted to 48,500 cubic meters. During the year 1914 the average yield, including all wells, even abandoned ones, was 10 cubic meters per well per day. The yield of the 10 wells worked during last June (1915) averaged 10 cubic meters per well per day. The author concludes from the data so far obtained that in future the average yield may be estimated as 20 cubic meters per well per day.

As to the quality and composition of the oil, there are not sufficient data from which exact figures can be derived, especially the bores have not been carried deeper than the upper layers of the oil deposits. The author, however, gives the results of new analyses, which indicate that the petroleum found so far is characterized by high density and a very small proportion of sulfur. The latter feature is of especial importance to Argentina, where the main fuel is oil, for the presence of a large proportion of sulfur in the oil would be a serious drawback to its utilization for fuel.

**Iron Ores of the Americas**, by C. K. LEITH—The distribution of the present production of iron ores by kinds is summarized by the aid of tables and charts. The distribution of the reserves is summarized by tables and charts. A comparison is made of the distribution of the present production and the distribution of reserves, bringing out the fact that there are large reserves of ore in the two Americas which are not now being drawn upon.

A summary is made of the factors which determine why certain ores are used and others not used. All these factors are summarized under the general term "availability." The points are made that the availability (and, therefore, value) is determined only in part by the intrinsic qualities of the ore and largely by the effort and money spent on the ore, and that intelligent formulation of laws of governmental control of reserves in the way of taxes or other measures requires careful consideration of this fact in order that opportunity may be kept open for the application of the human factors which so largely determine the availability and value of an ore body.

Because of the great variety of factors entering into the problem, it is difficult to forecast the distribution of future production of iron ores; but certain recent tendencies are enumerated which seem to present certain changes for the future.

**The Nitrate Industry**, by ENRIQUE CUEVAS—Caliche, the raw material from which the nitrate of commerce is extracted, was discovered in the great desert of northern Chile by the Indians, some time in the seventeenth century. The first nitrate company was organized in 1812 with very crude reduction methods employed. The present era in the industry dates from 1855 with the introduction of steam as a means of heating and evaporating the solutions.

In 1873, the Peruvian Government assumed a monopoly of the nitrate lands and made grants in a careless manner. This led to much difficulty encountered by Chile when that country was left in possession of this area at the close of the Pacific war. However, titles have since been generally cleared up and beneficial laws enacted, covering not only the matter of land disposal, but of labor and other important questions.

According to the latest official report of the inspector-general of the nitrate deposits, the zone of nitrate-bearing ground comprises 200,000 square kilometers, of which less than 3 per cent has been surveyed and prospected. In this surveyed portion alone there remains enough nitrate to supply the world for an additional 100 years, measured at the present rate of production. These calculations have been made on an extremely conservative basis, and take no account whatever of known areas of low-grade material.

The industry is divided into two principal operations: (1) mining and transportation of the crude material and (2) pro-

duction of nitrate. Methods employed in both branches leave room for improvement. Under present practice, considering average value of raw material, wages, etc., the cost of producing commercial nitrate is estimated at 50 cents United States currency per quintal (101.44 pounds).

Trade specifications require a content of nitrate of sodium equal to at least 95 per cent. This is used as a fertilizer. The refined product, with over 96 per cent nitrate of sodium, is applied to manufacturing uses, such as for glass, explosives, fusing mixtures, nitric acid, etc.

There can be no competition between Chilean nitrate and atmospheric nitrate under any conditions which may be foreseen at present. The deposits of the great Pampa Salitrera (nitrate plain) are too vast and the business of manufacturing and marketing the material is too well systematized, whereas atmospheric-nitrate manufacture exists under too many limitations.

A natural reduction in nitrate production has followed the outbreak of the European war, many of the important consuming markets having been cut off.

The author has appended detailed data regarding nitrate production, method of transacting nitrate sales, results of experiments showing the advantages of using nitrate of sodium as a fertilizer, with special reference to crops raised in the United States, and other items of value covering the entire field.

**The Coals of Brazil**, by I. C. WHITE—Impure coals 2 to 6 ft. in thickness of lower Permian age occur in the States of Rio Grande do Sul, Santa Catharina, Paraná, and thin beds extend into São Paulo, while lignitic coals of good quality of Upper Cretaceous or lower Eocene age are reported from the States of Para and Amazonas by Dr. Ganzaga de Campos.

The Permian coal formation covers several hundred square miles in South Brazil, its coals containing about 35 per cent of ash, of which 2 to 8 per cent is sulfur. By crushing, washing, and briquetting, the ash can be reduced to 14 per cent, and the excessive sulfur eliminated in 33 per cent of the coal, the resulting briquettes yielding a heat value of about 13,500 British thermal units, while 42 per cent of the coal by weight will make a fair grade of "slack" coal with about 25 per cent of ash. Used in the manufacture of producer gas and converted into power through the gas engine, the effectiveness is greater than equal weights of the best grades of Pocahontas or Cardiff coals when the latter are converted into power through the steam engine.

The lignitic coal of North Brazil, according to report, compares favorably with the lignites of the western United States, yielding fuel values slightly exceeding 10,000 British thermal units. The area and quantity of these lignitic coals are unknown.

The immense water powers of Brazil, available from her numerous waterfalls, cascades, and rapid rivers, will largely offset her deficiency in good coal, petroleum, and natural gas, but both of the latter may yet be found in North Brazil, when the great basin of the Amazon River has been properly explored by the drill of the petroleum and natural-gas operators.

**Mining Costs and Selling Prices of Coal in the United States and Europe, with Special Reference to Export Trade**, by G. S. RICE—In the United States, except in the anthracite district of Pennsylvania, coal-mining conditions are generally more favorable than in Europe. The mines are comparatively shallow, the coal beds are level or little folded; beds less than 2½ feet thick are seldom worked; except in the anthracite mines, less fire damp is encountered and less dead work is required.

The average value of coal in the United States on cars at the mine in 1913 is reported as \$1.18 per short ton (\$1.30 metric) for bituminous coal and \$2.13 per short ton (\$2.35 per metric and \$2.39 per long ton) for anthracite. In Wales in 1913 the average value per long ton at the mine for all kinds was \$2.86, and in Great Britain as a whole \$2.48 (\$2.44 metric). In the German Empire the average value for all kinds of coal f. o. b.



cars at the mine, in 1913, was \$2.50 per metric ton, and for Westphalian coal \$2.61.

Net mining profits in Great Britain and Germany are between 25 and 50 cents per ton, as compared with probably not more than 5 cents for bituminous coal in the United States. Evidently, in the United States, costs at the mine on export coal cannot be much reduced, but railroads may perhaps be able to lower their tariffs for such coal.

Because of low mining costs, the on-ship price of United States bituminous coal is less than that of corresponding British and German coals at their home ports. In 1913 the average declared value of all classes of British coal exported was \$3.40 per long ton (\$3.33 metric) and the price of best Welsh steam coals, f. o. b. Cardiff, ranged from \$4.50 to \$5.10 per ton (\$4.40 to \$5 metric). Westphalian steam lump coal, f. o. b. Hamburg, ranges from \$4 to \$5 per metric ton.

Compared with sailing distances from British coal ports, those from the chief United States export ports are 460 miles less to Atlantic ports of South America, and *via* the Panama Canal 2,560 miles nearer to Pacific ports. Compared with German ports, distances are 767 miles less to Atlantic coast ports

and 2,867 miles less to Pacific coast ports *via* the Panama Canal.

Yet in spite of higher prices at shipping ports and longer distances, coal exports to South America are chiefly from Great Britain. The reasons given are the claimed higher grade of British, particularly Welsh coals, and their better preparation, the heavy freight charges and cost of delivery that limit business to the best coal, the regularity of freight service from Great Britain, the large stocks of British coal kept on hand at ports of entry, and the financial arrangements that relieve South American customers from risks of transshipment, storage, and handling.

As regards these disadvantages, the best Pocahontas and New River coals are equal to the best Welsh steam coal, although possibly more friable. Some United States gas and coking coals may have a trifle more ash and sulfur than British coals, but this disadvantage can be more than offset by lower prices. Satisfactory storage and financial arrangements can be made by United States shippers, but unless regular service can be given, coal shippers in the United States will be at a great disadvantage as compared with those in Great Britain and Germany in normal times.

## NOTES AND CORRESPONDENCE

### TEMPERATURE CONTROL IN WOOD DISTILLATION PLANTS

*Editor of the Journal of Industrial and Engineering Chemistry:*

There has been considerable agitation during the past year in regard to temperature control in wood distillation plants. While the writer is much in favor of development along this line, and realizes that the maximum result per pound of wood distilled can be obtained only by the adaptation of scientific temperature control, he believes that before the matter can be approached in a practical manner applicable to plant conditions, those conditions will have to undergo a radical change.

Where the material undergoing destructive distillation is fairly uniform in size, and the retort is so arranged that the heat can be evenly distributed throughout the mass during distillation, temperature control by pyrometer readings becomes a fairly simple matter. This is evident in the destructive distillation of acetate of lime in the acetone process. It will be noted that the charge is, under the best systems, kept in constant motion, or where stationary retorts are used is charged in thin layers on trays. In both cases the object in view is a better heat distribution. Of as much importance as the size of the acetate charge, it is necessary to have it reduced to a fairly fine condition, the lumps generally showing upon analysis a high percentage of undecomposed calcium acetate after being drawn from the retort.

As regards wood distillation, the raw material will vary in size alone, as much as from 90 to 100 per cent, so that after heat has been applied for some time, the smaller pieces will have given up free water and have started to break down into valuable products, long before the larger pieces have become water-free; hence, we will have two reactions taking place in the retort at the same time. Now, it is necessary, if a plant, as at present designed, is to be run on a paying basis, that the retorts handle one full charge every 24 hours, and if the heat is held down low enough to retard all, or nearly all destructive distillation until the larger wood has been freed of its water, a complete distillation could not possibly be made within a 24-hour period, or at least the writer has never been able to accomplish it in that time. Running under normal conditions, with average wood, I have found that to get the best results from 20 to 22 hours had to be allowed for the distillation; but where the wood was at all rough, large or poorly seasoned, it was necessary to carry a much higher heat than under normal

conditions, long after the usual time, if the retort is to be expected within the 24-hour limit, so, that with wood varying in size and water content, as most of it does, I was able to obtain the best results by using the flow and nature of the distillate as a guide. Where experimental tests are run upon bark-free, well-seasoned and evenly sized wood, the distillation can be carried out very effectually and with a large increase in valuable products, with temperature controlled by pyrometer readings; but with the raw material delivered to the retorts as it now is, I believe by far the best results, as well as the most profitable, can be obtained by a careful recording of the nature of the wood charged in each retort, and then the control of the distillation by the liquor flow.

If some practical method could be devised for reducing the wood to a fairly uniform size, say blocks 12 in.  $\times$  from 3 to 4 in. square, and these blocks be loaded on the cars in trays so that a good heat flow could be maintained between them, temperature control would be reduced to a simple matter, and the valuable products of destructive distillation very materially increased; but before this can be done the proper adjustment of the wood condition and a retort to handle it must first be worked out.

DELTA CHEMICAL COMPANY  
WELLS, MICHIGAN  
January 7, 1916

R. B. GOETSCHUS

### OXALIC ACID SUBSTITUTES IN THE LAUNDRY

*Editor of the Journal of Industrial and Engineering Chemistry:*

Within the last year the rise in price of oxalic acid has brought forth many substitutes which have been offered to the laundry trade as sours. The laundrymen have purchased and used them and in a number of cases their introduction into the washing process has resulted in immediate trouble, the work finishing up a dirty yellow instead of a clear white.

Such a case was brought to the attention of the writer last week. The laundry in question was using one of these souring powders, and their white work was finishing up a nice yellow. A qualitative analysis of the powder showed it to consist of an acid fluoride of sodium. The stain was removed from a piece of goods with strong hydrochloric acid and found to contain a large quantity of iron and calcium. With this information the cause of the discoloration was easily seen. The addition of this

powder to a water containing calcium, magnesium and iron salts would cause the precipitation of calcium and magnesium fluorides and these by inclusion would carry down ferrous or ferric fluoride or both. Now, while it is true that both the ferrous and ferric fluorides are soluble in water it is also true that no amount of washing will free the gelatinous calcium and magnesium fluorides from the ferrous or ferric salts with which they are contaminated. As the calcium and magnesium fluorides are insoluble in water, and as this precipitation takes place in the presence of the fabric, and is also accelerated by heat, the pores of the fabric will retain, in spite of the rinse which follows, enough of the impure calcium and magnesium fluorides to produce the discoloration in question. The trouble is caused, therefore, by the action of such a powder on hard water and will increase or diminish as the amount of iron in the water increases or decreases. Repeated washing will of course increase the discoloration.

The detrimental effects of the precipitation of even perfectly white salts of such a nature in fabrics is too well known to require any comment, and the use of compounds producing them should be strongly discouraged.

LOCKPORT, NEW YORK  
November 16, 1915

E. D. KOEPPING

#### NOTE ON "THE PHENOL COEFFICIENT OF GERMICIDES"

*Editor of the Journal of Industrial and Engineering Chemistry:*

In THIS JOURNAL, 8 (1916), 45, there appears an article by Messrs. Kilmer, Clark and Hampton on the "Hygienic Laboratory Method for Determining the Phenol Coefficient of Disinfectants." Their experimental results show that a coefficient of 1.60 is obtained for "Camphenol" in a series of tests in which the culture medium used for growing the test organism was composed of 3 grams of beef extract, 20 grams of peptone and 1 liter of water, while a coefficient of 3.20 was obtained when the medium contained 3 grams of beef extract, 10 grams of peptone, 5 grams of salt and 1 liter of water. The authors say that they "are unable to offer any rational explanation" for the results.

It seems to me that there are two factors involved. The first is the phenol used. An examination of Table I shows that the phenol was much more active, that is, that killing occurred at  $2\frac{1}{2}$  and at 15 minutes with higher dilutions, than in any published results with which I am familiar. In experiments made in this laboratory with a similar medium (but a different make of phenol), the dilutions required for the  $2\frac{1}{2}$ -minute period

were 1-80 or 1-90, and for the 15-minute period 1-100 or 1-110. If 80 and 110 were used for calculating the coefficient, the result would be about 2.25. The use of different varieties of phenol would account, then, for a part, but only a part, of the discrepancy.

The other, and more important factor involved is the presence of salt in the culture medium. It is well known that salt accelerates the action of a disinfectant. Results obtained in this laboratory during the past two years show the extent of this acceleration very well. These results will appear shortly in the *Journal of Infectious Diseases*.

In the experiments described by Messrs. Kilmer, Clark and Hampton, 5 grams of salt were used per liter of medium, and 0.1 cc. of this was used for the test experiments. There was thus present in the 5 cc. of disinfectant 0.5 milligram of salt. Comparison of results on the killing power of "Camphenol" in Tables I and II shows that with the salt medium the disinfectant was 1.62 times as active in the  $2\frac{1}{2}$ -minute period and 1.67 times in the 15-minute, as when the medium containing no salt was used. While in the experiments made in this laboratory the amounts of salt were slightly greater, still they were of the same order. We used formic acid for the disinfectant. When 1.0 milligram of salt was present in 5 cc., the disinfectant was found to be 3 times as active as when no salt was present, and with 1.2 milligrams of salt the disinfectant was 4 times as powerful. It will therefore be seen that a very small amount of salt will very greatly influence disinfection, and the increased activity of "Camphenol" as shown in Table II can be accounted for on this basis.

It is not probable that every disinfectant is accelerated to the same degree by the presence of salt, but this could be fairly easily tested. If therefore, "Camphenol" was more sensitive to this accelerating action than was phenol, the phenol coefficient, as determined, would be higher.

The main idea which I wish to emphasize is that the salt content of the culture medium is a very important factor, and one which should not be overlooked in suggesting any standard medium for use with disinfectants. I believe also that more than one discrepancy in phenol coefficient determinations can be accounted for by this factor—the salt either being a recognized addition to a medium in one case but not in another, or getting into the medium in varying amounts by the use of broth obtained from different sources, such as meat and the various meat extracts.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
BOSTON, January 13, 1915

JOHN F. NORTON

## PERSONAL NOTES

The United States Civil Service Commission announces an open competitive examination on February 23, 1916, for the position of chemist, for men only, at a salary of \$1200 a year; also an open competitive examination, on February 29th, for pharmaceutical research chemist, for men only, at a salary of \$3000 a year. Another Civil Service examination will be held on April 12, 1916, for the position of junior chemist, departmental service. These examinations are open to all men who are citizens of the United States and who meet the prescribed requirements. Further information may be had by applying to the United States Civil Service Commission, Washington, D. C.

Dr. Charles R. Van Hise, President of the University of Wisconsin, has been elected president of the American Association for the Advancement of Science, in succession to Dr. W. W. Campbell.

Charles M. Hall, inventor of the process for recovering aluminum which bears his name, who died December 27, 1914, left an estate valued at \$10,000,860, according to testimony of

A. V. Davis, of Pittsburgh, an executor, before State Transfer Tax Appraiser Rice. The entire fortune was made in aluminum.

Sir Henry Enfield Roscoe, F.R.S., the distinguished British chemist, emeritus professor in the University of Manchester, died on December 18th, at his residence in West Horsley, England, at the advanced age of 81 years. A memorial service was held on December 22nd at the Rosslyn Hill Unitarian Chapel.

The first annual meeting of the Technical Section of the American Paper and Pulp Association will be held in New York City at the Waldorf-Astoria Hotel, February 16th and 17th. The committee meetings have been arranged for Wednesday, the general meetings of the Section being scheduled for the forenoon and afternoon of Thursday. The meeting in the afternoon will be attended by the proprietors of pulp and paper mills from all parts of the country, in addition to the chemists and engineers connected with the industry, who make up the membership of the Technical Section. It is planned to exhibit



apparatus, and short talks on the machinery shown will be given by representatives of the makers. The officers of the Technical Section are: Henry E. Fletcher, *Chairman*, W. G. MacNaughton, *Vice-Chairman*, and Thomas J. Keenan, *Secretary-Treasurer*, 117 East 24th St., New York.

Stanley Feather Hodgson, a Fellow in pure chemistry in the department of research in pure chemistry of the Mellon Institute of Industrial Research, died in St. Francis Hospital, Pittsburgh, January 7th, of pneumonia, after a brief illness of one week.

The Library of the Engineering Societies, 29 West 39th St., New York City, has taken over the library service formerly carried on by the Chemists' Club, and will, on request, make bibliographies, and furnish correct references, translations, abstracts and copies from the literature of engineering, including chemical engineering.

Mr. Clarence W. Marsh announces his establishment as an independent consulting and chemical engineering, at the Boston Safe Deposit & Trust Company Bldg., 201 Devonshire Street, Boston. Mr. Marsh has had the advantage of twelve years' practical experience as chief engineer and special investigator, and as director for the Hooker Electrochemical Company, and the Development and Funding Company of New York.

The Washington Academy of Sciences held the annual meeting of the Adacemy for receiving reports and the election of officers, at the Cosmos Club on January 13th. President Alsberg, of the Washington Section of the A. C. S., addressed the meeting on "The Chemical Analysis of Animal Nutrition."

At the meeting of the American Society of Mechanical Engineers, in the Engineering Societies Building, New York City, on January 11th, Mr. Walter N. Polakov, superintendent of power of the New York, New Haven and Hartford Railroad, discussed the question of standardization and predetermination of the cost of power. He demonstrated a simple method by which the owner of a power plant can, without the necessity of study of technical details of operation, determine just how close the cost of his own plant is to the possible minimum cost of such a plant, all variable factors beyond operating control being automatically adjusted.

Dr. Rudolph A. Witthaus, known for his work in chemistry and toxicology, who died on December 19th, leaves most of his estate of more than \$150,000 to the New York Academy of Medicine.

Dr. Eugene Woldemar Hilgard, professor of agriculture in the University of California from 1875 until his retirement in 1904, distinguished for his contributions to agricultural chemistry and geology, died on January 8th, in his eighty-fourth year.

Prof. Robert James Davidson, since 1891 professor of chemistry at the Virginia Polytechnic Institute and dean of the scientific department, died suddenly on December 19th, in his fifty-third year.

Mr. William B. Ruggles, for more than twenty years a prominent engineer in New York City, and recently engineering advisor to the Russian Government, died January 23rd of pneumonia at his home, Bergen Point, N. J., in his fifty-fifth year. He was the head of the Ruggles-Coles Engineering Company of 50 Church Street, which he founded. About a year ago at the request of the Russian Government, Mr. Ruggles went to Petrograd and visited the great wheat-growing provinces, where he designed plans for the storage and handling of wheat which called for the expenditure of more than \$100,000,000. Mr. Ruggles was the inventor of an iron ore drier extensively used on the Mesaba Range, and was interested in other corporations, being President of the Novella Cement Company and a director of the Buffalo Potash and Cement Corporation. Mr. Ruggles was a member of the Engineers', Cornell, Phi Upsilon, and New

York Athletic Clubs, and of the American Society of Mechanical Engineers.

Dr. P. A. Levene, member of the Rockefeller Institute for Medical Research, and director of the Chemical Laboratories, has been elected an ordinary member of the Rega Societies *Scientiarum Upsaliensis*, in recognition of his scientific activities.

The International Oxygen Company announce that on January 1st they inaugurated the eight-hour day at their works in Newark, N. J.

Dr. Alexander Silverman, head of the department of inorganic, analytical and physical chemistry, University of Pittsburgh, gave an illustrated lecture on "The Chemistry of Glass Making," before the regular meeting of the Chicago Section of the A. C. S., on January 21st.

Mr. Joseph E. Babb, Supt. Fort Pitt Oil & Paint Company, spoke on "Lubricating Greases: Their Composition and Methods of Analysis," at the regular meeting of the Pittsburgh Section of the A. C. S., held on January 20th.

Mr. F. R. Baxter, of the Vacuum Oil Company, gave a talk on "Oils," at the January 3rd meeting of the Rochester Section of the A. C. S. Mr. M. H. Eisenhart, of the Eastman Kodak Company, spoke on the "Manufacture of Acids," before the meeting of the Section on January 17th.

The ninety-first meeting of the Louisiana Section of the A. C. S. was held in New Orleans on January 21st, the program consisting of motion pictures on the following subjects: (1) "The Silk Industry," (2) "The Manufacture of Paper," (3) "City Sanitation—Sewage Disposal."

Dr. W. H. Frost, Past Assistant Surgeon, U. S. Public Health Service, gave an illustrated lecture entitled "An Outline of Studies by the U. S. Public Health Service on the Pollution of the Ohio River," before the January 12th meeting of the Cincinnati Section of the A. C. S.

The Cornell Section of the A. C. S. held a research meeting of the Section on January 25th, at which the following papers were presented: "The Electrolytic Production of Perchlorates," by E. L. Mack; "The Nitration Products of Phenoltetrachlorophthalin and Some of Its Derivatives," by J. J. Kennedy; "The Electrolysis of Solutions of the Rare Earths," by A. B. Ray.

The January meeting of the Detroit Section of the A. C. S. was held on January 20th with the following program: "Formaldehydized Capsules," by Wilbur L. Scoville, and "The Theory and Practice of Case Hardening," by Herman G. Kiefer. The Section held their annual smoker on February 3rd.

The New York Section of the American Electrochemical Society has arranged a symposium on "Electrochemical War Supplies," which it will hold jointly with the New York Section of the A. C. S. at the Chemists' Club, on February 11th. The program will include the following speakers: Lawrence Addicks, "Electrochemical War Supplies;" W. S. Landis, "Air-Saltwater;" E. D. Ardery (U. S. Army), "Hydrogen for Military Purposes;" Albert H. Hooker, "New War Products;" William M. Grosvenor, "Magnesium;" G. Ornstein, "Liquid Chlorine;" Geo. W. Sargent, "Electric Steel."

The regular January meeting of the Puget Sound Section of the A. C. S. was held January 29th. A paper on "Plasticity of Clays" was presented by R. F. McMichael of Auburn.

There will be held in Washington during the week of February 21-26th, inclusive, a "Safety-First" exhibit in which all the Government Departments are taking an active part, and when manufacturers and operators from all over the country may see what the Government of the United States is doing in "safety-first" work. A conference of State mine inspectors will be held at the office of the Bureau of Mines, February 24th.

# GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

## DEPARTMENT OF AGRICULTURE

**Zacaton as a Paper-Making Material.** CHARLES J. BRAND, JASON L. MERRILL. Department Bulletin 309. 27 pp. Paper, 5 cents. This bulletin gives a description of a new grass suitable for paper making, including the botanical history, distribution, laboratory tests, physical tests, etc. The following conclusions are drawn:

"Zacaton grass may prove to be a valuable paper stock, although at present it is a waste product and flourishes in a region remote from the paper-manufacturing sections.

"The grass can be chemically reduced to paper stock by the soda process under less drastic and less expensive conditions than those employed for the reduction of poplar wood.

"The well known process, methods, and machinery employed for the manufacture of pulp from poplar wood are entirely suitable for the treatment of this material. In place of the wood-sawing, chipping, and screening machinery, a grass cutter, and possibly a duster, is required.

"A production of 43 per cent of air-dry fiber from the air-dry grass is regarded as a very good yield, the fiber yield from poplar wood being from 46 to 48 per cent, and from esparto 43 per cent.

"For bleaching the stock it has been found necessary to use more bleaching powder than in the case of poplar stock.

"Paper manufactured from this stock has shown physical tests equal to those of a first-grade machine-finish printing paper.

"The paper has a very satisfactory appearance and feel."

**Phosphate Rock and Methods Proposed for Its Utilization as a Fertilizer.** WILLIAM H. WAGGAMAN AND WILLIAM H. FRY. Department Bulletin 312. 37 pp. Paper, 5 cents. This report discusses the various methods for treating phosphate rock which for purposes of discussion are classified as follows:

(1) Acid treatment, which includes the manufacture of superphosphate and phosphoric acid; (2) combined heating and acid treatment; (3) double decomposition by means of a silicate or an alkali; (4) processes used in connection with the steel industry; (5) processes in which the phosphorus or phosphoric acid is volatilized; (6) treatment dealing with the production of two or more fertilizer elements; (7) electrolysis; (8) enrichment or concentration of phosphates; (9) processes and apparatus for the mechanical treatment of phosphates; (10) miscellaneous processes.

The commercial applications of each of these types of processes are discussed and their advantages and disadvantages pointed out. The paper also includes a statement of the character and location of phosphate deposits in the United States and a discussion of the forms in which phosphoric acid is applied to soils. An appendix gives a chronological list of all U. S. patents which have been granted for processes intended for the production of soluble or available phosphates by any of the several processes described.

**The Corrosion of Fence Wire.** ALLERTON S. CUSHMAN. Farmers' Bulletin 239. 31 pp. Paper, 5 cents. This is a new

impression, without changes, of the paper printed in 1905. It is intended not only as an advisory publication regarding the selection of fence wire but also as a suggestion regarding methods of wire manufacture to secure durable qualities.

**Harmfulness of Headache Mixtures.** L. F. KEBLER, F. P. MORGAN AND PHILIP RUPP. Farmers' Bulletin 377. 16 pp. Paper, 5 cents. A reprint without change in reference to headache mixtures containing acetanilid, antipyrin, and phenacetin.

**Influence of Growth of Cowpeas upon Some Physical, Chemical, and Biological Properties of Soil.** C. A. LECLAIR. Journal of Agricultural Research, 5 (Dec. 6), 439-47.

**Translocation of Mineral Constituents of Seeds and Tubers of Certain Plants during Growth.** G. DAVIS BUCKNER. Journal of Agricultural Research, 5 (Dec. 13), 449-58.

**Fate and Effect of Arsenic Applied as a Spray for Weeds.** W. T. McGEORGE. Journal of Agricultural Research, 5 (Dec. 13), 459-64. "It has been shown herein that soils possess strong fixing power for arsenic and that when a sodium-arsenite spray is used for destroying weeds the arsenic will ultimately be deposited in the surface soil, there to remain in spite of the leaching effect of rains or irrigation.

"The chemical reactions involved in the fixation are a replacement of solution of iron, calcium, magnesium, and humus, owing in part to a hydrolysis of the sodium arsenite in solution, and also a combination with the dibasic and tribasic elements to form the difficultly soluble arsenites or arsenates."

**Beriberi and Cottonseed Poisoning in Pigs.** GEORGE M. ROMMEL AND E. B. VEDDER. Journal of Agricultural Research, 5 (Dec. 13), 489-93. As a result of the experiments it is believed that the so-called cottonseed poisoning of pigs is a deficiency disease, analogous to the disease known as beriberi in man, if not identical with it. Acute cottonseed poisoning corresponds to wet beriberi, and the chronic form to dry beriberi. This conclusion would indicate that the use of cottonseed meal as a feedstuff is permissible when combined with other materials that make up the deficiency of this material.

**Respiration Experiments with Sweet Potatoes.** HEINRICH HASSELBRING AND LON A. HAWKINS. Journal of Agricultural Research, 5 (Dec. 20), 509-17. "The experiments described in this paper seem to indicate that there is no general correlation between the total sugar content of the sweet potato and its respiratory activity. A simultaneous decrease in the reducing sugar content and the respiratory activity of given lots of roots indicates a correlation between reducing-sugar content and respiration, but seasonal changes and environmental conditions to which the sweet potatoes have been previously subjected tend to obscure any such correlation in different lots. Experiments with wounded roots indicate that the sugar content is not the limiting factor in the respiration of the sweet potato. The reducing sugars are the immediate source of respiratory material. The cane sugar is relatively stable in the sweet potato, and when once formed it does not appear to be readily utilized in the process of respiration, while starch and other carbohydrates are present in abundance."

**Carbohydrate Transformation in Sweet Potatoes.** HEINRICH HASSELBRING AND LON A. HAWKINS. Journal of Agricultural Research, 5 (Dec. 27), 543-60. This work continues the investigation described in the previous abstract. The plan in this work was to compare carbohydrate transformation occurring in sweet potatoes during a period of 10 to 12 days immediately after they had been dug with the changes taking place during a subsequent period of equal length. The experiments were carried out at 5, 15 and 30 degrees. It is concluded that the



carbohydrates are first converted to reducing sugar, and cane sugar is then synthesized from the reducing sugar.

**Variations in Mineral Composition of Sap, Leaves, and Stems of the Wild-Grape Vine and Sugar-Maple Tree.** O. M. SHEDD. *Journal of Agricultural Research*, 5 (Dec. 20), 529-42.

**Diuresis and Milk Flow.** H. STENBOCK. *Journal of Agricultural Research*, 5 (Dec. 27), 561-8.

**Petrography of Some North Carolina Soils and Its Relation to their Fertilizer Requirements.** J. K. PLUMMER. *Journal of Agricultural Research*, 5 (Dec. 27), 569-81. "Definite information is required on the behavior of the various soil-forming minerals to the forces of weathering before positive conclusions can be drawn on the availability of the plant food carried by the different minerals.

"The field results with the cotton plant indicate that there are some relationships existing between the mineral component of the soil and the requirements of this plant for the three inorganic fertilizer constituents, phosphoric acid, potash, and lime."

#### BUREAU OF MINES

**Annual Report of the Director.** VAN. H. MANNING. 105 pp. This report includes a discussion of the various problems which are under investigation and briefly summarizes the experimental and field work done during the past year on each subject.

**Extraction and Recovery of Radium, Uranium and Vanadium from Carnotite.** CHARLES L. PARSONS, R. B. MOORE, S. C. LIND AND O. C. SCHAEFER. *Bulletin* 104. 124 pp. Paper, 25 cents. This is the complete report on the cooperative work done by the Bureau of Mines and the National Radium Institute which is briefly described in *THIS JOURNAL*, 8 (1916), 48-53.

#### PUBLIC HEALTH SERVICE

**Hydrocyanic Acid Gas. Its Practical Use as a Routine Fumigant.** R. H. CREEL, F. M. FAGET AND W. D. WRIGHTSON. *Public Health Reports*, 30 (Dec. 3, 1915), 3537-50. This article discusses the conditions of use of hydrocyanic acid as a fumigant and reports upon experiments to test the effectiveness with various animals and bacteria.

#### SANITARY LEGISLATION

The following court decisions and legislative actions are reported in *Public Health Reports*, 30 (1915), on the pages indicated in parenthesis.

**Disposal of Sewage and Pollution of Streams by Distillery Waste.** Kentucky Court of Appeals decision in the case of *Kraver, et al. vs. Smith*, 177 S. W. Rep. 286. (P. 3303.) In this case the damage claimed was due to pollution of the stream from sewage including the discharge from a distillery. *Held*, that the city was responsible for the damage and liable to persons damaged since they permitted the distillery to discharge objectionable materials through municipal sewers. The distillery was relieved from any charge of nuisance but the city had authority to regulate the character of the sewage discharged into public sewers by such private manufacturing concern.

**Production, Care, and Sale of Milk and Milk Products.** Enid, Oklahoma, Ord. 891, July 6, 1915. (P. 3331.) This ordinance includes specifications as to the fat, total solids and gravity of milk, cream, and milk products.

**Production, Care, and Sale of Milk and Milk Products.** Cleveland, Ohio, Ord. 34648-A, June 21, 1915. (P. 3380.) This ordinance establishes a bureau of dairy and food inspection and defines the standards of quality for milk and milk products.

**Production, Care, and Sale of Milk and Milk Products.** Evanston, Illinois, Ord., March 26, 1915. (P. 3453.) This regulation includes specifications for the minimum fat and solid content of milk, cream, skimmed milk, butter milk, etc. Bacterial standards are also defined.

**The Nuisance Created by Garbage Disposal Plant.** Ohio Supreme Court decision in the case of *Toledo Disposal Company vs. State*, 106 N. E. Rep. 6. (Jan. 13, 1914.) (P. 3507.)

*Held*, that garbage disposal plants, operated under express contract with and legislative authority of a municipality, cannot be restrained from operation as a public nuisance if properly operated. The benefit to the general public is held to take precedence over any inconvenience to immediate surrounding premises.

**Sale of Ice.** Evanston, Illinois, Ord., March 26, 1915. (P. 3530.) This regulation includes a specification that no ice shall be sold or offered for sale unless the same "be free from sewage forms, from pathogenic bacteria, and contain no more than 100 bacteria per cubic centimeter in a total seven-day count at a temperature of 20° C. on agar and does not contain nitrates or nitrites in such amount as to indicate contamination as ascertained by standard methods of water analysis."

**Sale and Handling of Drinking Water.** Evanston, Illinois, Ord., March 26, 1915. (P. 3536.) This regulation includes the same requirement as to standard tests and bacteria in water as that prescribed for ice (see preceding abstract).

**Sale of Adulterated Food and Drugs.** Evanston, Illinois, Ord., March 26, 1915. (P. 3533.) This regulation includes specifications as to permissible preservatives and coloring matter and defines preservatives which are not permitted.

**Office of State Chemist Created.** Colorado State Act of May 8, Chapter 150. (P. 3578.) This regulation makes the head professor of the Department of Chemistry of the University of Colorado, "State Chemist" of Colorado, and designates the instructor in food and drug analysis of the Department of Chemistry of the University as "Assistant State Chemist." The authority and duties of these offices are defined.

**Production, Care, and Sale of Milk and Milk Products.** Ft. Smith, Arkansas, Ord. 1137, August 25, 1915. (P. 3594.) This regulation includes specifications as to the standards for milk and cream.

#### COMMERCE REPORTS—NOVEMBER, 1915 (Concluded)

A new sheet glass plant is to be built in Japan by the Asah Glass Company, the annual output of which will then be over 600,000 tons. (P. 792.)

The Bureau of Standards finds that an addition of 4 per cent of calcium chloride to the mixing water, accelerates the hardening of concrete, so that at the end of 2 days, the strength is 75 per cent of that normally obtained in one month. (P. 793.)

With enormous resources, the wood pulp and paper industry of Russia is very promising though its development has been hindered by lack of capital and technical knowledge. (P. 796.)

Paper is again being shipped from Oregon to Australia, after a lapse of several years in this trade. (P. 799.)

Conversion of peat into a valuable fertilizer by an inexpensive bacterial treatment, is proposed in Ireland. (P. 811.)

A company for the manufacture of bronze powder and aluminum powder, has been organized in France. (P. 835.)

#### COMMERCE REPORTS—DECEMBER, 1915

Efforts are being made to develop the production of alcohol from the nipa-palm in Borneo. (P. 852.)

In Nottingham, England, 700 tons of bones per week are consumed in the production of glue, animal fats, and fertilizers. (P. 853.)

In New Zealand, the government has assumed control of the kauri-gum industry. (P. 861.)

Waste molasses is being used successfully as fuel in Hawaiian sugar factories. (P. 885.)

The woods of Tasmania are not suitable for wood-pulp, according to the report of Mr. Henry E. Surface, of the U. S. Forest Service. (P. 889.)

Efforts to secure supplies of fiber from Brazil, to replace the curtailed supply from the Philippines and Mexico, have not been very successful. (P. 892.)

A company has been organized in Philadelphia to manufacture synthetic camphor from turpentine. (P. 897.)

The **beet sugar** production in the United States in 1915, is the largest ever recorded. (P. 899.)

Deposits of **molybdenum** and **tungsten ores** have been discovered in Chile. (P. 905.)

Shipments of **soya-bean oil** from Japan direct to the United States are increasing. (P. 935.)

Imports of Japanese **matches** into the United States are increasing. (P. 948.)

Practically all the Russian **beet sugar** factories have modern equipment, including several novel processes. (P. 954.)

The cultivation of **sugar cane** and **beets** in Chile is under consideration. (P. 958.)

Exportation of **logwood** from Jamaica and British Honduras, except to the United Kingdom, has been prohibited. (Pp. 961, 941.)

Discovery of extensive **platinum** deposits in Spain has been reported. (Pp. 993, 1037.)

The production of **tanning materials** in Venezuela from native plants including **divi-divi**, **mangrove**, **balata** and others is proposed, with a view to developing a local leather industry. (P. 5.)

**Invar** (nickel steel), formerly imported, is now being made in the United States. (P. 1019.)

Cultivation of **sesame** as an oil seed is tending to replace peanut cultivation in India. (P. 1030.)

A large part of the **gum tragacanth** output of Persia is now being shipped to the United States. (P. 1054.)

**Antimony** deposits in Honduras, hitherto unprofitable, are now being worked. (P. 1054.)

Of the constituents of **fertilizers** in Russia, phosphates may be obtained from deposits which have not yet been developed, and also from basic slag. **Potash** deposits have not yet been developed. (P. 1064.)

Imported mineral products of India are **coal**, **manganese ore**, **iron**, **copper**, **wolframite**, **bauxite**, and **pitchblende**. (P. 1066.)

A plant for the smelting of **tin ores** from Bolivia, is being erected at Perth Amboy. Hitherto most of this ore has been shipped to Europe. (P. 1067.)

Exports of newsprint **paper** and **paper pulp** from Canada to the United States show a marked increase. (P. 1087.)

Large amounts of **formaline** are being exported from the United States to Japan for use as a disinfectant in the silk industry. (P. 1112.)

An increased production of metallic **sodium** in the United States by either the Castner or Darling process is urged, in view of the increased demand for **sodium peroxide** and **cyanide**. (P. 1114.)

Exports of **rubber** from the Straits Settlements show marked increases. (P. 1122.)

A new Japanese **wood pulp** factory is being erected, with an annual output of 12,000 tons. (P. 1139.)

The production of **nitrate** in Chile is increasing and several new fields are about to be developed. (P. 1212.)

A new Philippine oil nut, "*chioschilon cunningianus*," contains 45 per cent of a dark, fatty, non-drying oil, suitable for use as a lamp oil. (P. 1214.)

The cause of the embargo on **logwood** from British possessions is stated to be the increased price of logwood extract from the United States to Canadian and other British purchasers. Raising of the embargo will be conditional upon resumption of the export of the extract under favorable conditions. (P. 1217.)

Possible sources of **logwood** are Mexico, Guatemala, Costa Rica and Cuba. (P. 1218.)

Important mineral products of Spain include ores of **antimony**, **iron**, **copper**, **manganese**, **mercury**, **silver**, **tin**, **zinc**, and **tungsten**; also **coal**, **phosphate rock** and **iron pyrites**. (P. 1236.)

Serious efforts are being made to promote a **natural indigo** industry in India, especially to provide a permanent market. (P. 1273.)

The **rubber** output of Belgian Congo has decreased owing to competition of plantation rubber. **Gum copal** is now the principal article of export, while **palm kernels** and **palm oil** are very important items. (Sup. 64a.)

Tunis is now second to the United States in the production of **phosphate**. (Sup. 79c.)

# SPECIAL SUPPLEMENTS ISSUED IN DECEMBER

Greece—7c	Ceylon—51a	British East Africa—65b
Italy—8c	Manchuria—52k	British West Africa—67b
Gibraltar and Malta—20a	French Indo-China—54c	French East Africa—70a
British West Indies—22c	Chosen (Korea)—55j	Tunis—79c
Nicaragua—34a	Malaysia—56d	
British Guiana—44b	Belgian Congo—64a	

# STATISTICS OF EXPORTS TO THE UNITED STATES

GREECE—Sup. 7i	ITALY—Sup. 8i	Nicaragua—Sup. 34i
Drugs and chemicals	Hemp	Gold
Gum mastic	Glue	Hides
Olive oil (crude)	Licorice	Rubber
Chrome ore	Olive oil (crude)	Silver
Magnesite	Pumice	Sugar
Pumice	Hides	
Tanning materials	Crude tartar	Ceylon—Sup. 51a
Amyl alcohol	Mercury	Citronella oil
JAMAICA—Sup. 22i	Beeswax	Cocanut oil
Annatto	Boric acid	Drugs
Sisal	Magnesite	Papain
Eustic	Sienna	Graphite
Hides	Talcum	Rubber
Logwood	Umbur	Manchuria—Sup. 52k
Logwood extract	MADAGASCAR—Sup. 70a	Hides
Orange oil		Soya bean oil
Sugar	Mangrove bark	Talcum
Wax	Graphite	

# BUREAU OF STANDARDS

**Annual Report of the Director.** Unnumbered Publication. 148 pp. This report summarizes the functions, organization, and investigations of the Bureau, including a statement of the general nature of conclusions reached in each of the more important technical and scientific researches in progress. Approximately 400 separate investigations are thus briefly reviewed.

**The Standardization of Bomb Calorimeters.** ANONYMOUS. Circular 11, 2nd Ed. 17 pp. This circular recommends methods of calibration and gives operating directions for the use of various types of bomb calorimeters. A description of the standard materials distributed by the Bureau, including methods for their use and a schedule of fees for testing calorimetric equipment, is included.

**Earth Resistance and Its Relation to Electrolysis of Underground Structures.** BURTON MCCOLLUM AND K. H. LOGAN. Technologic Paper 26. 48 pp. "Among the important factors which influence the amount of current leaving a street railway track or other grounded conductor-carrying current is the resistance of the soil between the current-carrying conductor and other conductors within the earth.

"It is the purpose of this paper to discuss the importance of the part played by the soil in the electrolysis problem, to describe some methods for determining the resistivity of soils to give the results of some experiments on earth resistivity, to point out some factors influencing the electrical conductivity of the earth, and to suggest certain benefits to be derived from a proper application of a knowledge of soil conditions in protecting underground structures from stray currents."

**Electrolysis and Its Mitigation.** E. B. ROSA AND BURTON MCCOLLUM. Technologic Paper 52. 143 pp. "This investigation has included a study of the physical laws governing electrolytic and self-corrosion in soils, an extended investigation of the effects of electric currents on plain and reinforced concrete, and a study of the work of previous investigators relating to the subject of electrolysis and its prevention. Many laboratory investigations have been carried out, and also experiments on



artificial pipe lines laid especially for the purpose of permitting experiments under actual conditions with various methods of electrolysis prevention. This work has been supplemented by a large amount of field work in various cities with a view of obtaining first-hand information in regard to the effectiveness of different methods of mitigation as they are commonly applied and to develop methods of making electrolysis surveys and giving any special information desired. The results of these investigations are being published in a number of special reports, a list of which is given at the end of this paper.

"The present report is confined principally to a discussion of the subject of the prevention of electrolysis in metallic structures, including gas and water systems and lead-covered cables. The discussion and conclusions presented here are based on the studies above referred to in so far as they yield definite results to the present time. The work is still incomplete, however, and much remains to be done in the investigation of special problems relating to some of the more important methods of electrolysis mitigation. As the work progresses supplementary reports will be made from time to time as the results of the investigation seem to justify."

**Protection of Life and Property against Lightning.** O. S. PETERS. Technologic Paper 56. This report includes a discussion of the relative advantages of different materials used as lightning conductors.

#### GEOLOGICAL SURVEY

**The Ellamar District, Alaska.** S. R. CAPPS AND B. L. JOHNSON. Bulletin 605 (1915). 125 pp., 10 plates, and 10 text figures. "This report gives the results of a detailed study of the geology and ores of the Ellamar district, which lies at the northeast border of Prince William Sound and includes part of the mainland, about half of Bligh Island, and a number of smaller islands. The Prince William Sound region is now one of the larger copper producers of Alaska and promises to hold that position, so that any information as to its very complex geology is of considerable importance."

**Rhode Island Coal.** G. H. ASHLEY. Bulletin 615 (1915). 62 pp., 5 plates, 3 text figures. "A brief discussion of the character and attempted utilization of Rhode Island coal, which has always had a certain interest to the people of that State as a source of local supply in competition with Pennsylvania coal. The author concludes that, as this coal is a high-ash, high-moisture, graphitic anthracite which requires peculiar handling, the best prospect for its present use is in producing electric power at the mines, either in steam engines or by means of specially devised producer-gas or water-gas plants. He adds that this can probably not be done until Rhode Island coal can be mined and delivered at the furnace for less than one-half the wholesale price of competing coals in Providence and Boston. The illustrations consist of a sketch of the Rhode Island coal field, views at several of the mines, and charts showing the composition and theoretical heating power of Rhode Island coal as compared with its competitors, and the relation of its carbon content to its fuel value."

**The Broad Pass Region, Alaska.** F. H. MOFFIT. With Sections on Quaternary Deposits, Igneous Rocks, and Glaciation. J. E. POGUE. Bulletin 608 (1915). 80 pp., 8 plates, 3 text figures. "Describes briefly the geography and geology of the Broad Pass region. . . . Although no commercial mineral deposits have been found in this region, yet what is known of the geology gives hope that such deposits may be found."

**Portland Cement Materials and Industry in the United States.** E. C. ECKEL, with Contributions by E. F. BURCHARD AND OTHERS. Bulletin 522, 2nd Ed. 401 pp., 19 plates, 2 text figures. "This report contains a brief sketch of the general status of the Portland cement industry, a discussion of the chemical and physical

properties necessary to a Portland cement material, and detailed descriptions of the available Portland cement resources of each State in the United States. Emphasis is laid on the fact that the value of cement material depends almost entirely on its location with respect to fuel supply, transportation routes, and markets. The illustrations consist mainly of maps showing the distribution of cement materials in certain parts of the country."

**Quicksilver Deposits of the Mazatzal Range, Arizona.** F. L. RANSOME. Bulletin 620-F. Contributions to Economic Geology, 1915, Part I, pp. 111-28. Published October 21. This investigation indicates that considerable quantities of ore containing sufficient available mercury to make it suitable for economic working is to be found in this district. However, not enough mining work has yet been done to determine with certainty that further development will be profitable.

**Iron-Bearing Deposits in Bossier, Caddo and Webster Parishes, Louisiana.** ERNEST F. BURCHARD. Bulletin 620-G. Contributions to Economic Geology, 1915, Part I, pp. 129-50. Published October 22. This report presents for each deposit examined the principal facts that are essential to determine the commercial availability of these ores. The writer, however, concludes that these deposits in most cases offer no encouragement for development in the near future.

**A Reconnaissance in the Kofa Mountains, Arizona.** EDWARD L. JONES. Bulletin 620-H. Contributions to Economic Geology, 1915, Part I, pp. 151-64. This report includes a discussion of the geological and geographical conditions and ore deposits of gold, copper, and lead, including certain placer deposits of this district.

**A Reconnaissance of the Cottonwood-American Fork Mining Region, Utah.** B. S. BUTLER AND G. F. LOUGHLIN. With Notes on History and Production, by V. C. HEIKES. Bulletin 620-I. Contributions to Economic Geology, 1915, Part I, pp. 165-226. In this report are given the topographical, geographical, and ore-deposits information which is of economic interest.

**Potash in Certain Copper and Gold Ores.** B. S. BUTLER (Compiler). Including a Note on Muscovite, by GEORGE STREIGER. Bulletin 620-J. Contributions to Economic Geology, 1915, Part I, pp. 227-36. "In this report have been brought together portions of some complete analyses of copper ores from different districts showing the potash content and the percentages of the commoner oxides. For each district are given the amount of ore available and the quantity that has been treated. The last item gives an approximation of the amount of tailings that have resulted from past operations.

"The ores of several of the large gold-producing districts of the West are notably rich in potassium, and although the tonnage in these deposits is usually small compared with that of the copper deposits, nevertheless in several places there have been large accumulations of tailings. . . . Some facts concerning a few of the larger districts are given."

**Evaporation of Potash Brines.** W. B. HICKS. Professional Paper 95-E. Shorter Contributions to General Geology, 1915, pp. 65-72. Published October 25. "According to the results set forth in this paper, the potassium is concentrated best in brines containing carbonates and chlorides, and poorest in those containing sulfates and carbonates, though a small amount of sulfate does not seem to hinder the concentration materially. In brines that contain several acid radicles the concentration of potassium may increase to a maximum as evaporation proceeds and then decline. The evidence at hand indicates that a large percentage of the potassium in a solution is lost during evaporation before the maximum concentration of potassium is attained. The loss is small until the potassium reaches a concentration of about 4 per cent, but it is very rapid during further evaporation. Therefore, in the commercial extraction

of potash from brines, especially those of the alkalies, it would seem best first to concentrate the solution by evaporation until it contained about 4 per cent of potassium, and then to subject the resulting bittern to other processes of manufacture. The most advantageous point of concentration would, however, have to be determined for each particular brine."

**Preliminary Report on the Diffusion of Solids.** C. E. VAN ORSTRAND AND F. P. DEWEY. Professional Paper 95-G. Shorter Contributions to General Geology, 1915, pp. 83-95. Published November 10. "The investigation of which this paper is a preliminary note has for its first object the determination of the coefficients of diffusivity over a considerable range of pressures and temperatures for solids and minerals. The investigation was first undertaken in connection with some experiments on the elasticity and plasticity of metals. Although it is believed that the results are essential for the construction of a complete theory of the physical properties of elastic and plastic bodies in the normal state or in a state of isostatic adjustment, it is realized that this is only one of many fields in which the results are of fundamental importance."

**The Production of Metals and Ores in 1913 and 1914.** J. P. DUNLOP. Mineral Resources of the United States, 1914, Part I, pp. 415-25. Published November 20. This is a summary only of the data which has been separately published in the various chapters which give in detail for each metal or mineral the important statistics.

**The Production of Silica (Quartz) in 1914.** FRANK J. KATZ. Mineral Resources of the United States, 1914, Part II, pp. 443-48. Published October 14. "The marketed production of silica from quartz veins, pegmatites, and quartzite in 1914 was 153,401 short tons, valued at \$360,502, against 97,902 short tons, valued at \$201,488 in 1913. This was an increase of 55,499 short tons, or 57 per cent, in quantity and of \$159,014, or 79 per cent, in value.

"Increase in sales of crude quartz in 1914 as compared with 1913 was 49,332 short tons, or 65 per cent, in quantity and \$34,378, or 63 per cent, in value. The sales of ground quartz increased 6,167 short tons, or 26 per cent, in quantity and \$124,636, or 85 per cent, in value. The average price per ton for crude was 72 cents in 1914; in 1913 it was 73 cents; in 1912, 82 cents; and in 1911, 91 cents. This decline in average price is due to the increased sales of quartz for smelting. Quartz, which was ground for pottery, paints, and fillers, was purchasable crude for about \$2 a ton in Maine, Connecticut, and Maryland. The average price per ton for ground quartz was \$9.09; in 1913 it was \$6.23; in 1912, \$7.94; and in 1911, \$8.30. In 1914, of the total quantity here recorded, 80.51 per cent was marketed in crude form and 19.49 per cent as ground, and of the total value received, 75.36 per cent was for ground quartz and 24.64 per cent for crude."

Data are also given separately for flint or chert, sand and sandstone, tripoli, and diatomaceous earth.

**Statistics of the Clay-Working Industries in the United States in 1914.** JEFFERSON MIDDLETON. Mineral Resources of the United States, 1914, Part II, pp. 455-548. Published October 23. "The present report, except the section on clay mining, deals with the products of the clay-working industries, and the tables are made up to show the output of manufactured clay products and not the production of clay.

"The year 1914 in the clay-working industries was not one of general prosperity. The total value of all clay products marketed in the year—the best criterion by which the status of the industry can be judged—was \$164,986,983, compared with \$181,289,132 in 1913, a decrease of \$16,302,149, or 8.99 per cent; but on the other hand, compared with 1908, there was an increase in 1914 or nearly twice that amount (\$31,789,221, or 23.87 per cent). In fact only in the preceding four years has the total

value of clay products exceeded that of 1914, so that although the condition of the industries was somewhat unsatisfactory in 1914, compared with its condition only a few years ago, it should be considered gratifying."

**The Production of Abrasive Materials in 1914.** FRANK J. KATZ. Mineral Resources of the United States, 1914, Part II, pp. 549-68. Published October 26. "The total value of the abrasive materials which are considered in this chapter and which entered trade during 1914 decreased about 21 per cent, as compared with the value for 1913. There was a decrease in both domestic production of natural and artificial abrasives and also in their importation. The value of natural abrasives produced decreased about 25 per cent; of artificial abrasives, about 16 per cent; and of imports, about 20 per cent.

Among the natural abrasives a gain was shown in the production of pumice. There was a decrease in quantity and value of all other abrasive products. The total estimated value of all the abrasive materials consumed in the United States during 1914 is given in the table following.

Natural abrasives.....	\$1,200,143
Artificial abrasives.....	1,685,410
Imports.....	728,710
Total value.....	\$3,614,263

In the following table is given the value of natural abrasives produced in 1914.

Millstones.....	\$ 43,316
Grindstones and pulpstones.....	639,344
Oilstones and scythestones.....	167,948
Emery.....	2,425
Garnet.....	145,510
Abrasive quartz and feldspar.....	(a)
Diatomaceous (infusorial) earth and tripoli.....	142,428
Pumice.....	59,172
Total.....	\$1,200,143

(a) See chapter on silica (quartz).

**The Production of Magnesite in 1914.** CHARLES G. YALE AND HOYT S. GALE. Mineral Resources of the United States, 1914, Part II, pp. 569-86. Published October 28. "The magnesite consumed in the United States during 1914 amounted to 122,000 short tons of calcined and 13,000 short tons of crude, imported, and 11,293 short tons of raw, domestic, a total equivalent to about 132,000 short tons of calcined magnesite. Thus only 4 per cent of the magnesite used in this country in 1914 was of domestic production. Nearly 93 per cent was imported from Austria and Hungary for making refractory bricks and other articles; the remaining 3 per cent was imported chiefly from Greece, either directly or through ports in Holland, Germany, and England. The principal consumption is in the Eastern States and is supplied by importation, whereas the entire domestic production comes from California and is used almost entirely on the West coast."

The various uses of magnesite are discussed, particularly in the manufacture of paper, for oxychloride and sord cement, for generation of carbon dioxide and for magnesia paints.

**The Production of Coal in 1914.** C. E. LESHER. Mineral Resources of the United States, 1914, Part II, pp. 587-746. Published November 29. "Total production of coal in 1914, 513,525,477 short tons; spot value, \$681,490,643.

"*Pennsylvania anthracite*—Total production in 1914, 81,090,631 long tons (equivalent to 90,821,507 short tons); spot value, \$188,181,399.

"*Bituminous coal and lignite*—Total production in 1914, 422,703,970 short tons; spot value, \$493,309,244.

"The year 1914 will be remembered as one of general depression in the coal-mining industry, comparable to some extent to the disastrous year 1908, yet the total production in 1914 was exceeded in but two previous years, 1912 and 1913. The decrease from 1913, when the production amounted to 569,960,219 tons, was 56,434,742 tons, or 9.9 per cent."



## BOOK REVIEWS

**Analysis of Dyestuffs.** By ARTHUR G. GREEN. Pp. ix + 144, with 31 analytical tables, 1915. Charles Griffin and Company, London; J. B. Lippincott Company, Philadelphia, American agents. Price, \$3.00, net.

In this volume Prof. Green has assembled his various extensive publications on this subject that have appeared between 1893 and 1913 in the *Journal of the Society of Dyers and Colourists* and in the *Journal of the Society of Chemical Industry*; these have, in part, been incorporated with Knecht, Rawson and Lowenthal's work "A Manual of Dyeing" (Lippincott, 1910). He has brought them up-to-date and has provided them with concise and very suitable introductory, connecting and supplementary matter. There is more useful and readily accessible analytical and identification information on coal tar and other dyes contained in this publication than in any other now extant. Every color analyst will therefore welcome it as a valuable guide in his work. For complete and final identification, recourse, as Prof. Green explicitly says, must be had to other works of reference. This book does not, in general, pretend to do more than to enable the analyst to ascertain, with the least expenditure of time, a comparatively small group of dyes to which the thing under examination belongs. That alone is a big time-saver, also of great value, and no other present publication approaches this one in that valuable respect.

Because of the multitude of commercial dyes it is obviously impossible to construct "fool-proof" analytical tables, and the tables in this book will have to be used intelligently by any analyst, particularly since in many cases directional details as to manipulative operations are not as full as many would wish. No doubt with this matter now made so readily available the gaps that now exist, or seem to exist, in this publication, will be filled in in subsequent editions.

Since this publication is in part addressed to the practical dyer and in part to the analyst and the line could not always be clearly drawn it is all the more necessary for each of them to pay close attention to the manipulative directions, the full text and the notes, and sympathetically to coöperate with their author and to try to understand him, which is not at all a difficult matter, and not try to find as many ways as possible to misunderstand him, as some unfortunately do.

The subject matter is divided into nine chapters: Chapters I-III, dealing with dyestuff chemistry and classification, contain as concise, lucid and correct a statement of this broad subject as can be found anywhere; Chapter IV treats of identification of dyes in substance; Chapter V of identification of dyes on animal fiber; Chapter VI of dyes on vegetable fiber; Chapter VII treats of indigo assay and identification in substance and on fiber; Chapter VIII identification of pigments and lakes; Chapter IX deals with the determination of the constitution of azo dyes and is the most complete and detailed publication on this subject available anywhere, giving also identification reactions for many of the reduction and oxidation products of azo dyes. An index of 18 pages (4 to text, 14 to tables) concludes the book.

No doubt, actual use of the analytical tables in instructional and actual commercial work by the general chemical public will suggest a system of cross-referencing within the respective tables and to the descriptive matter and cautions in manipulation in the text which may be incorporated to advantage in later editions; very likely cross-reference, at appropriate places, to some standard work on dyes such as the Schultz "Farbstofftabellen" may be developed, all of which would serve to

heighten the "fool proofing" and also to make final identification less time-consuming. This work, as it stands, leaves all dyers and analysts greatly in debt to Prof. Green for the immense labor he has performed in sifting out and co-ordinating the analytical data.

BERNHARD C. HESSE

**Commercial Paints and Painting.** By ARTHUR SEYMOUR JENNINGS. x + 224 pp. 47 illustrations. New York: D. Van Nostrand & Co., 1914. Price, \$2.00.

The subject of which this work treats is one upon which the most divergent opinions are held by different authorities. The truth is that the fundamental principles upon which the art of applying protective coatings depends, have hardly as yet been demonstrated. Most of the subject still remains as a mass of empirical information without the principles by which the information derived from one set of experiments may properly be transferred to another set. The present work is intended to give information not to the chemist, nor to the paint manufacturer, nor to the decorator, but to the engineer and architect who is called upon to specify what paints shall be used and how they shall be applied. It is this class of persons who are at the present time in most serious need of information regarding painting which will enable them to draw up specifications and to plan the supervision of the work in such a way as to realize the maximum of benefit to their clients, and it is unfortunately true that this very class has had up to the present time less reliable information upon which to draw than any other class of persons having to do with the subject of paints and painting. The architect or the engineer is not himself a practical painter; neither is he a chemist who can be charged with knowledge of the chemical and physical principles involved in paint manufacture and application but, nevertheless, the duty is imposed upon him of deciding upon the testimony of others what paints shall be selected, what preparation the surface to receive it shall receive, and how it shall be applied. It may fairly be said that neither the chemist nor the practical painter has as yet given him, in any complete or satisfactory form, the facts and the principles which should be his guide. This is partly due to a lack of knowledge as to what chemical and physical elements are really at work in the destruction of paint in service, partly to the fact that almost everyone who has taken up the subject of painting, particularly with a view to writing articles and books, has had another motive than the simple desire to ascertain and set forth the truth, for it most frequently happens that the investigators and writers have been committed to the interests of some commercial painting or manufacturing enterprise; and partly also the present state of uncertainty is due to the enormous difficulties which stand in the way of ascertaining by tests what are the best paints for a given purpose and how to apply them, for up to the present time it is generally true that the attempts at imitating in the laboratory the effects of a service test of five or ten years have been unsuccessful and misleading.

A considerable part of this book is devoted to the mechanical appliances used in applying paints and to specifications for painting. The latter are almost entirely English, for the book is English, though published in New York.

The work contains much valuable information and it appears to be substantially free from bias, but it leaves much to be desired as a guide to the engineer in its lack of the enunciation of distinct principles which may be safely followed.

PARKER C. McILHINEY

# NEW PUBLICATIONS

By IRENE DEMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

**Air-Brakes: References to Books and Magazine Articles.** CARNEGIE LIBRARY OF PITTSBURGH. 8vo. 55 pp. Carnegie Library, Pittsburgh.

**Crass Moulder.** ALEX PURVES. 8vo. 170 pp. Price, \$0.75. E. & F. N. Spon, London.

**Carburation: A Handbook of Carburation.** A. B. BROWNE. 8vo. 137 pp. Price, \$2.00. J. Wiley & Sons, New York.

**Chemistry: Die Bedeutung der Chemie fuer den Weltkrieg.** R. ANSCHUTZ. 8vo. Price, \$0.50. F. Cohen, Bohn.

**Chemistry: General Chemistry for Colleges.** ALEX SMITH. 662 pp. Price, \$2.25. The Century Co., New York.

**Chemistry: Historical Introduction to Chemistry.** T. M. LOWRY. 8vo. 599 pp. Price, \$2.25. The Macmillan Co., New York.

**Chemistry: Teacher's Handbook to Accompany "Foundations of Chemistry."** A. A. BLANCHARD and F. B. BERTRAM. 16mo. 111 pp. Price, \$0.24. American Book Co., New York.

**Coal: Die Chemie der Kohle.** W. HINRICHSSEN and S. TACZAK. 8vo. Price, \$4.00. W. Engelmann, Leipzig.

**Coal Distillation, Gasification and By-Products.** J. E. CHRISTOPHER. 8vo. 90 pp. Price, \$0.75. T. Wall, London.

**Coal-Tar Industry, British. Its Origin, Development and Decline.** W. M. GARDNER. 8vo. 448 pp. Williams & Norgate, London.

**Conductivities and Viscosities in Pure and in Mixed Solvents.** H. C. JONES. 8vo. 175 pp. Price, \$2.00. Carnegie Institution, Washington.

**Corrosion of Iron: A Summary of Causes and Preventive Measures.** L. C. WILSON. 12mo. 178 pp. Price, \$2.00. Engineering Magazine Co., New York.

**Crystal Theories: Statische und kinetische Kristalltheorien, Part 2.** J. BECKENKAMP. 8vo. Price, \$6.50. Gebrueder Borntraeger, Berlin.

**Diesel Engines for Land and Marine Work.** A. P. CHALKLEY. 4th Ed. 8vo. 386 pp. Price, \$2.00. Constable & Co., London.

**Electric Motors: Elektromotoren.** B. THIERBACH and O. R. BARTH. 8vo. Price, \$0.75. Hachmeister und Thal, Leipzig.

**Electric Dictionary: A Cyclopaedia of Words, Phrases and Data Used in the Electric Arts, Trades and Sciences.** N. HAWKINS and OTHERS. 8vo. 505 pp. Price, \$2.00. T. Rudel & Co., New York.

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**Seals and Cements: Their Nature, Manufacture and Use.** E. A. DANCASTER. 8vo. 224 pp. Price, \$1.25. Crosby Lockwood, London.

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**Paints: The Light-Reflecting Value of White and Colored Paints.** H. A. GARDNER. 13 pp. Educational Bureau Paint Mfrs. Association of the U. S. Philadelphia. Bulletin 50, January, 1916.

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# MARKET REPORT—JANUARY, 1916

WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON JANUARY 20TH.

## INORGANIC CHEMICALS

Acetate of Lime, gray.....	100 Lbs.	5.75	@	6.00
Alum, lump.....	100 Lbs.	5.00	@	5.25
Aluminum Sulfate, high grade.....	100 Lbs.	5.00	@	5.25
Ammonium Carbonate, domestic.....	Lb.	8 1/2	@	9 1/4
Ammonium Chloride, gray.....	Lb.	8 1/2	@	9
Ammonium Phosphate, commercial, 98 100%.....	Lb.	11	@	11 1/4
Aqua Ammonium, 16%, drums.....	Lb.	2 1/2	@	—
Arsenic, white.....	Lb.	4 3/4	@	5 1/4
Barium Chloride.....	Ton	—	@	120.00
Barium Nitrate.....	Lb.	15	@	16
Barytes, prime white, foreign.....	Ton	19.00	@	23.00
Bleaching Powder, 35 per cent.....	100 Lbs.	14.00	@	15.00
Blue Vitriol.....	Lb.	23	@	24
Borax, crystals, in bags.....	Lb.	5 1/4	@	6
Boric Acid, powdered crystals.....	Lb.	10 1/4	@	10 3/4
Brimstone, crude, domestic.....	Long Ton	22.00	@	22.50
Bromine, technical, bulk.....	Lb.	5.00	@	6.50
Calcium Chloride, lump.....	Ton	—	@	11.78
Calcium Chloride, granulated.....	Ton	—	@	14.78
Caustic Soda, 74 per cent.....	Lb.	5 1/4	@	5 1/2
Caustic Soda, 76 per cent.....	Lb.	5 1/4	@	6
Chalk, light precipitated.....	Lb.	4 3/4	@	5 1/2
China Clay, imported.....	Ton	11.00	@	16.00
Feldspar.....	Ton	8.00	@	12.00
Fuller's Earth, foreign, powdered.....	100 Lbs.	80	@	1.05
Glauber's Salt, in bbls.....	100 Lbs.	60	@	75
Green Vitriol, bulk.....	100 Lbs.	75	@	85
Hydrochloric Acid, commercial, 18%.....	100 Lbs.	2.50	@	3.00
Hydrochloric Acid, C. P., conc., 22%.....	100 Lbs.	3.00	@	3.50
Iodine, resublimed.....	Lb.	4.25	@	4.30
Lead Acetate, white crystals.....	Lb.	—	@	12 1/2
Lead Nitrate.....	Lb.	16 1/2	@	16 3/4
Litharge, American.....	Lb.	90	@	1.00
Lithium Carbonate.....	Lb.	10	@	12
Magnesium Carbonate.....	Lb.	30.00	@	35.00
Magnesite, "Calcined".....	Ton	1.85	@	2.15
Mercuric Chloride, commercial.....	Lb.	7 1/2	@	8
Nitric Acid, 36%.....	Lb.	9	@	9 1/2
Nitric Acid 42%.....	Lb.	30	@	32
Phosphoric Acid, sp. gr. 1.750.....	Lb.	35	@	1.00
Phosphorus.....	Lb.	1.50	@	1.70
Plaster of Paris.....	Bbl.	53	@	54
Potassium Bichromate, casks.....	Lb.	5.50	@	—
Potassium Bromide.....	Lb.	50	@	60
Potassium Carbonate, calcined, 80 @ 85%.....	Lb.	50	@	—
Potassium Chlorate, crystals, spot.....	Lb.	30	@	35
Potassium Cyanide, bulk, 98-99 per cent.....	Lb.	55	@	60
Potassium Hydroxide.....	Lb.	3.70	@	3.75
Potassium Iodide, bulk.....	Lb.	—	@	—
Potassium Nitrate.....	Lb.	1.75	@	2.00
Potassium Permanganate, bulk.....	Lb.	225.00	@	250.00
Quicksilver, flask, 75 lbs.....	Lb.	7 1/4	@	—
Red Lead, American, dry.....	Lb.	55	@	65
Salt Cake, glass makers'.....	100 Lbs.	36	@	38
Silver Nitrate.....	Oz.	10.00	@	12.00
Soapstone in bags.....	Ton	1.85	@	2.10
Soda Ash, 48 per cent.....	100 Lbs.	10 3/4	@	11
Sodium Acetate.....	Lb.	1.50	@	1.60
Sodium Bicarbonate, domestic.....	100 Lbs.	3 1/2	@	3 3/4
Sodium Bicarbonate, English.....	Lb.	30	@	32
Sodium Bichromate.....	Lb.	1.50	@	—
Sodium Carbonate, dry.....	100 Lbs.	25	@	50
Sodium Chlorate.....	Lb.	15	@	—
Sodium Fluoride, commercial.....	Lb.	3.00	@	3.25
Sodium Hyposulfite.....	100 Lbs.	3.10	@	—
Sodium Nitrate, 95 per cent, spot.....	100 Lbs.	85	@	1.10
Sodium Silicate, liquid.....	100 Lbs.	2	@	2 1/2
Sodium Sulfide, 30%, crystals, in bbls.....	Lb.	5	@	7
Sodium Sulfite, crystals.....	Lb.	22 1/2	@	23
Strontium Nitrate.....	Lb.	2.20	@	2.60
Sulfur, flowers, sublimed.....	100 Lbs.	1.80	@	2.15
Sulfur, roll.....	100 Lbs.	2.00	@	2.50
Sulfuric Acid, chamber, 60%.....	100 Lbs.	2.50	@	3.00
Sulfuric Acid, conc., sp. gr. 1.842.....	100 Lbs.	2.50	@	3.00
Sulfuric Acid, oleum (fuming).....	100 Lbs.	9.00	@	13.00
Talc, American.....	Ton	75	@	80
Terra Alba, American, No. 1.....	100 Lbs.	14	@	—
Tin Bichloride, 50%.....	Lb.	48	@	50
Tin Oxide.....	Lb.	6 1/2	@	—
White Lead, American, dry.....	Lb.	18 1/2	@	19
Zinc Carbonate.....	Lb.	12	@	18
Zinc Chloride, commercial.....	Lb.	8 3/4	@	8 1/2
Zinc Oxide, American process.....	Lb.	6 1/2	@	7
Zinc Sulfate.....	Lb.	—	@	—

## ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.....	Lb.	1.15	@	1.20
Acetic Acid, 28 per cent, in bbls.....	Lb.	6 1/2	@	7
Acetic Acid, glacial, 99 1/2%, in carboys.....	Lb.	32	@	36

Acetone, drums.....	Lb.	35	@	40
Alcohol, denatured, 180 proof.....	Gal.	50	@	52
Alcohol, grain, 188 proof.....	Gal.	2.62	@	2.64
Alcohol, wood, 95 per cent, refined.....	Gal.	55	@	57
Amyl Acetate.....	Gal.	4.50	@	5.50
Aniline Oil.....	Lb.	95	@	1.00
Benzoic Acid, ex-toluol.....	Lb.	4.00	@	4.10
Benzol, 90 per cent.....	Gal.	80	@	90
Camphor, refined in bulk, bbls.....	Lb.	42	@	—
Carbolic Acid, U. S. P., crystals, drums.....	Lb.	1.25	@	1.30
Carbon Bisulfide.....	Lb.	6	@	15
Carbon Tetrachloride, drums, 100 gals.....	Lb.	16	@	20
Chloroform.....	Lb.	70	@	75
Citric Acid, domestic, crystals.....	Lb.	64	@	64 1/2
Cresol, U. S. P.....	Gal.	1.15	@	1.25
Dextrine, corn (carloads, bags).....	100 Lbs.	3.10	@	3.20
Dextrine, imported potato.....	Lb.	12	@	13
Ether, U. S. P., 1900.....	Lb.	15	@	20
Formaldehyde, 40 per cent.....	Lb.	9 1/2	@	10
Glycerine, dynamite, drums included.....	Lb.	50	@	—
Oxalic Acid, in casks.....	Lb.	50	@	51
Pyrogallic Acid, resublimed bulk.....	Lb.	1.25	@	1.45
Salicylic Acid.....	Lb.	4.00	@	4.15
Starch, cassava.....	Lb.	3 3/4	@	4 1/2
Starch, corn (carloads, bags).....	100 Lbs.	2.25	@	2.36
Starch, potato.....	Lb.	6	@	6 1/2
Starch, rice.....	Lb.	8	@	10
Starch, sago.....	Lb.	3 1/4	@	3 1/2
Starch, wheat.....	Lb.	5	@	6
Tannic Acid, commercial.....	Lb.	75	@	76
Tartaric Acid, crystals.....	Lb.	65	@	67

## OILS, WAXES, ETC.

Beeswax, pure, white.....	Lb.	47	@	55
Black Mineral Oil, 29 gravity.....	Gal.	13	@	14
Castor Oil, No. 3.....	Lb.	17 3/4	@	18 1/4
Ceresin, yellow.....	Lb.	10	@	14
Corn Oil, crude.....	100 Lbs.	8.05	@	8.10
Cottonseed Oil, crude, f. o. b. mill.....	Gal.	61	@	62
Cottonseed Oil, p. s. y.....	Lb.	9 1/8	@	9 1/4
Cresote, beechwood.....	Lb.	—	@	—
Cylinder Oil, light, filtered.....	Gal.	20	@	25
Fusel Oil, crude.....	Lb.	3.45	@	3.70
Japan Wax.....	Lb.	13	@	—
Lard Oil, prime winter.....	Gal.	92	@	96
Linseed Oil, raw (car lots).....	Gal.	72	@	—
Menhaden Oil, crude (southern).....	Gal.	—	@	—
Naphtha, 68 @ 72°.....	Gal.	30	@	35
Neat's-foot Oil, 20°.....	Gal.	95	@	97
Paraffine, crude, 117 & 119 m. p.....	Lb.	3 1/2	@	4
Paraffine Oil, high viscosity.....	Gal.	24 1/2	@	25
Rosin, "R" Grade, 280 lbs.....	Bbl.	—	@	5.85
Rosin Oil, first run.....	Gal.	21	@	32
Shellac, T. N.....	Lb.	21	@	22
Spermaceti, cake.....	Lb.	25	@	26
Sperm Oil, bleached winter, 38°.....	Gal.	74	@	75
Spindle Oil, No. 200.....	Gal.	19 1/2	@	20
Stearic Acid, double-pressed.....	Lb.	14 1/4	@	15
Tallow, acidless.....	Gal.	78	@	80
Tar Oil, distilled.....	Gal.	30	@	31
Turpentine, spirits of.....	Gal.	58	@	—

## METALS

Aluminum, No. 1, ingots.....	Lb.	53	@	55
Antimony, ordinary.....	Lb.	42 1/2	@	—
Bismuth, New York.....	Lb.	3.50	@	—
Copper, electrolytic.....	Lb.	24 1/2	@	—
Copper, lake.....	Lb.	24 1/2	@	—
Lead, N. Y.....	100 Lbs.	5.90	@	—
Nickel, electrolytic.....	Lb.	50	@	—
Nickel, shot and ingots.....	Lb.	45	@	—
Platinum, refined.....	Oz.	87.50	@	90.00
Silver.....	Oz.	56 3/4	@	—
Tin.....	100 Lbs.	41.62 1/2	@	—
Zinc, N. Y.....	Lb.	18 3/4	@	—

## FERTILIZER MATERIALS

Ammonium Sulfate.....	100 Lbs.	4.10	@	—
Blood, dried.....	Unit	3.25	@	—
Bone, 4 1/2 and 50, ground, raw.....	Ton	35.00	@	—
Calcium Cyanamid.....	Unit of Ammonia	2.45	@	—
Calcium Nitrate, Norwegian.....	100 Lbs.	—	@	—
Castor Meal.....	Unit	—	@	—
Fish Scrap, domestic, dried, f. o. b. works.....	Unit	3.85	@	10
Phosphate, acid.....	Unit	80	@	85
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	2.75	@	3.00
Tennessee, 70-80 per cent.....	Ton	5.00	@	5.50
Potassium "muriate," basis 80 per cent.....	Ton	490.00	@	—
Pyrites, furnace size, imported.....	Unit	13 1/4	@	—
Tankage, high-grade; f. o. b. Chicago.....	Unit	3.10	@	10

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## EDITORIALS

### SPRING MEETING OF AMERICAN CHEMICAL SOCIETY

The Fifty-Second Meeting of the American Chemical Society will be held at the University of Illinois, Urbana-Champaign, from Tuesday, April 18th, to Friday, April 21st, inclusive. The Beardsley Hotel, Champaign, has been chosen as headquarters; all meetings will be held at the University of Illinois.

The provisional program, printed elsewhere in this issue, includes as a special feature the dedication of the new chemistry building University of Illinois, when addresses will be made by Governor Edward J. Dunne of Illinois, President Edmund J. James, University of Illinois, W. R. Whitney of the U. S. Naval Board, and Professor Alexander Smith of Columbia University. The public lectures will be on the "Production and Use of Radium," by C. L. Parsons of the U. S. Bureau of Mines, and Dr. C. F. Burnham of Baltimore. A special excursion has been arranged to Danville, Illinois, where the following will be visited: Hegeler Brothers' Zinc Smelter and Sulfuric Acid Plant, Western Brick Company's Kilns, Three Rivers Coal Company's Strip Coal Mine.

### COÖPERATION IN FOREIGN TRADE

An address by Joseph E. Davies, Chairman of the Federal Trade Commission, before the National Foreign Trade Council, at New Orleans, discusses the epochal opportunities that now confront American business in foreign trade, which has suddenly become a large factor in our national outlook.

Mr. Davies summarizes the general problems connected with the development of foreign trade as follows: production, shipping, banking and credit facilities, creation of markets and meeting of international competition.

Eighty-five per cent of the thousands of replies that the Trade Commission has received from a questionnaire directed to the business men of the United States disclose a demand for permission to coöperate in foreign trade, under Federal regulation.

Conditions of foreign competition which existed in the world's markets prior to the war are illustrated by typical examples of the effectiveness and comprehensive character of foreign methods:

"A combination of non-competing manufacturing plants of Great Britain, for instance, are equipped to establish, and have established, joint selling agencies, with branch offices and warehouses, and with such effective organizations that they are equipped to handle any kind of service within their lines, from the sale of a handsaw to the building of a railroad.

"Much of the oriental business of Germany, is alleged to have been acquired through so-called rings, \* \* \* \* \* The markets are scientifically studied and assiduously cultivated. In one of these rings, 48 different German manufacturers participated. Its organization with the local bank and home bank connections was complete. It had within its organization facilities for selling to a Chinaman a five cent file, or for planning, financing, and completing the industrial development of an entire province, opening harbors, building railways and telegraph lines, sinking mines, erecting factories, installing light and power plants, and even to clothing the people and marketing of products. \* \* \* \* \*

"Prior to the war, in Germany, approximately 600 cartels or manufacturing and selling syndicates, of a high degree of integration in industry and capacity, were projecting their activities

into foreign markets. It is generally recognized that at the same time there were approximately 130 international cartels of a similar character; and it may occasion surprise to know that the control of a smelting and refining plant in Colorado was owned by such a little known international organization.

"At the University of Kiel there has existed, and does now exist, an institute for the study of world trade, subsidized by the Imperial Government of Germany, and organized with a corps of highly trained economists. In Turkey, during the last several years, a German trade paper has been published daily in both French and German.

"The Imperial Government of Japan has projected its enterprise into foreign countries, with its government monopolies of salt, camphor, and tobacco. In Chosen, which is a new name for Korea, it is significant that there has been established an institute for the development of native Japanese chemical and industrial engineers. It is generally recognized that exporting and marketing Japanese firms threaten the complete domination of the Chinese trade.

"These manifestations of activity in Europe and in the Orient are indicative of the kind and character of competition that will be met in foreign trade in the future. Subsequent to the war these conditions will be emphasized and activities will be intensified by the spur of economic necessity in some of the nations of Europe. Under conditions such as these, the embarkation of American enterprise into foreign trade and the maintenance of its rightful place there, will require the strongest initiative and the highest order of business intelligence."

Two-thirds of our exports consist of foodstuffs and materials to be used in manufacture abroad; these practically sell themselves, so that here our main problem is that of conserving these natural resources.

"The remaining one-third of our exports are manufactured articles, and consist generally of two classes—specialties and staples. Here demand must be created; and foreign competition must be met. In specialties, the demand is largely created and the competition met through the popular character of the product. In staples, which constitute the large bulk of international trade in manufactured goods, the condition differs. The development of the demand is difficult, and the competition to be met most severe. \* \* \* \* \*

"Relatively few of the larger organizations of the country manifest a desire to enter into extensive coöperation in foreign trade. They do not seem to feel the need of coöperative effort, because of their ability and capacity to project their own enterprises. In that connection it may be said, with some reservation, that a very substantial part of our foreign trade has been developed through large organizations of this character. This development of our foreign trade is characterized by the fact that the ownership and management of plants reside in a single corporation, and is in distinct contrast in the manner in which the foreign trade of some European countries has been developed, where similar results have been obtained through the syndicated relations of smaller manufacturers who retain the individual ownership and individual control of their respective plants."

The demand for coöperation comes especially from the manufacturer of staples. In many lines of manufacture it is impossible for a small concern to engage directly in foreign enterprise: cost is prohibitive, risk is too great, warehousing and credit facilities are individually impossible.

The census taken by the Federal Trade Commission discloses that misapprehension as to the application of the anti-trust laws to foreign commerce, and doubt as to the legality of such enterprise in the foreign fields amounted in many instances to a prohibition of any action in the foreign market.

"It is the opinion of the Federal Trade Commission that enterprise in foreign trade should not be impeded by conditions of this kind. In the absence of injury to any American interest a greater degree of coöperation in export trade than is allowed in domestic trade may be beneficial to the country. If this is not now permitted by law, new legislation, to that end, properly safeguarding the public interest, should be enacted."

## ORIGINAL PAPERS

## RESEARCH ON THE CORROSION RESISTANCE OF COPPER STEEL

By D. M. BUCK<sup>1</sup> AND J. O. HANDY<sup>2</sup>

Received January 22, 1916

In order to obtain further definite information relative to the influence of varying amounts of copper and other elements when alloyed with steel, an extended series of service tests was undertaken by the authors in the spring of 1914.

Following work which had been done by one of us,<sup>3</sup> we continued the practice of conducting the tests on full size, uncoated sheets, under exact service conditions, extreme care being taken so to plan the work that those differences found in the various grades of steel used could be safely ascribed to the influence of the particular element which had been added.

In addition to repeating work which had already been done on the effect of the addition of approximately 0.25 per cent copper, we have included in this test steels with a copper content as low as 0.04 per cent, as well as steels with higher amounts up to and including 2 per cent copper.

As will be seen from Tables I to III, we also made additions of phosphorus, silicon, aluminum, sulfur, roll scale, and, following a suggestion by a colleague<sup>4</sup> that the addition of cold steel to the middle ingots of the heat would cause them to outlast the first poured ingots, a similar amount of cold steel turnings was added to one of the ingots in exactly the same manner in which the copper had been added to the others.

Some work has also been done on the influence of annealing temperatures higher than the average practice, and we have kept careful records of inside and outside sheets of the pack,<sup>5</sup> and of the presence or absence of mill scale on the surface of the sheets at the time of exposure, to determine whether or not these differences in initial protection affected the ultimate time of failure of the sheets.

## STEELS USED IN TESTS

Several heats of open-hearth and Bessemer steel were used in the tests. Table I gives the additions as they were made: the grade numbers given here are those used throughout this paper. It will be noted that in one instance ten ingots were used from a single heat, and that they differed one from the other only in the amount and kind of element which was added. In Tables II and III appear the final analyses of the sheets rolled from these ingots.

In the manufacture of basic open-hearth heat No.

<sup>1</sup> Metallurgical Engineer, American Sheet and Tin Plate Company, Pittsburgh, Pa.

<sup>2</sup> Director of Laboratories of the Pittsburgh Testing Laboratory, Pittsburgh, Pa.

<sup>3</sup> THIS JOURNAL, 6 (1913), 447; *Iron Age*, June 3, 1915; *Iron Trade Review*, June 10, 1915.

<sup>4</sup> Institute of Industrial Research, Bull. 5.

<sup>5</sup> Sheets are rolled in packs and the two outside sheets of the pack always carry on their surfaces much more mill scale (magnetic oxide of iron) than do the inside sheets.

7750, an effort was made to produce a wild, oxidized heat. The steel was melted "hot;" ore was fed faster than usual and continued even after carbon had been reduced to 0.12 per cent. Silica sand was added instead of dolomite. The heat had a very wild appearance, rose strongly in the moulds, and in addition, we had a running stopper in the ladle giving a divided stream, which of course favored oxidation. Analyses of the sheets from this heat by the Ledebuhr method showed an oxygen content averaging only 0.03 per cent, which is no higher than that in normal open-hearth steel.

Basic open-hearth heat No. 8857 was made without

TABLE I STEELS USED IN TESTS AND ADDITIONS MADE TO MODIFY THEM BASIC OPEN-HEARTH HEAT

HEAT No. 6807 Grade	HEAT No. 8805(d) Grade	Ingot No.	MATERIAL	ADDITIONS	AMOUNT
2	2	1	None		
3	3	2	Copper		0.25% (d)
4	4	3	Copper		0.50% (d)
5	5	4	Copper		1.00% (d)
6	6	5	Copper		2.00% (d)
7	7	6	None		
8	8	7	Phosphorus		0.100% (d)
9	9	8	Silicon		0.300% (d)
10	10	9	Aluminum		8 ozs.
11	11	10	Sulfur		0.100% (d)
		11	Cold steel		6 lbs.
HEAT No. 8815 Grade	HEAT No. 7699(b) Grade	Ingot No.			
12	12X	2	Copper to ladle		0.25% (d)
13	13X	2	Copper to mould		0.25% (d)
14	14X	3	None		....
HEAT No. 7750 Grade		Ingot No.			
19		4	Copper		0.25% (d)
20		6	Copper		0.25% (d)
21		7	Roll scale		20 lbs.
22		7	Roll scale		20 lbs.
23		8	Silicon		0.10% (d)
24		9	Phosphorus		0.10% (d)
		3	None		....
HEAT No. 8857 Grade		Ingot No.			
25		2	None		
26		3	Copper		0.35% (d)
HIGH SULFUR BESSEMER HEAT [RESIDUAL (NOT ADDED) SULFUR]					
Grade		Ingot No.			
15		(c)	Copper		0.25% (d)
16		(c)	None		....
NORMAL BESSEMER HEAT					
Grade		Ingot No.			
17		(c)	Copper		0.25% (d)
18		(c)	None		....

(a) About 0.04 per cent residual copper.

(c) See test.

(b) About 0.05 per cent residual copper.

(d) Aimed at.

the addition of manganese or other deoxidizer at any stage.

Basic open-hearth heat No. 8805 corresponds to heat No. 6807 (grades 2 to 11 inclusive) and the same additions were made in exactly the same way and in the same order. The composition is quite similar to No. 6807 *except that the copper (residual) is about 0.04 per cent in all grades except those to which copper was added.* Comparison of the results on sheets from these two heats affords information relative to the influence of comparatively small copper contents. The grade numbers for heat No. 8805 are the same as for No. 6807 except that an "X" has been added to each.

Basic open-hearth heat No. 7699 corresponds to



heat No. 8813 and the additions were the same. *This heat, however, contained 0.05 per cent residual copper.*

#### SHEET MANUFACTURE AND EXPOSURE OF TEST PIECES

All of the operations of blooming, rolling, sheet rolling, etc., were conducted according to regular mill practice and were under the personal supervision of the authors. Enough sheet bars were taken from the

required for our tests were taken at regular intervals from the piles, an average product being thus obtained.

Each sheet was stamped with a distinguishing mark, and they were numbered consecutively from 1 to 24. In the case of the grades 2X to 14X inclusive, and also grades 25 and 26, six sheets of each were selected

TABLE II—LOSS IN OUNCES PER SQUARE FOOT PER MONTH FOR EACH PERIOD OF EXPOSURE IN TESTS AT SCOTTDALÉ AND MCKEESPORT, PENNSYLVANIA

GRADE	PERCENTAGES PRESENT						ANNEALING		SCOTTDALÉ TESTS			MCKEESPORT TESTS			GRAND	RANK	ELEMENT	
	C	Mn	S	P	Si	Cu	° F.	mo.	6.5	9.53	Av.	8.2	10.9	Av.				
2	0.06	0.41	0.039	0.032	0.004	0.272	1400	0.1411	0.1361	0.1386	0.1386	0.1134	0.1057	0.1095	0.1241	9	Copper	
							1600	0.1405	0.1382	0.1393	0.1393	0.1041	0.1045	0.1043	0.1218		Copper	
3	0.06	0.43	0.045	0.041	0.004	0.549	1400	0.1423	0.1345	0.1384	0.1384	0.1089	0.1047	0.1068	0.1226	8	Copper	
							1600	0.1374	0.1338	0.1356	0.1356	0.1043	0.0961	0.1002	0.1179		Copper	
4	0.07	0.43	0.039	0.036	0.004	1.085	1400	0.1389	0.1319	0.1354	0.1354	0.1039	0.1007	0.1023	0.1188	3	Copper	
							1600	0.1375	0.1353	0.1364	0.1364	0.0991	0.0962	0.0976	0.1170		Copper	
5	0.06	0.42	0.042	0.040	0.004	2.180	1400	0.1314	0.1294	0.1304	0.1304	0.1005	0.0941	0.0973	0.1138	1	Copper	
							1600	0.1332	0.1303	0.1317	0.1317	0.0966	0.0905	0.0935	0.1126		Copper	
6	0.06	0.45	0.047	0.035	0.004	0.018	1400	0.3723	0.4202	0.3962	0.3962	0.1843	0.2215	0.2029	0.2996	19	None	
							1600	0.2632	0.3831	0.3231	0.3231	0.1634	0.2007	0.1820	0.2526		None	
7	0.06	0.44	0.047	0.089	0.009	0.016	1400	0.3040	0.3564	0.3302	0.3302	0.1589	0.1682	0.1635	0.2469	16	Phosphorus	
							1600	0.2692	0.3258	0.2975	0.2975	0.1460	0.1620	0.1540	0.2257		Silicon	
8	0.06	0.41	0.045	0.034	0.319	0.016	1400	0.3521	0.4747	0.4134	0.4134	0.2016	0.2027	0.2021	0.3078	20	Sulfur	
							1600	0.3186	0.3909	0.3547	0.3547	0.1527	0.1656	0.1593	0.2569		Silicon	
9	0.06	0.43	0.047	0.036	0.007	0.017	1400	0.3764	0.4732	0.4248	0.4248	0.2103	0.2335	0.2219	0.3233	22	Aluminum	
							1600	0.3591	0.4758	0.4174	0.4174	0.1932	0.1890	0.1911	0.3043		Aluminum	
10	0.06	0.43	0.075	0.028	0.008	0.019	1400	0.4327	0.5144	0.4735	0.4735	0.2341	0.2926	0.2633	0.3684	24	Sulfur	
							1600	0.4211	0.5206	0.4708	0.4708	0.1960	0.2464	0.2212	0.3460		Sulfur	
11	0.05	0.44	0.037	0.030	0.003	0.014	1400	0.3746	0.4538	0.4142	0.4142	0.1923	0.2204	0.2063	0.3103	21	Steel	
							1600	0.3023	0.3693	0.3358	0.3358	0.1717	0.1823	0.1770	0.2564		Steel	
12	0.06	0.46	0.028	0.035	0.003	0.242	1400	0.1386	0.1381	0.1383	0.1383	0.1073	0.1030	0.1051	0.1217	5	Copper	
							1600	0.1406	0.1394	0.1400	0.1400	0.1107	0.1056	0.1081	0.1241		Copper	
13	0.06	0.56	0.034	0.033	0.010	0.266	1400	0.1388	0.1401	0.1394	0.1394	0.1043	0.1064	0.1053	0.1224	7	Copper	
							1600	0.1431	0.1377	0.1404	0.1404	0.1079	0.1073	0.1076	0.1240		Copper	
14	0.08	0.60	0.035	0.032	0.006	0.014	1400	0.3344	0.3477	0.3410	0.3410	0.1785	0.1745	0.1765	0.2588	17	None	
							1600	0.2729	0.3104	0.2916	0.2916	0.1788	0.1914	0.1851	0.2384		None	
15	0.06	0.50	0.140	0.093	0.006	0.256	1400	0.1332	0.1458	0.1395	0.1395	0.1020	0.1021	0.1020	0.1208	4	Copper	
16	0.06	0.47	0.142	0.096	0.004	0.008	1400	0.4221	0.5018	0.4619	0.4619	0.2547	0.2353	0.2450	0.3535	23	None	
17	0.07	0.48	0.048	0.112	0.012	0.260	1400	0.1280	0.1358	0.1319	0.1319	0.1028	0.0963	0.0995	0.1157	2	Copper	
18	0.07	0.49	0.052	0.112	0.010	0.004	1400	0.3301	0.3911	0.3606	0.3606	0.1895	0.1922	0.1908	0.2757	18	None	
19	0.07	0.29	0.029	0.016	0.009	0.265	1400	0.1403	0.1366	0.1384	0.1384	0.1074	0.1037	0.1055	0.1220	6	Copper	
20	0.06	0.31	0.039	0.018	0.005	0.102	1400	0.1332	0.1478	0.1473	0.1473	0.1155	0.1125	0.1140	0.1307	10	Copper and scale	
21	0.06	0.26	0.030	0.017	0.005	0.014	1400	0.2849	0.2984	0.2916	0.2916	0.1649	0.1711	0.1680	0.2296	14	Scale	
22	0.06	0.29	0.033	0.018	0.123	0.016	1400	0.3026	0.3342	0.3184	0.3184	0.1604	0.1606	0.1605	0.2394	15	Silicon	
23	0.06	0.29	0.035	0.068	0.006	0.015	1400	0.2366	0.2571	0.2468	0.2468	0.1406	0.1476	0.1441	0.1955	12	Phosphorus	
24	0.06	0.30	0.027	0.016	0.004	0.014	1400	0.2752	0.2939	0.2845	0.2845	0.1677	0.1684	0.1680	0.2263	13	None	
50	0.02	0.03	0.031	0.005	0.002	0.041	1400	0.1588	0.1577	0.1582	0.1582	0.1156	0.1178	0.1167	0.1375	11		

product of each ingot to give us a large excess of sheets for our tests. The bars were taken from the piles at such points as to represent the whole ingot from top to bottom, thus securing the average product of the ingot. All grades were given exactly the same treatment in all of the manufacturing operations, and each sheet received the customary one (straightening) pass through the cold rolls.

All sheets (except those annealed at higher temperature) were annealed at one time in the same furnace, thus securing uniform heat treatment. To determine the possible influence of higher annealing temperature, one-half of the sheets of grades 2 to 14, inclusive, were annealed at a temperature about

TABLE III—LOSS IN OUNCES PER SQUARE FOOT PER MONTH FOR EACH PERIOD OF EXPOSURE

GRADE	PERCENTAGES PRESENT						MCKEESPORT TESTS			ELEMENT
	C	Mn	S	P	Si	Cu	8.2	10.9	Av.	
2X	0.06	0.49	0.033	0.029	0.004	0.290	0.1033	0.1037	0.1045	Copper
3X	0.04	0.45	0.033	0.033	0.004	0.555	0.1021	0.1035	0.1028	Copper
4X	0.05	0.46	0.033	0.031	0.004	0.990	0.1038	0.1022	0.1030	Copper
5X	0.05	0.46	0.031	0.025	0.011	1.940	0.1001	0.0979	0.0990	Copper
6X	0.06	0.48	0.034	0.032	0.002	0.041	0.1293	0.1296	0.1294	None
7X	0.06	0.46	0.031	0.085	0.003	0.040	0.1187	0.1210	0.1198	Phosphorus
8X	0.06	0.43	0.028	0.030	0.332	0.036	0.1352	0.1267	0.1309	Silicon
9X	0.06	0.47	0.032	0.029	0.006	0.037	0.1241	0.1301	0.1271	Aluminum
10X	0.06	0.46	0.082	0.028	0.004	0.044	0.1493	0.1810	0.1651	Sulfur
11X	0.06	0.46	0.033	0.032	0.010	0.037	0.1257	0.1314	0.1285	Steel
12X	0.06	0.53	0.033	0.033	0.004	0.270	0.1046	0.1012	0.1029	Copper
13X	0.06	0.41	0.031	0.022	0.006	0.314	0.1072	0.1047	0.1059	Copper
14X	0.06	0.41	0.031	0.024	0.006	0.050	0.1173	0.1167	0.1170	None
25	0.06	0.15	0.032	0.012	0.005	0.017	0.1922	0.2195	0.2058	None
26	0.06	0.16	0.030	0.012	0.004	0.404	0.1096	0.1055	0.1075	Copper

200° F. higher than the normal temperature for sheets. The remainder of the sheets of these grades and all other grades were annealed at the usual temperature (1400° F.). After the annealing process the sheets were laid out in piles and the twenty-four (24) sheets

in the same manner as above, and were numbered from 1 to 6. All sheets were 26 gauge, 26 in. × 96 in.

A strip 2 in. wide was cut lengthwise from each sheet, and these strips were given the same distinguishing numbers as the sheets from which they were cut, and were sent to the laboratories, where each one was carefully analyzed. As soon as this work had been completed, and we were thus assured that no mistakes had been made in marking the sheets, they were corrugated and forwarded to Scottdale and McKeesport, Pennsylvania. Twelve (12) sheets of each grade, 2 to 24 inclusive, were exposed at each station, while the other grades 2X to 14X, 25 and 26 were exposed at McKeesport only.

Meanwhile, there had been obtained in the open market, from three different sources, three lots of one of the so-called "pure irons," which on analysis proved to have a copper content of 0.041 per cent. Several sheets of each lot were exposed exactly as received, without pickling or cleaning of any kind (this has been the invariable practice on all corrugated sheets of all grades in this test and in all previous tests made by one of us).

All of the grades above mentioned, including the so-called "pure iron" (grade 50), were exposed as roof panels at McKeesport on July 7, 1914, and at Scottdale on July 9, 1914. At approximately the same time that the full size sheets were exposed, a series of 2 in. × 4 in. test pieces cut from the 2 in. strips before mentioned, and consisting of one piece from each sheet (636 in all), was exposed. These

test pieces were cleaned by a very light wash of sulfuric acid, dipped in ammonia water to neutralize all acid, then thoroughly washed, dried, weighed and arranged in wooden racks in such a manner as to afford all free and equal exposure to the weather.

The method of removing, cleaning and weighing these test pieces will be discussed later. The results obtained are given in Tables II and III.

#### INSPECTION OF EXPOSED SHEETS

At the time of exposure of the full size corrugated sheets careful notes were taken concerning the physical appearance of the sheets as affected by the amount of mill scale which was present, and as to whether they were outside or inside sheets of the packs. During the progress of the test, this feature was carefully watched, and the time of ultimate failure of sheets whose surfaces were comparatively free from mill scale was compared with others of the same grade, whose surfaces were well covered with mill scale. From these observations, we concluded that the influence of this original surface oxide is slight, and is lost in the early stages of rusting, for no difference in final failure could be noticed. The photographs shown on pages 212 and 213 were taken from time to time during the tests, and show in a graphic manner the progress of the corrosion at various stages.

Careful inspections of the sheets were made approximately once every two months. At the first inspection, distinct differences were noticed in the physical conditions of the various panels: the corrosive action of the atmosphere had produced a decided difference in color, the steels with a copper content of .25 per cent or more being distinctly darker than the others which contained only a trace of copper; at the same time, these dark brown panels were smoother to the touch than the others, and the rust was denser and more adherent. Inasmuch as this same phenomenon had been noticed in former tests, it was thus indicated, even at this early stage, which steels would be the most resistant. It was also noted that several of the panels to which ingredients other than copper had been added, *e. g.*, sulfur and aluminum, gave indications that the rate of corrosion was proceeding even faster than with those steels to which no additions had been made. The fact that such early inspections are valuable, and that the relative merits of the various steels and irons can be predicted with fair accuracy, is borne out by the results of later inspections, and by the order of failure of the various panels.

The peculiar piebald appearance of the sheets (photographs were taken immediately after exposure of the sheets) in Cuts A-1, 2, and 3, is caused by the irregular distribution of mill scale. The outside sheets show a uniform dark color while the inside sheets are light in the areas where mill scale was absent and *vice versa*.

It will be noted that the twelve (12) sheet panels have been divided into two panels of six (6) sheets each. In the cases of Grades 2 to 14 inclusive the left half of these consists of sheets annealed at 1400°,

while those in the right half were annealed at 1600°. In all other cases the two halves received identical treatment.

Referring to Cuts E-1, 2 and 3, an unusually severe wind storm occurred at Scottdale on Nov. 18, 1915, which blew away all fragments of sheets which were hanging by one end, only those sheets remaining which were in good condition and which still contained a considerable amount of uncorroded metal.

The rate of corrosion of the various grades may be observed by studying Photographs A, B, C, D and E, of the Scottdale test, and F, G, H and I, of the McKeesport test. While the corrosion at McKeesport was somewhat slower than at Scottdale, yet by a study of the photographs and tables, it will be seen that the relations between the various grades are approximately the same.

We call particular attention to the photograph of the Scottdale test taken December 1, 1915, 17 months after the test was erected. At this time all of the non-copper steels and the "pure iron" had completely failed, while every panel to which copper had been added was intact.

#### RELIABILITY OF TESTS ON SMALL PIECES

It has been claimed<sup>1</sup> that tests made by determining the losses in weight on exposure of comparatively small test pieces are inaccurate and misleading. A study of the tables which we present herewith, showing the weight losses due to corrosion of the various grades of steel and iron, in the shape of 2 in. × 4 in. test pieces, together with the photographs showing the conditions of the large size sheets, will prove that the results accord remarkably, and that the weight losses correspond to the relative endurance of the large sheets.

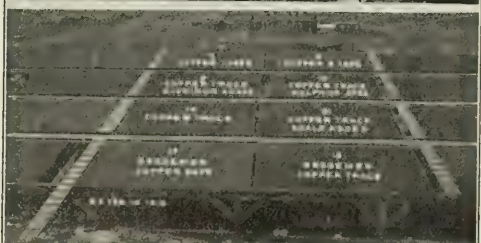
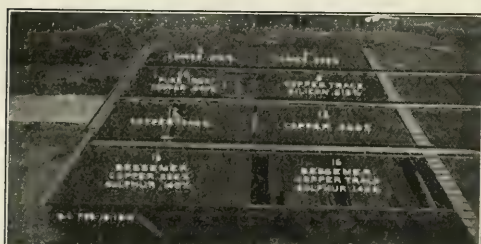
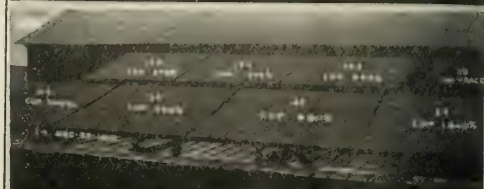
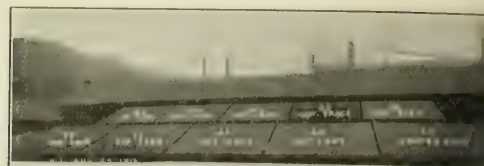
In these experiments, we adopted the practice of removing and cleaning one-half of the small test pieces after the lapse of several months, allowing the others to remain exposed for some time longer. This was done in an effort to determine if there was any tendency of the rust film to behave differently on different sheets. It was thought that the sponge-like rust which is normally formed on non-copper steels might accelerate corrosion more than the dense adherent film on copper steels. That this idea was correct, is shown by the results (discussed below).

#### CLEANING OF SMALL TEST PIECES

To clean the rust from the test pieces before final weighing, we used an ammoniacal solution of ammonium citrate. This solution completely removes the rust in about 12 hours, with the minimum attack upon the underlying metal. Careful experiments show that the attack on bare iron and steel by this solution is practically nil. On rusted pieces, due no doubt to electrolysis, it is a little greater, but still negligible compared with the total losses obtained. Furthermore it is approximately the same on all grades used in this test. This is further substantiated by the fact that the order of final failure of the large sheets coincided almost exactly with the weight losses obtained on the small pieces by this method.

<sup>1</sup> Cushman, *Proc. Am. Iron and Steel Institute*, 1915.











This report does not include details of the various inspections nor detailed tables showing losses of individual test pieces, but presents tables of summaries giving average results. The losses are in each case expressed in ounces per square foot of exposed surface per month, and the results are averages of from six to twelve determinations in each case. Complete detailed notes may be found at the authors' offices, and are available to anyone who wishes to study them.

#### RESISTANCE TO CORROSION OF VARIOUS GRADES

Table II summarizes the results on all grades which were exposed in both locations, and compares losses during each entire period of exposure, and also grand averages. The column headed "RANK" gives the order of resistance to corrosion of the various grades—1 being best, and 24 poorest. In this ranking we have compared only those grades annealed at 1400° F. In this list there are ten grades to which copper was added in amounts from 0.25 to 2.00 per cent.<sup>1</sup> These have taken the ten highest positions, and there is a remarkable uniformity in corrosion rate among them, the greatest loss being 0.1307 and the lowest 0.1138. Higher amounts than 0.25 per cent copper give slightly better results, but the differences are so small as to be negligible, especially when considering the added cost.

The so-called "pure iron" with a copper content of 0.041 per cent takes 11th place, while the other

(Table II), we find that as low a copper content as 0.04 seems to have materially lessened corrosion—compare 6X with 6, 14X with 14, and 10X with 10, etc.: from the latter we learn that 0.04 per cent copper partially neutralizes the influence of as much as 0.082 per cent sulfur.

Panel 25, from a heat to which no deoxidizer was added, and which was comparatively low in manganese, shows a corrosion rate greater than that of normal basic open-hearth steels, indicating no benefit because of lower manganese but a possible detriment, from the steel not having been deoxidized. Panel 26 from the same heat, with copper addition, is quite the equal of other steels to which copper was added.

Table IV(A) indicates the relative rates of corrosion in the two different atmospheres, of all varieties of steel tested. On plain steels we find that the corrosion in the coke regions, that is, at Scottdale, is nearly twice as great as that at McKeesport in a normal mill district. The difference is very much less when considering copper-bearing steels, the ratio being approximately as follows:

All steels: 100 at McKeesport to 173 at Scottdale  
Copper steels: 100 at McKeesport to 133 at Scottdale  
Plain steels: 100 at McKeesport to 190 at Scottdale

From Table IV(B) we learn that the benefit of higher annealing temperatures in the case of plain steels is approximately 12 per cent greater endurance, while for copper steels it is practically negligible.

TABLE IV—AVERAGE CORROSION PER MONTH (FROM

STEELS AVERAGED	(A) BOTH TEMPERATURES	
	Scottdale	McKeesport
Grades 2 to 50.....	0.2596	0.1502
Copper steels.....	0.1376	0.1037
All others.....	0.3528	0.1857

grades which have only the usual traces of copper take positions from 12 to 24, the poorest being those to which sulfur was added (No. 10) and which contained high sulfur residually (No. 16), the latter showing losses approximately three times as great as the copper steels.

The addition of aluminum, silicon and cold steel in each case has slightly increased the corrosion rate (compare Nos. 9, 8 and 11 with No. 6). A phosphorus addition has somewhat lessened the corrosion (compare No. 7 with No. 6 and No. 23 with No. 24): this is in line with some of our previous work.

Grades 19 to 24, although from a heat which was supposed to be highly oxidized, have shown somewhat lower losses than the other heats. From other work we have done, we ascribe this to the somewhat lower sulfur content (compare Nos. 6 and 14 with No. 24).

In studying the results on Grades 15, 16, 17 and 18 (Bessemer), we note the accelerating effect of very high sulfur. At the same time, the addition of 0.25 per cent copper to the same steel has entirely neutralized this influence and the results are quite comparable to those obtained with normal copper steels.

Considering Table III, Grades 2X to 14X, to which the same additions were made as to Nos. 2 to 14

<sup>1</sup> In grade No. 20, the steel was so wild that it was very difficult to add the copper properly, and some was lost.

TABLE I: RESULTS IN OUNCES PER SQUARE FOOT

	(B) FROM GRAND AVERAGE		(C) GRADES 2 TO 24	
	1400°	1600°	Scottdale 1st period 2nd period	McKeesport 1st period 2nd period
	0.1206	0.1196	0.1379 0.1369	0.1066 0.0917
	0.3021	0.2686	0.3383 0.5122	0.1875 0.2343

In determining the losses of the weighed test pieces, the authors adopted the practice of removing them from the racks at different periods. At the end of these periods, which were 6.5 and 8.2 months, respectively, we removed one-half of the test pieces and cleaned and weighed them. The remaining half we left exposed for approximately 3 months longer, at the end of which time they also were taken down, cleaned and weighed. Various conclusions may be drawn from a study of corrosion rates during these two periods of exposure.

In Table IV(C) in the Scottdale test we notice that in the first period the rate of corrosion of copper steels was 0.1379 and of the same steels in the second period, 0.1369, showing that the corrosion rate does not increase for successive periods of exposure, while with the plain steels, we find a decided increase in the second period over the first, viz., 0.3383 in the first to 0.5122 in the second, a 51 per cent increase in corrosion rate. Similar results were obtained in the McKeesport test.

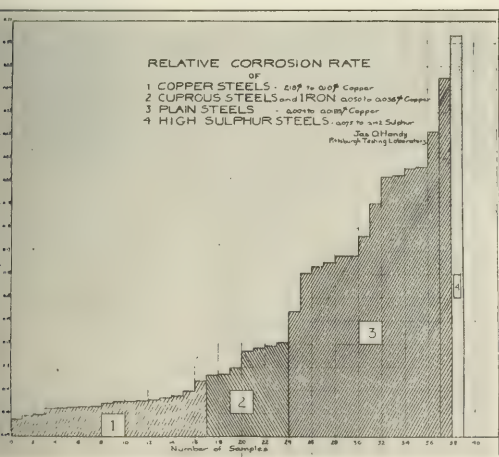
TABLE V—COMPARISON OF COPPER STEELS OF NORMAL ANALYSIS WITH OTHER STEELS TO WHICH NO ADDITIONS WERE MADE: (FROM TABLES I AND II)

TEST	Period	Copper steels 0.25% Cu (2-12-13-17)	Plain steels (6-14-18)	"Pure Iron" (50)	Low copper steels (6X) (14X)	
Scottdale	1st	0.1366	0.3456	0.1588	.....	.....
	2nd	0.1394	0.4737	0.1554	.....	.....
McKeesport	1st	0.1069	0.1841	0.1156	0.1293	0.1173
	2nd	0.0905	0.2325	0.1244	0.1307	0.1147

In Table V, we have set apart the copper steels which free in copper content with the amount used in the average material which is placed on the market, that is, 0.25 per cent, and we have compared these with plain steels to which no additions have been made, and also with so-called "pure iron." Such comparisons have been made both in the Scottsdale test and in the McKeesport test. We find again that with copper steels, as in Table IV(C), the corrosion rate does not accelerate in the second period of exposure, whereas with plain steels, the reverse is true, the corrosion ratio being 100 : 177. The pure open-hearth iron containing 0.04 per cent copper has shown greater total corrosion loss than the copper steels, yet, probably due to its copper content, it ranges itself with the copper steels, in that the corrosion rate is not increased in the second period. The same statement applies to the normal open-hearth steels containing 0.04 per cent copper, as will be noted by the results on samples 6X and 14X. It will also be noted that Grade 6X, a normal open-hearth steel with 0.041 per cent copper is nearly as good as No. 50 (pure iron with 0.041 per cent copper), while Grade 14X with 0.05 per cent copper is better than No. 50. (The test results have been shown at the different stages of testing to many parties of metallurgists and other investigators of corrosion problems.)

#### ADDITIONAL "PURE IRON" TESTS

In addition to the tests reported above, one of the authors<sup>1</sup> has conducted some tests, the results of which are further corroborative evidence on the behavior of low copper "pure irons" under atmospheric in-



fluences, and also on the progress of rusting during successive periods of exposure. A description of these tests follows:

At the request of one of the authors, two manufacturers of "pure iron" furnished sheets of their material, which were analyzed, corrugated and included in the weather exposure tests at McKeesport. Test pieces were also cut from the sheets and the losses of weight determined by exposure, in the Pittsburgh

atmosphere, under the same conditions, with copper-bearing steels and plain steels. The sheets were of 26 gauge, except in the case of Type A, 1st lot, which had a thickness of 0.022 in. instead of 0.0185 in. They were first exposed on July 16, 1914, November 7, 1914 and August 5, 1914, respectively. The analyses of the "pure iron" sheets were as follows:

PERCENTAGES	Type A: Low-copper		Type B
	1st lot	2nd lot	0.04 to 0.05% Cu
Carbon.....	0.013	0.020	0.014
Manganese.....	0.04	0.094	0.049
Phosphorus.....	0.004	0.005	0.003
Sulfur.....	0.030	0.018	0.033
Silicon.....	0.002	0.002	0.002
Copper.....	0.027	0.020	0.045
Oxygen.....	0.031	...	...
Aluminum.....	0.005	...	...

TYPE A, 1ST LOT—Observations showed that in less than 1 month this lot was rusting badly and the rust had the light brown color which had been found to be characteristic of the more rapidly corroding steels; in less than 2 months the same sheet had become very rough, resembling in this respect the most rapidly rusting steels containing added sulfur and silicon; in 9 months it had become as thin as paper at the edges; in 12 months it had frayed and broken at the bottom, but did not break transversely when pressed; in 15 months it had broken through near the bottom, though fairly strong at the upper end; after 18 months, one square foot of it had rusted away at the bottom, and it was cracked half way up; it cracked transversely when lightly pressed near the top.

TYPE A, 2ND LOT showed a thick, light brown rust after about 2 months' exposure; after 4 months, there was a thick, light brown scale; after 6 months, the sheets were thin at the bottom, but could not then be broken by light pressure; after 9 months, the sheets were rusted away at the bottom—one sheet was full of holes in the lower half and the rusting had proceeded further than in the case of the 1st lot at this period; after 12 months the sheets had become detached and were rusted so badly that they could be broken easily by hand in any part.

The more rapid corrosion of the second lot of this "pure iron" is believed to be due to the lower copper content.

TYPE B—It will be noticed that this type of "pure iron" contained more than twice as much copper as the "pure iron" of Type A. The percentages of copper in the different sheets were 0.043, 0.044 and 0.048, which places it in the class with the "pure iron" in the main test and with the sheets 6X and 14X, already described as being far more durable than plain steel or "pure iron" of Type A, especially in the 2nd lot. After 6 months, they were graded as showing no more corrosion than the copper-bearing steels which had been exposed for 7 months; after 8 months they were graded as being no longer as resistant to corrosion as the copper-bearing steels containing approximately 0.25 per cent copper—the rust was quite rough, resembling 7X, 14X and the "pure iron" in the main test; after 11 months, while the rust was rough and deep, there was no perceptible thinning at the edges and no sagging; after 14 months, one sheet broke when lightly pressed; after 17 months, one sheet was perforated and cracked—the second sheet was cracked and had a small perforation while the third sheet was not then broken through.

QUANTITATIVE WEIGHT LOSSES of the test pieces exposed for approximately equal periods, though at slightly different seasons, in the Pittsburgh atmosphere were as follows:

	Time	Loss in ounces per sq. ft.
Type A, 1st lot	6 mo. (Oct. to Apr.)	2.70
Type A, 2nd lot	5 1/2 mo. (Nov. to Apr.)	2.34
Type B,	5 1/2 mo. (Oct. to Apr.)	1.64

<sup>1</sup> Mr. Handy.



The test pieces, of which there were three in each case, were, after cleaning with ammonium citrate solution and weighing, exposed for three months longer.

Time, 3 mo. (May to Aug.)	Loss in oz. per sq. ft.	Copper percentage
Type A, 1st lot	1.26	0.027
Type A, 2nd lot	1.66	0.019
Type B	0.99	0.045

It will be seen that, when exposed under exactly the same conditions, the losses of weight were inversely proportional to the small and slightly varying copper percentages.

The following experiment shows the comparison between weight losses during one, two and three months' exposures of *separate* test pieces of "pure iron," Type A, 2nd lot.

	Loss in oz. per sq. ft.
June 1st to July 1st	0.74
" " August 1st	1.42
" " September 1st	2.27

It had been noticed in other experiments that the copper-bearing steels showed less loss of weight for equal periods of exposure, after the first dense rust coating had formed. These experiments show that the nearly equal corrosion loss during the second month and the greater corrosion loss during the third month place this low copper "pure iron" in the same class of inferior weather-resisting material with plain steel free from copper.

#### CORROSION LOSSES (OZ. PER SQ. FT.) OF COPPER-BEARING STEEL, PLAIN STEEL AND "PURE IRON"

Test pieces were exposed in racks for *one-month periods* in the Pittsburgh atmosphere. The results in the following table do not represent progressive rusting, a new test piece having been exposed on the first of each month.

	Copper-bearing steel 0.25% Cu	Plain steel	"Pure iron" 0.045% Cu
May	0.52	0.90	0.64
June	0.38	0.65	0.49
July	0.56	0.95	0.76
August	0.54	0.75	0.68

Test pieces were exposed for from 1- to 5-month periods in the Pittsburgh atmosphere with the following results. These results represent progressive losses, six (6) pieces having been exposed at the start and one taken down at a time at the end of each month.

Period exposed Months	Copper-bearing steel 0.25% Cu	Plain steel	"Pure iron" 0.045% Cu
1	0.52	0.90	0.64
2	0.64	1.82	0.92
3	0.95	3.00	1.41
4	1.13	3.64	1.46
5	1.13	4.41	1.61
6	1.17	5.53(a)	1.76

(a) This piece of plain steel was at this time reduced from an original weight of 18.3 grams to 0.9 gram, and was wholly disintegrated.

From the above tables, it will be noticed that the progress in rusting under the original rust coat is much more rapid in the case of the plain steel than in the case of the copper-bearing steel, and materially less rapid in the case of the copper-bearing steel than in the case of the "pure iron." However, this "pure iron" contains enough copper to account for its approximating in corrosion resistance the copper-bearing steel. It is of great interest to note that corrosion practically stopped in the case of the copper-bearing

steels after the fourth month: the rust had formed an efficient protective coating.

#### SUMMARY

Sheet steel or iron containing COPPER shows greatly increased corrosion resistance when exposed to atmospheric conditions. The most effective amount of copper to be used for this purpose is approximately 0.25 per cent. Smaller amounts of copper down to as little as 0.04 per cent have a considerable influence in lessening corrosion, but the results are not as good as with the higher amount mentioned above. Work previously done by one of us has indicated that 0.15 per cent copper is in nearly all cases as efficient as 0.25 per cent. Higher amounts of copper, up to 2 per cent, give little or no added benefit. Copper is as necessary in the so-called "pure irons" to insure corrosion resistance as it is in normal open-hearth and Bessemer steels.

PHOSPHORUS added to open-hearth steel slightly lowers the corrosion rate. SILICON, while probably without effect in the amounts normally present in open-hearth and Bessemer steels, accelerates corrosion when added in amounts from 0.10 to 0.30 per cent. The addition of small amounts of ALUMINUM probably has little influence on corrosion: the above tests indicate it to be harmful rather than beneficial. The addition of SULFUR to steel greatly increases the corrosion rate and when residually present in abnormal amounts, it is probably also detrimental from a corrosion standpoint. The addition of COLD STEEL to molten steel does not lower the corrosion rate, but, if it has any influence at all, it is to increase the corrosion.

LOSS IN WEIGHT DETERMINATIONS ON SMALL TEST PIECES are found to be accurate and valuable when determining the relative corrosion resistance of various sheet metals. The method of cleaning such test pieces with ammoniacal ammonium citrate solution is found to be the most convenient and accurate thus far investigated.

#### CONCLUSIONS

I—Copper increases the resistance of steel and iron to atmospheric corrosion:

- 1—Its influence is apparent when the copper content reaches only 0.03 per cent.
- 2—Its effect is almost at a maximum when the copper reaches 0.05 per cent.
- 3—The best amount of copper for commercial steel has been found to be 0.25 per cent.

II—Steel containing 0.25 per cent copper outlasts "pure iron" containing 0.04 per cent copper.

III—Steel containing 0.05 per cent copper lasts as long as "pure iron" containing 0.04 per cent copper.

IV—Sulfur in steel accelerates corrosion very markedly.

V—Sulfur oxides in the air accelerate the corrosion of steel.

VI—Copper in steel counteracts or retards both the corroding influences noted in IV and V.

# PREPARATION OF PURE IRON AND IRON-CARBON ALLOYS<sup>1</sup>

By J. R. CAIN, E. SCHRAMM AND H. E. CLEAVES

Received January 24, 1916

## INTRODUCTION

The fundamental importance of the iron-carbon thermal equilibrium diagram in the scientific metallurgy of iron and steel and its utility to practical workers have long been realized, and accordingly this subject has received attention from many points of view and from many investigators during the past two decades.

In view of this fact, it might seem superfluous to add to the existing literature except for the following considerations. Earlier workers have for the most part confined their attention to special portions of the diagram or to disputed questions of theory. Their thermal studies have not been carried out with the degree of accuracy now attainable. They have practically, without exception, employed commercial materials of varying degrees of purity. In two papers<sup>2</sup> published in 1913 Prof. H. M. Howe, as a result of a thorough examination of the literature, has fixed the most probable position of the equilibrium lines. His net conclusions are that "this calculated line is not entitled to great weight because of the weakness of the

of the materials used in some of the more important recent investigations. A glance at the table will show the justice of the conclusions quoted above. The analyses are incomplete even for the impurities ordinarily determined, and entirely ignore the possible presence of other impurities, such as Cu and Ni; but so far as they go, they indicate a very appreciable degree of contamination by S, Si, Mn, elements which we know exert a marked effect on the critical ranges. It may be said that the iron-carbon diagram has never been worked out with pure iron-carbon alloys. The present paper describes the preparation of a series of high degree of purity to be used as the basis of a more accurate study of the equilibrium diagram than has heretofore been attempted.

For the production of pure iron on a fairly large scale, the electrolytic refining method was obviously most suitable and was therefore adopted in this work. Pure carbon was made by calcining in a Dixon graphite crucible the pure sugar used as stock for Bureau of Standards analyzed sample No. 17. The latter contains, as the only impurity of importance for present purposes, 0.003 per cent ash, and the carbon obtained from it has an ash content of 0.17 per cent.

## MAKING THE ELECTROLYTIC IRON

The electrolytic method, using soluble anodes, has been frequently employed in similar investigations<sup>1</sup> and its essentials are well known, so that we give details only for the sake of completeness and because, in one respect, our method deviates from that usually followed, namely, in the use of porous anode compartments. The first iron was made on a small scale. The essential details of the bath are as follows: Two cylindrical anodes of ingot iron<sup>2</sup> about 2 in. in diameter by 5 in. long, contained in porous clay cups; three cathodes of sheet iron, each 4 in. square; electrolyte, 25 to 30 per cent FeCl<sub>2</sub> solution (made by dissolving the ingot iron in chemically pure hydrochloric acid), prepared as nearly neutral as possible; current density about 0.5 to 0.7 ampere per square decimeter; temperature during electrolysis approximately that of the room. No attempt was made to determine the yield or to secure high current efficiency. Good adherent deposits were obtained, the greatest thickness being about 0.5 cm. Owing to the unfavorable current distribution when working with anodes and cathodes of such unequal sizes, the thickness of deposit was not uniform all over the plates. Qualitative tests of the sludge from the anode cells showed that there

TABLE I.—PERCENTAGE COMPOSITION OF IRON-CARBON ALLOYS USED BY VARIOUS INVESTIGATORS IN DETERMINATIONS OF CRITICAL POINTS

No.	AUTHORITY	Date	C	Si	Mn	P	S
1	Carpenter and Keeling (a)	1904	0.38	0.06	Trace	0.03	0.01
2	Carpenter and Keeling	1904	1.85	0.09	..	..	..
3	Carpenter and Keeling	1904	3.98	..	..	..	..
4	Carpenter and Keeling	1904	4.50	0.12	..	..	..
5	Carpenter and Keeling	1904	2.63	..	..	..	..
6	Carpenter and Keeling	1904	2.85	..	Trace?	..	..
7	Heyn (b)	1904	2.85	0.04	0.03	..	..
8	Heyn	1904	0.95	0.04	0.06	..	..
9	Rosenhain (c)	1910	1.14	0.09	0.40	0.014	0.018
10	on Brayshaw's steel A <sub>2</sub>	1908	1.00	..	0.25	..	..
11	Benedicks (d)	1903	0.64	..	..	..	..
12	Charpy and Grenet (e)	1903	0.64	..	..	..	..
13	Charpy and Grenet	1903	0.93	..	..	..	..
14	Charpy and Grenet	1903	0.93	..	..	..	..
15	Charpy and Grenet	1903	1.50	..	..	..	..
16	Brayshaw (f) No. W <sub>2</sub>	1910	1.15	0.21	0.31	0.011 ±	0.012 ±
17	Brayshaw No. W <sub>2</sub>	1910	1.16	0.10	0.37	0.014	0.023
18	Brayshaw No. A <sub>2</sub>	1910	1.14	0.09	0.40	0.014	0.018
19	Levy (g)	1913	0.23	0.039	0.05	0.013	0.010
20	Levy	1912	0.92	0.14	0.123	0.009	0.011
21	Howe and Levy (h)	1913	0.027	..	0.26	0.005	0.024
22	Howe and Levy	1913	0.105	0.013	0.24	0.015	0.028
23	Howe and Levy	1913	0.214	0.039	0.05	0.013	0.010
24	Howe and Levy	1913	0.227	0.039	0.05	0.013	0.010
25	Howe and Levy	1913	0.235	0.039	0.05	0.013	0.010
26	Howe and Levy	1913	0.244	0.050	Nil	Nil	0.007
27	Howe and Levy	1913	0.382	0.027	0.22	..	0.004
28	Howe and Levy	1913	0.40	0.103	0.16	0.014	0.012
29	Howe and Levy	1913	0.563	0.18	0.15	0.013	0.013
30	Howe and Levy	1913	0.89	0.144	0.17	0.018	0.013
31	Howe and Levy	1913	0.73	0.141	0.07	0.012	0.019
32	Howe and Levy	1913	0.92	0.14	0.123	0.009	0.011

(a) Carpenter and Keeling, *Jour. Iron and Steel Inst.*, **65** (1904), 244; collected Researches of the Nat'l Phys. Lab., **1**, p. 227.

(b) Heyn, "Verh. des Vereins zur Beförderung des Gewerbflusses," **904**, p. 371.

(c) Rosenhain, *Proc. Inst. Mech. Eng.*, **1910**, p. 688.

(d) Benedicks, *Jour. Iron and Steel Inst.*, **77** (1908), 218.

(e) Charpy and Grenet, *Bull. Soc. d'Encouragement pour l'Industrie Nationale*, **1903**, p. 480.

(f) Brayshaw, *Proc. Inst. Mech. Eng.*, **1910**, pp. 525, 537, 656, 670.

(g) Howe, *Bull. Am. Inst. Mining Eng.*, **1913**, p. 1068.

(h) Howe and Levy, *Ibid.*, **1913**, p. 1076.

vidence," and that "much better data are needed, reached with pure materials and with the many causes of error reduced to a minimum." In Table I, compiled from Prof. Howe's papers, are given analyses

<sup>1</sup> Published with the permission of the Director of the Bureau of Standards.

<sup>2</sup> "A<sub>2</sub>, the Equilibrium Temperature for A<sub>1</sub> in Carbon Steel," *Bull. Am. Inst. Mining Eng.*, **1913**, p. 1066; "A Discussion of the Existing Data as to the Position of A<sub>2</sub>," *Ibid.*, **1913**, p. 1099.

<sup>1</sup> Lenz, *J. prakt. Chem.*, **108** (1869), 438; Cailletet, *Compt. rend.*, **80** (1875), 319; Roberts-Austen, *Jour. Iron and Steel Inst.*, **1** (1887), 71; Arnold and Hadfield, *Stahl u. Eisen*, **1894**, p. 526; Hicks and O'Shea, *Electrician*, **1895**, p. 843; Winteler, *Z. Elektrochem.*, **4** (1898), 338; Haber, *Ibid.*, **4** (1898), 410; Abegg, *Stahl u. Eisen*, **1901**, II, p. 736; Skrabal, *Z. Elektrochem.*, **10** (1904), 749; C. F. Burgess and Hambuechen, *Trans. Am. Electrochem. Soc.*, **5** (1904), 201; Maximowitsch, *Z. Elektrochem.*, **11** (1905), 52; Ryss and Bogomolny, *Ibid.*, **12** (1906), 697; Cowper-Cowles, *C. A.*, **3**, 1371; S, 3013; S, 3648; C. F. Burgess and Watts, *Trans. Am. Electrochem. Soc.*, **9** (1906), 229; Amberg, *Z. Elektrochem.*, **14** (1908), 326; Kern, *Trans. Am. Electrochem. Soc.*, **3** (1908), 103; Müller, *Metallurgie*, **6** (1909), 145 (contains bibliography); Pfaff, *Z. Elektrochem.*, **16** (1910), 217; Tucker and Schramm, *This Journal*, **2** (1910), 237; Watts and Li, *Trans. Am. Electrochem. Soc.*, **25** (1914), 529; Yensen, University of Illinois, *Bull.*, **72**, 1914.

<sup>2</sup> Analysis as follows: C, 0.016; S, 0.022; Mn, 0.029; P, 0.001; Si, 0.002; and Cu, 0.15.



was an accumulation of manganese and copper derived from anodic impurities. The porous cups therefore seemed to be of service in preventing anode impurities from migrating to the cathodes, and they were accordingly used in one of the larger baths to be described later. In another similar tank the cups were omitted. Table II shows that the cathode deposits from the bath without the cups were a little higher in copper than the others but were otherwise of similar quality. It was found that there was much oxidation of the surface layers of the electrolyte as the electrolysis went on, resulting in the production of basic salts of

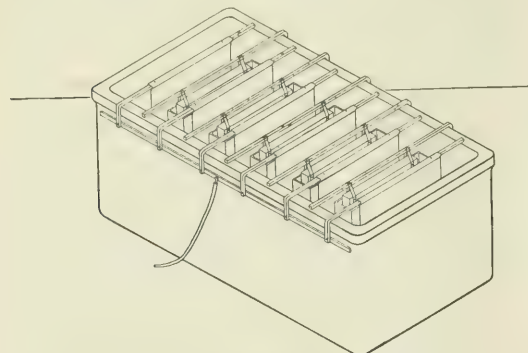


FIG. I.—TANK FOR PREPARING ELECTROLYTIC IRON

iron, which floated in the bath and which migrated to some extent to the cathodes. With the intention of avoiding or minimizing this oxidation, the small bath was provided with a hydraulically sealed cover having windows for observation and conduits for the current leads. The air in the space over the electrolyte was displaced with purified carbon dioxide and the electrolysis conducted as before. This method led to no marked improvement and it was abandoned, especially as there seemed to be a tendency toward higher percentages of carbon in the cathodic deposits. Although the greater part of the sediment settled to the bottom, the bath was never quite free from turbidity caused by these basic salts, and there is no doubt that

TABLE II.—PERCENTAGE COMPOSITION OF ELECTROLYTIC IRON FROM VARIOUS SOURCES

Source	C	S	P	Mn	Si	Cu	Ni and Co purity	Total Anal- ysis by
1(a, b).....	0.004	0.002	Trace	Trace	0.003	0.005	0.011	0.026 B. S.
2(c, b).....	0.004	0.003	Trace	Trace	0.006	Trace	0.011	0.024 B. S.
3(d, b).....	0.004	0.006	Trace	Trace	0.008	0.006	0.011	0.035 B. S.
4(e).....	0.004	0.004	Trace	Trace	0.005	0.008	0.011	0.033 B. S.
5(f).....	0.063	0.002	0.005	0.009	0.005	...	...	0.084 Müller
6(g).....	0.008	Trace	0.002	0.009	0.014	...	...	0.033 Stead
7(h).....	0.008	0.004	Trace	Trace	0.006	0.011	...	0.029 B. S.
8(i).....	0.009	0.003	Trace	Trace	0.006	0.006	...	0.024 B. S.

(a) B. S. (with porous cups).

(b) Bureau of Standards analysis of anodes from which this iron was made: C, 0.013 per cent; S, 0.020 per cent; P, 0.003 per cent; Mn, 0.025 per cent; Si, 0.003 per cent; Cu, 0.024 per cent; and Ni + Co, 0.021 per cent. (Cf. Burgess and Crowe, *Bull. Bur. Stand.*, 10 (1914), 342.)

(c) B. S. (with porous cups).

(d) B. S. (from small tank).

(e) B. S. (without porous cups).

(f) A. Müller, *Métallurgie*, 6 (1909), 152.

(g) H. C. H. Carpenter.

(h) Langbein-Pfahhauser.

(i) C. F. Burgess.

the deposits were contaminated by them in slight degree. This was of no consequence, inasmuch as these impurities were either volatilized or were reduced to iron in subsequent melting operations. The analysis of the iron stripped from cathodes of the small electrolytic bath is given in Table II. About 2 or 3 kg. were made in this bath.

The large electrolytic bath is shown in Fig. I. The anode cups were molded from a mixture of equal parts by volume of alundum cement and of clean white Ottawa sand; after careful drying in an oven the cups were burned at a temperature of 1000° to 1100° and were then found to have a satisfactory degree of porosity. The current density during electrolysis varied from 0.3 to 0.4 ampere per sq. dm. The electrolyte contained 23.3 per cent FeCl<sub>2</sub> (made from the ingot iron previously described) and 10.3 per cent NaCl, and was nearly neutral. Analyses of electrolyte from the anode and cathode compartments made after a week's run were as follows:

	PER CENT IRON Anode compartment	Cathode compartment
Original.....	9.52	7.88
After one week's run.....	8.82	7.53

The character of the deposits is shown by Figs. II and III. Deposits of 5 to 7 mm. thickness were obtained; the characteristics of these were about the same as of those made in the smaller bath. They were very hard and brittle in consequence of contamination by hydrogen. On removal from the bath and after washing with distilled water they corroded rapidly in the air. No account was taken of this surface oxidation, inasmuch as the iron was to be used for making iron-carbon alloys in such a way that the oxidized compounds of iron would be reduced to metal and the hydrogen expelled. About 12 to 15 kg. of iron were made for use in preparing the alloys. In Table II are given analyses of this iron made with and without the use of porous anode compartments, and for comparison analyses of electrolytic iron from other sources.

#### MELTING THE ELECTROLYTIC IRON

The next step for the further utilization of the electro-deposited iron is to melt it into ingots. The material as taken from the bath is brittle

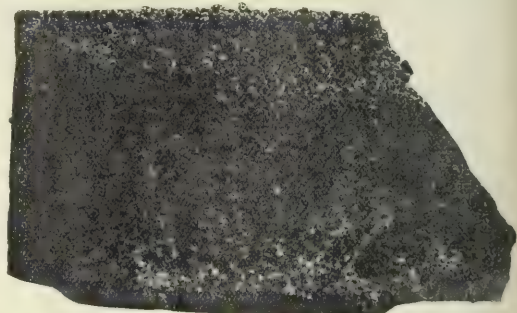


FIG. II.—CATHODE DEPOSIT

and is contaminated with occluded chlorides from the electrolyte, with hydrogen, and with oxidized compounds of iron. Annealing at 600° to 800° suffices to remove most of the hydrogen and some of the chlorides; this renders the iron more malleable and resistant to corrosion, but to attain a still higher degree of purity and to simplify subsequent operations the iron must be fused, preferably in a reducing atmosphere, and held in a state of fusion for some

minutes. Owing to the high melting point of iron ( $1530^{\circ}$ ), to its strong tendency to combine with or to be contaminated by substances likely to be present as vapors in electrically heated furnaces (Si, S, C, Pt, and the like), or as gases in the products of combustion of a fuel-fired furnace ( $\text{CO}$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ), and especially because of the corrosive action on crucibles of molten oxides of iron, with resulting possible contamination of the melt by slags, etc., it is evident that great care must be taken in the choice of furnaces and crucibles for work of this kind. While it is true that iron in the molten condition containing as little as 0.1 to 0.2 per cent of the impurities ordinarily determined has been produced commercially for some time, the conditions of laboratory preparation on a small scale are entirely different and lead to new difficulties.

1—Contamination by the hearth, or crucible material, or by gases, is less in large-scale operations, owing to the relatively smaller surface exposed compared with the weight of metal being handled.

2—Additions, such as ferro alloys, aluminum, or titanium for purification of the melt, as used commercially, are not permissible in an investigation of this kind.

3—The use of slags for protection from the products of combustion or for eliminating impurities and controlling composition in desired ways is excluded.

The importance of the conditions for melting pure iron and its alloys to secure products of very high purity does not seem

to have been recognized sufficiently in the past, and we shall therefore give full details of our methods.

#### FURNACES

**ELECTRIC FURNACES**—For ease and convenience of manipulation a furnace used for melting pure iron should maintain continuously a temperature of not less than  $1600^{\circ}$ . The temperature required eliminates furnaces wound with nickel or nichrome; molybdenum or platinum-wound furnaces are not desirable for work in high vacua, owing to volatilization of these metals with resulting contamination of the melt and destruction of the heater. Tungsten windings could no doubt be used, but no suitable furnace of this type was available at the Bureau. Our work with electric furnaces has been confined, therefore, to those employing carbon in some form as resistor. A furnace of the kryptol type, shown in Fig. IV, was constructed and has been found satisfactory. The Arsem vacuum furnace,<sup>1</sup> shown in Fig. V, was extensively used and is

very suitable for work of this character. The Helberger crucible furnace was used for melting some of our alloys. This furnace is intended to be used with conducting crucibles, but our work was done with amorphous carbon tubes as resistors. Because of the lack of protection of these from the oxidizing action of the air their life is inconveniently short. The resistance of Acheson graphite tubes was found to be too low to permit the desired temperatures to be reached. There were difficulties in securing good electrical contact between the terminals and the resistor so that this style of furnace as used by us is not to be recommended for work at  $1600^{\circ}$  or above. The difficulty common to all the types of electric furnaces used (unless the precautions mentioned later were observed) was that the melts were contaminated by volatile sulfur, silicon, or carbon derived from the resistors used. This contamination was least in the Arsem furnace when protecting the crucible, as shown in Fig. V, and was greatest in the Helberger furnace and in the kryptol furnace when using amorphous carbon as resistors.

Table III shows the amounts of contamination in-

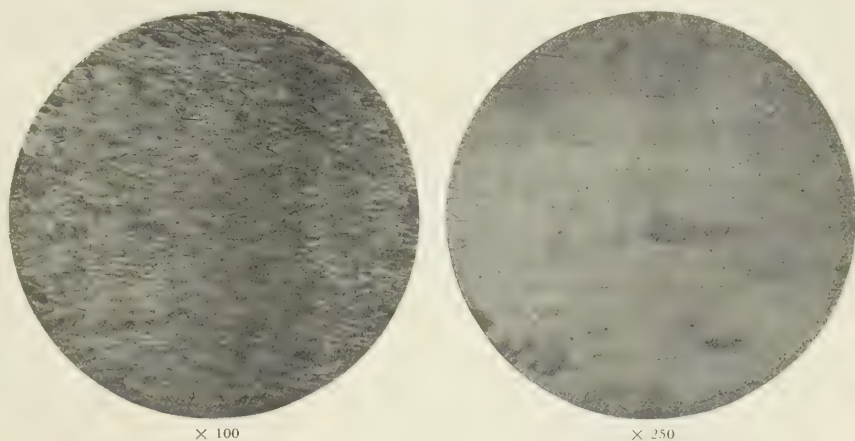


FIG. III.—ELECTROLYTIC IRON AS DEPOSITED; SECTION PERPENDICULAR TO THE ELECTRODE

roduced by melting pure iron in various types of furnaces. An analysis of the amorphous carbon used as filling material in the kryptol furnace and for the resistor tubes of the Helberger furnace showed 0.75 per cent sulfur and 0.07 per cent silica. The high

TABLE III.—PERCENTAGE COMPOSITION OF BUREAU OF STANDARDS ELECTROLYTIC IRON AFTER MELTING IN VARIOUS FURNACES

Manner of melting	C	Si	S	Mn	P	Cu
Original iron not melted...	0.004	0.001	0.004	Trace	Trace	...
In kryptol furnace filled with Acheson graphite...	0.012	0.01	0.004	Trace	Trace	...
In Helberger furnace.....	...	0.014	0.024	Trace	Trace	...
In Arsem furnace.....	0.010	0.007	0.007	Trace	Trace	0.012
In Helberger furnace and re-melted in Arsem furnace.	0.009	0.004	0.005	Trace	Trace	...
In gas furnace.....	0.012	0.003	0.02	Trace	Trace	...

sulfur in the amorphous carbon resistors is due to the use of petroleum coke in their manufacture. Analyses of the best grades of petroleum coke obtained by the Geological Survey showed percentages of sulfur ranging from 0.63 to 1.37 per cent. After having discovered these defects in amorphous carbon we discontinued its use, employing granular Acheson graphite of the best grade for the kryptol furnace, and a graphite

<sup>1</sup> W. C. Arsem, *Trans. Am. Electrochem. Soc.*, 9 (1906), 152.



spiral for the Arsem furnace. A resistor from the Arsem furnace contained 0.02 per cent sulfur and 0.03 per cent silica. The results were satisfactory. It may be concluded that if carbon resistance furnaces are intended for making melts with minimum contamination by volatile substances from the heating element, the best material available at present is first-quality graphite; and that the resistors should be carefully analyzed to insure against impurity before

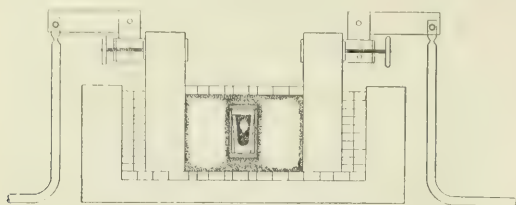


FIG. IV—KRYPTOL FURNACE WITH CRUCIBLE IN POSITION

installing them in the furnace. It is further evident that if the refractory walls of the furnace are in immediate contact with the heater, the former should be made of material not likely to react with the heated carbon. Such reaction would cause not only possible contamination of the melt, but also irregularities in the working of the furnace. For this reason ordinary fire clay or silica bricks, or any others containing silica in considerable amount, are excluded. In our own kryptol furnace commercial magnesite bricks were used, and while they were not all that could be desired they proved serviceable, provided the resistor was renewed occasionally.

**GAS FURNACES**—Two types of gas furnace, shown in Figs. VI and VII, were used and no difficulty was experienced in maintaining the necessary temperatures. The furnace shown in Fig. VI was a standard type except in respect to the blowpipe, which is similar to that used in tool forges, or for brazing purposes. A preheater raised the temperature of the necessary volume of air to about 350°. In some experiments made with this furnace pure platinum wire was melted, indicating that a temperature in excess of 1750° had been attained. The refractory lining supplied by the manufacturers was found to have a very short life under these conditions, so that we later covered it with alundum cement, or with a mixture of alundum cement and clay, which prolonged the life. The surface combustion furnace (Fig. VII) proved to be very suitable. This furnace has already been illustrated and briefly described.<sup>1</sup> The same trouble was experienced with the original refractory lining, and repairs were again made with alundum and clay. The highest temperature reached in this furnace, 1670°, was obtained when burning about 180 cubic feet of city gas per hour. In using this type of furnace for pure melts, the crucible must be protected from the large amount of very fine dust blown out of the contact material during operation.

#### CRUCIBLES

A few preliminary experiments with clay crucibles showed that it would be out of the question to use

<sup>1</sup> Lucke, *THIS JOURNAL*, 5 (1913), 801.

these for melting pure iron-carbon alloys. The clays used for making the crucibles which we tried were not sufficiently refractory and were badly corroded by the iron oxide which coats the surface of all melts made in gas-fired furnaces. This did not occur in the electric furnaces, but here the reducing atmosphere, which prevented oxidation, also caused the introduction of relatively large amounts of silicon from the clay. Alundum crucibles were tried, but gave the same trouble as those of clay. Crucibles made of electrically fused or sintered magnesia from two different sources were given a trial in the various types of furnaces, but with these also there was more contamination of the melts by silicon than seemed desirable (Table IV).

TABLE IV—PERCENTAGE COMPOSITION OF ALLOYS MADE IN CRUCIBLES OF COMMERCIAL PURE MAGNESIA

No.	METHOD OF MELTING	C	Si	S
P 27	Gas and vacuum furnaces	0.584	0.056	0.004
P 28	Gas and vacuum furnaces	0.022	0.029	0.030
P 29	Gas and vacuum furnaces	0.367	0.015	0.029
P 41	Single melt in Helberger furnace	0.886	0.024	0.013
P 39	Melted twice in Helberger furnace	0.688	0.054	0.026
P 31	Helberger and vacuum furnaces	0.210	0.032	0.020
P 32	Helberger and vacuum furnaces	0.252	0.022	0.010
P 33	Helberger and vacuum furnaces	0.094	0.041	0.024
P 35	Helberger and vacuum furnaces	0.146	0.050	0.029
P 37	Helberger and vacuum furnaces	0.088	0.050	0.039
P 40	Helberger and vacuum furnaces	0.765	0.033	0.013
P 42	Helberger and vacuum furnaces	0.058	0.070	0.016
P 36	Melted twice in kryptol furnace	0.927	0.045	0.019

As it had become evident that the desired results could not be secured with any kind of crucible on the market, we began the experiment of making our crucibles of various grades of chemically pure magnesia

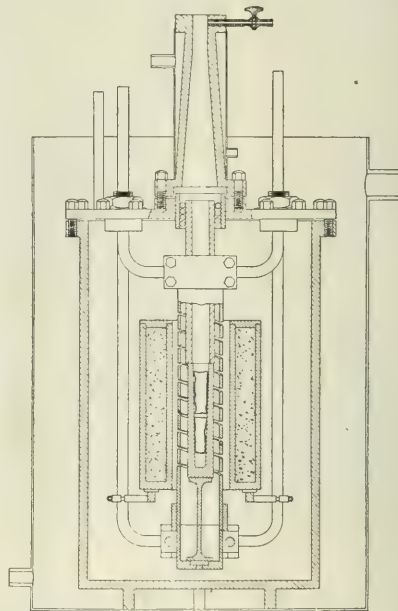


FIG. V—ARSEM FURNACE WITH CRUCIBLE AND PROTECTING TUBE IN PLACE

calined in the electric furnace at 1600° to 1800°. Although our product contained usually not over 0.05 to 0.10 per cent silica the alloys melted in crucibles made from such magnesia still carried too much silicon (see Table IV). Because of the difficulty of securing from chemical dealers magnesia suffi-

ently low in silica, the high cost of a good grade of his material, and the need of large quantities for several contemplated investigations, we decided to prepare our own material. An endeavor was made to develop a method free from too many complicated manipulations. As raw material we used two or three grades of pharmaceutical magnesium carbonate

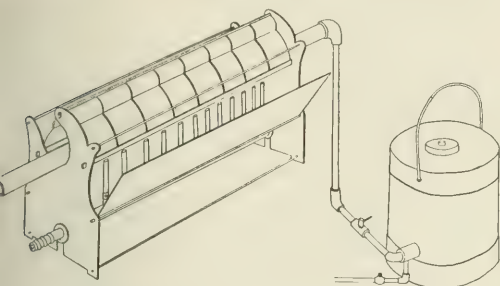


FIG. VI—SMALL GAS FURNACE WITH PREHEATER

carrying 0.1 or 0.2 per cent silica, and later a calcined Grecian magnesite with about 3.5 per cent silica. Attempts to prepare silica-free magnesia from these sources by dissolving them in hydrochloric acid, evaporating the solutions to dryness and baking, followed by solution of the  $MgCl_2$ , filtration and precipitation of magnesium carbonate by ammonium carbonate were not very successful on the scale tried, or the technique was difficult and the product unsatisfactory, as well as expensive. After trials of several other methods we developed the following procedure, which has produced a magnesium oxide carrying usually not over 0.01 per cent silica, and at low cost:

The Grecian magnesite was dissolved in commercial acetic acid (70 per cent), using a slight excess of the latter; more of the magnesite was then added until the solution was alkaline to litmus paper, after which the solution was diluted with about twice its volume of water, the whole thoroughly stirred and allowed to stand in barrels for a day or two; at the end of this time the clear solution was siphoned off into a large wrought-iron basin and rapidly evaporated over a large Fletcher burner, adding fresh liquid at intervals until a sufficient amount of the magnesium acetate had separated. The evaporation was then carried to the point where the solution solidified on cooling, after which the decomposition of the acetate into oxide was effected by directing the flame from a large Teclu burner over the surface of the separated salts. The magnesium oxide so obtained is contaminated by carbon, undecomposed acetate, and a little iron, but after calcining is quite suitable for use in making crucibles. The calcining was done in large gas furnaces which gave a temperature of from  $1550^{\circ}$  to  $1650^{\circ}$ . The magnesia, as taken from the iron basin, was moistened slightly with water and made up into large balls, which were placed inside an ordinary No. 20 plumbago crucible coated on the inside with alundum cement, or lined with an Acheson graphite crucible. The crucible was carefully covered during the calcining operation, which

lasted about two hours. As a result of this treatment the magnesia had shrunk to about one-third its original volume, all the carbon had burned out, and the silica content was very slightly increased. We found it important to blow air through the furnace for several minutes after shutting off the gas, in order to remove the last traces of products of combustion carrying sulfur. If these are allowed to remain in the furnace during the cooling period, the magnesia takes up some sulfur; our best material contained less than 0.01 per cent of this element. Calcining in the gas furnace at the temperature named gives a product which still shrinks a little when used in crucibles heated to higher temperatures, but we had no serious trouble with crucible failures on this account.

Two sizes of crucibles were used which, together with the molds employed for making them, are shown in Fig. VIII. The calcined material was mixed with about 10 per cent by weight of uncalcined magnesia and the whole wet with water until it formed a pasty

TABLE V—PERCENTAGE OF SILICA IN MAGNESIA FROM DIFFERENT SOURCES

SOURCE	$SiO_2$
Calcined Grecian magnesite	3.15 and 4.61
University of Illinois electrically calcined $MgO$	1.99
Magnesium aluminate tube	5.39
$MgO$ reagent (uncalcined) A	0.03
$MgO$ reagent (uncalcined) B	0.07
Bureau of Standards $MgO$ prepared from acetate	0.008
Bureau of Standards $MgO$ calcined in gas furnace	0.013 and 0.017
Crucible made from Bureau of Standards calcined $MgO$	0.025

mass. The thin brass cups used for lining the molds were put in place and there was introduced into the mold a sufficient amount of the material (ascertained by preliminary trials); a pressure of 5,000 to 10,000 pounds per square inch was applied to the head of the plunger and kept there a minute or two after the plunger had been driven down as far as it would go. The mold was then opened by removing the rings, the

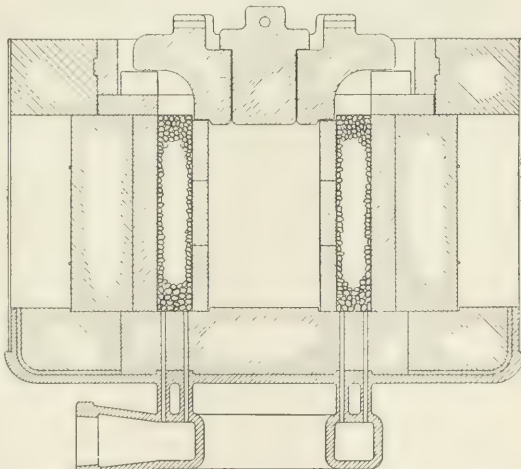


FIG. VII—SURFACE COMBUSTION CRUCIBLE FURNACE

brass cup carrying the crucible removed, and the plunger taken out. The crucibles were dried at  $100^{\circ}$  to  $120^{\circ}$  for a day and the brass cups stripped off by melting the solder from the joints. They were then either used directly for melts, or after heating to  $1200^{\circ}$  to  $1600^{\circ}$  in a gas or electric furnace. The



latter procedure is necessary for all crucibles that are to be used in vacuum furnaces.

#### PROCEDURE IN MAKING ALLOYS

We first attempted to make ingots in the following manner:

The iron as stripped from the cathodes was dried, broken into small pieces, and placed in one of the larger magnesia crucibles (Fig. VIII), together with a suitable quantity of carbon. These were brought gradually to temperatures above the melting point of iron and left in the furnace for 10 or 15 minutes. After cooling,

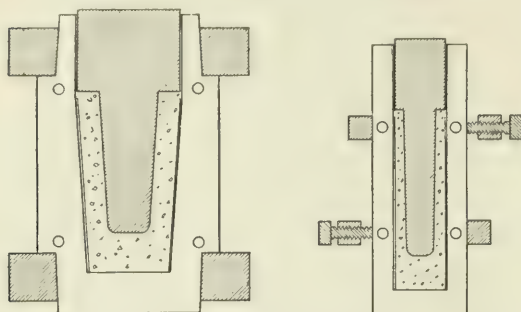


FIG. VIII—CRUCIBLE MOLDS

the crucibles were removed and broken away from the ingots. This procedure, while apparently wasteful, was necessary for several reasons: (1) Magnesia crucibles are extremely fragile at high temperatures and any attempt to handle them results in breakage with resultant loss of melts; (2) with the small mass of metal which we used (100 g.) it would be impossible to pour successfully; and (3) even if it could be accomplished, pouring would be objectionable because of the added danger of contamination. Moreover, the loss of the crucible is not serious, since the material can be recovered and worked up into new crucibles repeatedly.

The ingots obtained in the manner above described were found to be very unsound and full of blowholes; in this respect there was little difference between those made in the various furnaces. This seemed surprising in view of the difference in atmosphere over the melt in a gas furnace, where the conditions are oxidizing to iron, and in an electric furnace, where carbon dioxide, water vapor, or oxygen—the gases which would oxidize iron at high temperatures—are present only in very small amounts. It would thus appear that the blowholes in iron may be caused by carbon monoxide as well as by any or all of the other gases named, and that the maintenance of a reducing atmosphere is no guarantee of freedom from blowholes. That the melts made in the kryptol furnace were made under reducing conditions is evident from Fig. IV, which shows that the crucibles are completely covered with carbon at all times; this is further evident from an oxygen determination made on drillings from an ingot melted in the kryptol furnace. The percentage of oxygen in this ingot, notwithstanding the fact that no deoxidizer had been used, was 0.03.<sup>1</sup> The weight of these ingots was about 100 g.

<sup>1</sup> We are indebted to J. A. Aupperle, metallurgist of the American Rolling Mill Co., for this analysis.

Fig. IX(a) is a photograph of a split ingot, showing the unsound structure.

The introduction of a regulated amount of carbon into the alloys gave a good deal of trouble. In the gas furnace the amount of oxidizing gases was so great, relative to the weight of carbon introduced, that the latter was all burned out before the melting operation was completed, even when special precautions were taken to protect the crucibles. These difficulties were finally overcome by using the following procedure which has been fairly satisfactory: The electrolytic iron was first melted down in the larger crucibles in a gas or electric furnace. The ingots of pure iron so made were sawed into longitudinal strips of convenient size for insertion into the smaller magnesia crucibles (Fig. VIII) and the necessary amount of carbon was added. The crucible was placed in the vacuum furnace with the protecting chimney in place as shown in Fig. V. The furnace was evacuated to 0.2 mm., and the current through the heater was increased gradually until the iron had melted and dissolved the carbon; this point was determined by observation through the window. As soon as this stage was reached a violent ebullition took place; sometimes the contents of the crucible were ejected. We attribute this principally to the expulsion of gases from the cavities in the ingots. In 10 or 15 minutes the surface of the melt became quiescent and the operation was ended. After cooling, the ingots were removed by breaking the crucibles.

Fig. IX(b) shows the sound structure of these ingots, which were usually entirely or nearly free from blowholes. After discarding the surface down to clean metal, the ingots were turned down to the size required for the thermal test specimens, Fig. IX(c), re-

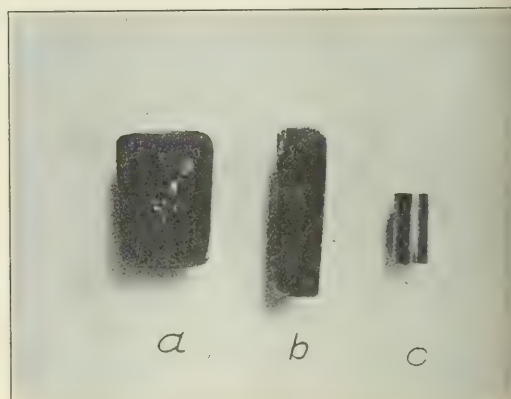


FIG. IX—SPLIT INGOTS AND TEST SPECIMEN

taining the chips for analysis. Complete analyses of typical samples are given in Table VI. For comparison, Table VII is given, showing the results of attempts by two earlier workers to make pure iron-carbon alloys.

We are now building a larger vacuum furnace for producing large ingots of pure iron and iron-carbon alloys, which will be examined either as made or after forging, rolling, and application of heat treatment

to physical properties, magnetic and electrical characteristics, resistance to corrosion, and related properties. Reports of progress in this work will be issued as they are justified. Later we shall deal with the effect of alloying elements other than carbon on the properties of iron.

TABLE VI—PERCENTAGE COMPOSITION OF TYPICAL BUREAU OF STANDARDS IRON-CARBON ALLOYS

C	Si	S	P	Mn	Cu	Ni and Co	Total
0.084	0.007	0.009	Trace	Trace	0.020	0.011(a)	0.047
0.376	0.013	0.009	Trace	Trace	0.005	0.011(a)	0.038
0.395	0.008	0.013	Trace	Trace	0.012	0.011(a)	0.044
0.597	0.010	0.008	Trace	Trace	0.004	0.011(a)	0.033
0.624	0.004	0.010	Trace	Trace	0.008	0.011(a)	0.033
0.692	0.006	0.011	Trace	Trace	0.008	0.011(a)	0.036
0.860	0.006	0.006	Trace	Trace	0.007	0.011(a)	0.030
1.087	0.006	0.006	Trace	Trace	0.013	0.011(a)	0.036
1.797	0.010	0.005	Trace	Trace	0.018	0.011(a)	0.044
2.240	0.005	0.005	Trace	Trace	0.020	0.011(a)	0.041
2.560	0.005	0.005	Trace	Trace	0.014	0.011(a)	0.035
3.27	0.006	0.006	Trace	Trace	0.016	0.011(a)	0.039

(a) The figures given for nickel and cobalt do not represent individual determinations for each specimen since the amount of sample was sufficient to allow of these being carried out. Four representative analyses of pure iron and iron-carbon alloys having given the result indicated, it is assumed that these elements were present in that amount in all the samples.

TABLE VII—DEGREE OF CONTAMINATION (PERCENTAGES) OF IRON MELTS MADE BY OTHERS

	C	Si	P	S	Mn
Miller's electrolytic iron	0.0630	0.0053	0.0045	0.0024	0.0090
Miller's electrolytic iron after re-melting in <i>vacuo</i> in "pure MgO crucible" (a)	0.017	0.089	0.028	0.037	0.025
F. Burgess' electrolytic iron	0.009	0.006	0.001	0.010	Trace
F. Burgess' electrolytic iron melted with sugar carbon in magnesia crucible by Howe (b)	2.954	0.040	0.050	0.035	None

(a) A. Müller, *Metallurgie*, 6 (1909), 159.

(b) Howe, *Bull. Am. Inst. Mining Eng.*, 1913, p. 1118.

#### DISCUSSION OF THE SOURCES OF CONTAMINATION

**SILICON**—In our earlier experiments, where we were obliged to make crucibles of magnesia higher in silica than at produced by the acetate method already described, we noted that occasionally an alloy of very low silicon content would result from a melt made in a crucible relatively high in silica. The use of our purified magnesia had eliminated all trouble from silicon contamination in melts, but we later decided to make some experiments to determine the relationship between the introduction of silicon and temperature of melting. For this purpose a series of runs was made in the vacuum furnace varying independently the temperature of melting and the silica content of crucibles. One per cent of carbon was added to all these melts since in the presence of carbon there is additional likelihood of contamination of silica at high temperatures. The results in Table VIII show that if the temperature is not allowed to rise much above 1600°, crucibles containing as much as 0.9 per cent silica may be used safely. This is of importance when a great deal of work is being done, for it enables one to use repeatedly the same crucible material until the silica becomes dangerously high.

TABLE VIII—FACTORS GOVERNING CONTAMINATION OF MELTS BY SILICON

Temperature of melting (degrees)	SiO <sub>2</sub> in crucible melt Per cent	Si in sample melt Per cent	Temperature of melting (degrees)	SiO <sub>2</sub> in crucible melt Per cent	Si in sample melt Per cent
1610	0.57	0.007	1720	1.27	0.040
1610	0.67	0.007	1780	1.20	0.042
1610	0.75	0.007	1770	0.19	0.007
1610	0.91	0.006	1720	0.24	0.006
1610	1.14	0.015	1760	0.31	0.021
1610	1.66	0.023	1740	0.60	0.031
1650	1.35	0.032			

**SULFUR**—As has been shown, contamination by sulfur may result from the use of gas furnaces or of petroleum coke carbon in electric furnaces. On abandoning the use of gas furnaces and employing

Acheson graphite as resistor material this difficulty disappeared, as is apparent from a comparison of Tables V and VII.

**MANGANESE AND PHOSPHORUS**—Both these elements have been reduced to mere traces (less than 0.001 per cent) in all our alloys.

**COPPER**—This impurity, one of the most difficult to guard against, is present in objectionable quantities in some of our melts and to some extent in all. The ingot iron used for anodes contains copper which is not completely removed in the electrolytic refining process, so that our deposits contain about 0.005 per cent of this element. This copper persists through the melting operation, and unless great care is taken, more is introduced, owing to the use of copper connections in furnaces. In particular, the copper blocks used in the vacuum furnace must be smooth and make good contact with the graphite heater, since any arcing causes the vaporization of considerable quantities of copper with resulting contamination of the melt.

**NICKEL AND COBALT**—Our anode iron contains 0.02 per cent (Ni + Co); in the electrolytic refining this is reduced to 0.01 per cent which persists through the melting operations.

**MAGNESIUM**—As all our melting was done in magnesia crucibles it was thought desirable to look for this element as a possible impurity. Several analyses of ingots made in the regular way showed that Mg was not present in any determinable quantity. A rather interesting result, however, was obtained on analyzing some ingots which had been melted at high temperatures (over 1700°). It was found that these contained appreciable amounts of Mg (from 0.005 to 0.01 per cent). Furthermore, the samples were so brittle that the pieces broke while turning in the lathe. It appears at least possible that there may be a direct connection between the two circumstances, though our present data are not sufficient to justify a definite conclusion to that effect.

**OXYGEN**—Unfortunately, the Bureau is not at present prepared to make accurate oxygen determinations on this class of material, but it is hoped later to publish analyses of some of the alloys for this element, if it is found to be present. In our method of preparation, starting with an ingot already low in oxygen and carburizing in a vacuum furnace where the carbon monoxide resulting from interaction of oxides or oxygen with carbon would be removed as formed, the deoxidation would tend toward completion, and accordingly the alloys should contain but small residual amounts of oxides and oxygen.

#### SPECTROSCOPIC EXAMINATION

In order to confirm the results of the chemical analyses for small quantities of impurities, the arc spectra of a number of samples of iron and iron-carbon alloys were studied by Dr. K. Burns<sup>1</sup> of this Bureau, to whom we are indebted for the data given below:

**MAGNESIUM**—The spectra fully confirmed the chemical tests. Line 2851.1 Å showed strong in two samples containing 0.007 and 0.010 per cent Mg while it was very faint or absent in

<sup>1</sup> For an account of the methods used, cf. K. Burns, *Bull. Bur. Stand.*, 12 (1916), 179-196.



unfused irons and in alloys which failed to give magnesium by the chemical method.

**SILICON**—Line 2881.5A showed presence of silicon in the alloys, but unfused iron showed no traces.

**MANGANESE**—Several manganese lines show in various samples of electrolytic iron that have been melted. These lines are absent from the spectrum of unmelted electrolytic iron. The faintness of the manganese lines as compared with those given by a specimen containing 0.01 per cent of this metal indicate a very low manganese content.

**CHROMIUM**—The statements made in regard to manganese also apply to chromium.

**COPPER**—Lines 3247.7 and 3274.1A are always present though so faint as to be questionable in unmelted specimens.

**NICKEL AND COBALT**—Several nickel and cobalt lines show faintly in the various samples.

In the course of the examination of the arc spectrum of pure iron several faulty identifications have been corrected.

2795.542 ascribed to magnesium is iron;

3369.555 ascribed to nickel is iron and nickel;

3412.347 ascribed to iron is probably cobalt; and

3443.645 ascribed to iron is no doubt cobalt.

No attempt has as yet been made to clear up all the doubtful identifications in the iron spectrum; the above list is given to show the possibilities in this direction which may be realized by means of the use of pure iron.

#### METHODS OF CHEMICAL ANALYSIS

The analyses recorded in this paper were carried out according to well-known principles with suitable precautions, and the methods are given below merely for reference.

The chips obtained when making the thermal test specimens were thoroughly mixed before weighing portions for analysis. Chips from high-carbon alloys which contained admixed graphite were finely ground and mixed before weighing.

**CARBON** was determined by the barium-carbonate titration method devised by one of the authors.<sup>1</sup> The chips (1 to 5 g.) were burned in purified oxygen, passing the products of combustion into a solution of barium hydroxide; the barium carbonate was filtered and washed in an atmosphere free from carbon dioxide (see the original for details of apparatus used), and the barium carbonate was titrated against standard hydrochloric acid, using methyl orange as indicator.

**SULFUR** was determined by dissolving 5 g. of the metal, contained in an appropriate evolution apparatus having all ground-glass connections, in concentrated hydrochloric acid, the gases given off being passed into an ammoniacal solution of hydrogen peroxide. After complete solution of the metal the contents of the evolution flask were boiled for 10 minutes while a slow current of purified hydrogen was passed through the solution. The ammoniacal peroxide solution was transferred to a beaker and boiled a few minutes, then the solution was slightly over-neutralized with hydrochloric acid and the sulfur precipitated at boiling temperature as barium sulfate. After digestion for a sufficient length of time the precipitate was filtered, washed, ignited and weighed, and the percentage of sulfur calculated.

**SILICON**—Five to 10 g. of metal were dissolved in an Erlenmeyer flask in hydrochloric acid (equal volumes of water and hydrochloric acid of specific gravity 1.20), the solution evaporated to dryness and the flask heated on the hot plate at about 200° for an hour. The residue was digested with hydrochloric acid of the same strength as that used for dissolving; the insoluble matter containing the silica was filtered off, washed with dilute

hydrochloric acid and water, ignited in a platinum crucible and weighed, after which the silica was volatilized with hydrofluoric acid and its amount determined from the change in weight of the crucible after again igniting. The results were then calculated to silicon.

**PHOSPHORUS**—The usual method of precipitation as ammonium phosphomolybdate was employed, and the phosphorus estimated by comparing the volume of the precipitate with that produced by treating a standard steel in the same way.

**MANGANESE**—The sodium bismuthate method was used.

**COPPER**—Ten to 20 g. of metal were dissolved in a slight excess of hydrochloric or sulfuric acid, and hydrogen sulfide passed into the hot solution until all the copper was precipitated. The precipitate was filtered off, and, after washing the paper carrying it, was transferred to a porcelain crucible, and the whole ignited until all the carbon was burned off. A little potassium bisulfate was added and the copper oxide brought into solution by fusion, following by leaching with water and filtration. The solution was compared with a standard solution colorimetrically, either by an ammonia or ferrocyanide method, or by both.

**MAGNESIUM**—Ten to 20 g. of metal were dissolved in aqua regia, the solution evaporated to dryness, and dehydrated. The residue was dissolved in 1 : 1 HCl and silica removed by filtration. The iron was extracted by the ether method. After the removal of the iron, hydrogen sulfide was passed through the solution (acidified with acetic acid) to precipitate copper, etc. Manganese and residual iron were removed from the filtrate by bromine and ammonia and the magnesium precipitated as magnesium-ammonium phosphate. The accuracy of the above procedure was checked by running duplicates to which small amounts of a magnesium salt had been added.

**NICKEL AND COBALT**—The solution of 10 g. of the iron in  $\text{HNO}_3 + \text{HCl}$  was evaporated to dryness, dehydrated, taken up with HCl of 1.1 specific gravity, filtered, the filtrate evaporated to a small volume, and the iron removed by the ether method. Copper was precipitated with hydrogen sulfide, and the iron and manganese in the filtrate were precipitated by ammonia and bromine. The filtrate was acidified with acetic acid, and nickel and cobalt were precipitated as sulfite from the boiling solution. The two metals were either weighed as oxides or deposited electrolytically from ammoniacal solution, the two methods giving concordant results. The oxides (or metals) were dissolved in hydrochloric acid, the solution was neutralized, and finally made acid with acetic acid and the cobalt precipitated as  $\text{K}_2\text{Co}(\text{NO}_2)_6$ . After filtering and igniting this precipitate at a low temperature, the cobalt was dissolved, reprecipitated with hydrogen sulfide, and finally weighed as  $\text{CoSO}_4$ . The nickel was determined by the dimethylglyoxime method in the filtrate from the cobalt. The sum of these determinations checked very closely with the total (Ni + Co) found directly.

#### SUMMARY

Methods have been developed for producing laboratory samples of iron-carbon alloys, of a very high degree of purity; sources of contamination of melts and means of eliminating them have been described; a method for producing magnesia of a satisfactory degree of purity for making crucibles to be used in work of this kind has been developed; a procedure for making small ingots, which are sound and free from blowholes, without the use of deoxidizers has been worked out. A series of iron-carbon alloys containing 99.96 per cent of the two elements has been prepared, to serve as a basis for the redetermination of the iron-carbon equilibrium diagram.

BUREAU OF STANDARDS  
WASHINGTON, D. C.

<sup>1</sup> J. R. Cain, "Determination of Carbon in Steel and Iron by the Barium Carbonate Titration Method," *Technologic Paper No. 33* of the Bureau of Standards.

# RECOVERY OF GALLIUM FROM SPELTER IN THE UNITED STATES

By W. F. HILLEBRAND AND J. A. SCHERRER

Received February 5, 1916

Some months ago a few grams of gallium of American production were received by one of us (S.) from Mr. F. G. McCutcheon, Chemist of the Bartlesville Zinc Company, Bartlesville, Oklahoma. Recently the other (H.) received 50 g. more from Mr. McCutcheon.

The first material contained a little indium and a trace of calcium, as determined spectroscopically by Dr. K. Burns at the Bureau of Standards. The second lot is of similar composition, presumably. A yet incompletest test by one of us (H.) indicates an indium content probably of less than one percent.

The metal or alloy is a liquid resembling mercury in appearance, but it wets glass and porcelain and adheres so tenaciously that if agitated in a glass vial the contents can be seen only as a coating on the walls. This latter property is not in evidence if the metal is covered with hydrochloric or sulfuric acid.

Although gallium melts at about 30°, it is said to remain liquid far below this temperature, indefinitely when less inoculated with solid gallium.

Inquiry of Mr. Kurt Stock, Superintendent of the Bartlesville Zinc Company, brought out some exceedingly interesting information, as shown by the following extracts from his letter of reply, dated October 21, 1915:

"His attention [Mr. McCutcheon's] was drawn to peculiar sands and drops, in appearance like mercury, which seemed to be made of zinc-lead dross plates after these had been exposed to the weather for a time. Mr. McCutcheon, with the help of his two assistants, made a great number of tests, proving the material to be an alloy of gallium and indium with small amounts of zinc \* \* \* \* \*"

"Your hope that a new source of supply for both metals has been opened up, with the prospect of continued manufacture, is not shared by me, as the conditions leading to the concentration of gallium and indium are very unusual and are based on the normal state of the spelter market. You are aware that the present demand for high-grade spelter has led zinc smelters to the practice of redistillation, and it is the final leady residue from such continued redistillation that carries gallium in noticeable quantities \* \* \* \*. We are not at all sure which of the large variety of ores is responsible. Gallium is not found in all dross and where it is found it does not occur continuously \* \* \* \* \*"

"That the amount in the original ores must be extremely small can well be realized when you consider that the residue from the continued distillation of about 12,000 lbs. of spelter weighs about 60 lbs., and represents our raw material from which we can obtain a few grams of the alloys. However, we have at present about 45 tons of dross on hand, which we suspect carries gallium."

"A very interesting feature is that both gallium and indium are volatile at the temperature prevailing in our ore furnaces, where a maximum of 1350° C. is reached for only a few hours, and they resist distillation if kept for three weeks and longer at that temperature at which we operate our redistilling furnaces, namely about 1000° C."

"Please be assured that we shall leave nothing untried to save these rare metals, but do not get impatient if results are not forthcoming for a while \* \* \* \* \*"

"You may use this very general information any way you desire."

It will be of interest to determine if this metal, hitherto such a rarity, possesses qualities of value in itself or when combined in small amounts with other metals, and if it has such, whether their importance will justify continued production after the price of spelter falls.

So far as known to us, the only uses for gallium that have been so far suggested are in alloy with aluminum as cathode material in metal vapor lamps<sup>1</sup> and for the production of optical mirrors. The fact that it wets quartz would seem to negative the suggestion that it might be suitable in quartz thermometer tubes for measuring temperatures too high for glass instruments. The authors would gladly receive further suggestions.

Also of interest is the particular source of this gallium. Mr. Stock assures us that it comes from domestic ores, probably from certain as yet undetermined ones of Joplin. Its presence has been reported in the past in a number of domestic blends, including one from Joplin. A very recent statement from Mr. Stock is to the effect that the dross produced of late shows no gallium and that the amount of gallium at first thought to be available will not come up to expectations: "I am more convinced than ever that gallium will remain a rarity and that a commercial production is out of the question."

Since the foregoing was written, spectroscopic tests have been made at the Bureau of Standards by Dr. K. Burns upon seven samples of zinc ore kindly supplied by Mr. S. M. Rodgers of the American Steel and Wire Company. Germanium was also included in the metals looked for. The data concerning the precise sources of some of the ores tested are unfortunately meager, particularly with respect to Nos. 2, 4 and 7, but the presumption is strong that No. 4 came from the Joplin district. Of special interest is the fact that this ore showed more of both gallium and germanium than any of the others. The tests obtained by Dr. Burns follow, accompanied by his comments:

SPECTROSCOPIC TESTS OF ZINC ORES				
No.	KIND AND SOURCE OF ORE	Germanium	Gallium	
1	Sulfide—Sunset, Idaho.....	Moderate	Moderate	Moderate
2	Sulfide—Australia.....	Not found	Moderate	Moderate
3	Sulfide—Frisco, Idaho.....	Weak	Moderate	Moderate
4	Sulfide—Missouri.....	Strong	Strong	Strong
5	Carbonate—Monarch, Leadville.....	Absent	Moderate	Moderate
6	Carbonate—Doctor Mine, Almont, Colo.....	Moderate	Not found	Not found
7	Carbonate—Utah, Nevada.....	Very weak	Rather weak	Rather weak

"By means of the carbon arc the spectrum was examined in the region 2800 Å to 3600 Å. Large amounts of iron were present in all these samples. This makes the determination of indium by our method not very accurate, as the most sensitive lines of indium coincide either with carbon lines or with iron lines. It is certain, however, that indium is not present in these ores in quantities approaching one-tenth of the gallium found in ores marked 'moderate.'"

BUREAU OF STANDARDS, WASHINGTON, D. C.

<sup>1</sup> T. W. Vogel, *Zentralblatt*, 1910, I, 703. German patent.



## A PROPOSED METHOD FOR THE PROFITABLE UTILIZATION OF WASTE SULFITE LIQUOR

By HERMAN V. TARTAK

Received December 23, 1915

The utilization of the waste liquors resulting from the manufacture of paper pulp by the sulfite process is a problem that has received as much careful attention and systematic study perhaps as that of any other waste product of the present day. The technical literature contains reports of many exhaustive investigations on different phases of this problem. Over 150 patents have been secured for utilizing the waste sulfite liquor. In spite of all this experimental work, however, this material is still classed as a waste. Considering the amount, it is one of the most valuable waste materials known to industrial chemistry.

Most of the paper mills get rid of the waste liquor by emptying the same into streams. An estimate of the quantity of this material discharged annually into the streams of this country is given in the following table taken from Water-Supply Paper 226 of the United States Geological Survey:

AMOUNT OF SULFITE WASTE LIQUOR DISCHARGED INTO STREAMS OF THE UNITED STATES DURING 1906

	Million gallons
Maine.....	560,000,000
Massachusetts.....	45,000,000
Michigan.....	175,000,000
New Hampshire.....	380,000,000
New York.....	1,000,000,000
Ohio.....	41,000,000
Oregon.....	52,000,000
Pennsylvania.....	217,000,000
Virginia.....	84,000,000
West Virginia.....	89,000,000
Wisconsin.....	540,000,000
All other states.....	44,000,000
	3,227,000,000

When one takes into account that of this enormous quantity of liquor discharged annually into streams there is 10 per cent by weight, or more than 2.5 billion lbs. of solid matter, largely organic, it must be conceded that its disposal is a problem of no small magnitude. In fact, the pollution of streams in this manner is one of the most serious water pollution problems confronting this and several foreign countries. "The seriousness of the problem is the direct result of two factors—the tremendous volume of such waste liquors and their high content of organic matter of extremely undesirable character."

Besides the usual objections to the addition of organic matter to streams, some of the paper mills of Oregon and other western states have met with the further objection that the sulfite liquor may be toxic and poisonous to fish. This latter objection is an important one when the waste liquors are discharged into streams where the salmon canning industry has reached considerable proportions.

At the suggestion of the Crown Willamette Paper Company of Portland, Oregon, Professor Charles Marchand, of the Pernot Laboratories of the same city, decided to devote some of his time and attention to the utilization of waste sulfite liquor. He began work during the summer of 1914 and carried out his investigations intermittently for some months. He finally succeeded in devising a process which, from small laboratory tests, indicated that it is possi-

ble to make alcohol profitably from the waste liquor and also to detoxicate the liquor so that it is not harmful to fish after it is diluted somewhat with water. The paper manufacturing company mentioned above desired to try the process on a scale sufficiently large that the results obtained would give some idea of its actual commercial value. The requirements specified by internal revenue laws regulating alcohol distilleries, however, are such that an experimental distillery could not be arranged for by the parties concerned without much inconvenience and considerable expense. The federal laws do accord to the agricultural experiment stations special privileges which make the establishment of an experimental distillery a comparatively simple matter. For this reason, the agricultural experiment station of this state was requested to take part in the work and establish what is known under the federal laws to be an "agricultural experiment distillery" for making alcohol for denaturation only.

Because of the great importance of the problem to this state and this country in general, the experiment station authorities decided to take up the work. An "agricultural experiment distillery" with proper stills, fermenting vats, etc., for handling 500 gallons of liquor, was established at the plant of the Crown Willamette Paper Company at Oregon City, Oregon, and Professor Charles Marchand, Mr. Vance P. Edwardes and the author undertook the necessary experimental work. Practically all of the details of the experiments were carried out by Professor Marchand and Mr. Edwardes, the writer having charge of the experimental plant and acting largely in an advisory capacity. The following is a brief description of the process used in the experiments:

The amount of sulfurous acid, free and combined, in the waste liquor is first quantitatively estimated by acidifying a known quantity of the liquor with sulfuric acid and then distilling the sulfur dioxide into a definite quantity of sodium hydroxide and finally titrating the excess of alkali. A determination of reducing sugar is also made, after the removal of tannin, by the usual reduction method with Fehling's solution. Sufficient diluted commercial sulfuric acid (the concentrated acid diluted 1 to 3) is then added to the liquor taken for treatment to be the reacting equivalent of the free and combined sulfurous acid present. This will give an excess of sulfuric acid because a portion of the sulfurous acid in the liquor is present as free acid.

The liquid is then evaporated, preferably *in vacuo*, to half its volume at a temperature not exceeding 85° C. A temperature higher than this may destroy some of the fermentable sugar. By this evaporation all but a trace of the sulfurous acid is removed. The sulfur dioxide driven off by the evaporation may be passed into milk of lime and magnesia to prepare new cooking acid.

The last trace of sulfurous acid remaining in the evaporated liquor is transformed into sulfuric acid by means of an oxidizing agent. This is a very vital step in the process because it finally effects the com-

lete removal of sulfur compounds which are anti-ferments. Potassium permanganate seems to be one of the cheapest materials which can be used for this process.

After the oxidation of the remaining sulfurous acid is accomplished, the liquor is then neutralized with calcium hydroxide, using litmus paper to indicate the point of neutrality. Great care should be taken not to add an excess of the milk of lime; the liquid is next allowed to cool and is drawn off from the calcium sulfate, which settles out, into the fermenting tank.

The concentrated liquor contains, as a rule, about 70 per cent of fermentable sugar. Finally ordinary brewers' yeast is added and the fermentation is carried on for 40 to 60 hours at a temperature around 17° C. During the fermentation the liquid is agitated (or a little air is forced through it) to favor the process; the former method is preferable, because in the latter there is some loss of alcohol.

Finally, the alcohol is distilled off in the usual manner by means of a continuous still.

Several experiments were carried out by the above described process making some variation with the length of the time of fermentation, the acidity of the liquor fermented and the concentration of the liquor. The results of these experiments are summarized in Table I.

The figures for dextrose are somewhat high. Under

about 48 hours. In some of the experiments a small portion of the liquor was allowed to ferment over 100 hours without any further production of alcohol.

The treatment of every 500 gallons of liquor required about 23 lbs. of sulfuric acid and 0.5 ounce of potassium permanganate. The apparent percentages of fermentable sugar in the liquor before and after concentration indicate that the digestion with sulfuric acid increases the quantity of fermentable sugar; there seems to be no other way of accounting for the increase in sugar during the concentration of the acidified liquor. The yield of alcohol was somewhat low considering the theoretical yield. The low yield was undoubtedly due to volatilization permitted by the imperfectness of the apparatus used. The writer believes that a yield of 1 per cent of absolute alcohol could be obtained with a properly constructed and controlled plant.

A few tests, made to ascertain the quantity of sulfur dioxide removed by the sulfuric acid treatment, indicated that the quantity of sulfur dioxide liberated was approximately 0.8 per cent of the original liquor.

The solids of the liquor are reduced nearly 30 per cent by the above described process and the liquor remaining after the distillation of the alcohol is, when somewhat diluted, apparently not noticeably toxic

TABLE I—RESULTS OF FERMENTATION EXPERIMENTS WITH THE TREATED WASTE SULFITE LIQUOR

EXPT. No.	Gallons of liquor treated	Gallons of liquor after treatment	Per cent concentration	Gallons of concentrated liquor after fermentation	Fermentation period, Hours	Fermentation temp., ° C.	PER CENT FERMENTABLE SUGAR			Percentage by volume from original liquor YIELD OF ALCOHOL		
							In original liquor	In concentrated liquor before fermentation	after fermentation	Per cent of sugar fermented	Abs. alc.	Theoretical yield abs. alc.
1.....	490	200	40.8	?	?	?	2.80	5.75	2.71	3.04	(a)	(a)
2.....	1270	432	34.0	394	60-72	23.3-25.5	1.70	5.40	2.60	2.80	(b)	(b)
3.....	488	245	50.2	181	36-56	18.3-24.0	3.33	6.66	3.43	3.23	0.80	0.84
4.....	505	253	50.1	181	40-50	22.2-24.4	2.98	7.47	3.19	4.28	0.76	0.80
5.....	552	237	43.0	186	36-46	20.0-22.2	2.91	6.88	2.30	4.58	0.79	0.83
6.....	515	259	50.3	200	45-55	23.3-25.0	3.02	7.66	2.44	5.22	0.86	0.90

(a) The distillation was lost because of imperfect apparatus. (b) Acetic acid fermentation set in before distillation.

the conditions which prevailed the experimental work had to be accomplished in a limited time and consequently in making the determination of fermentable sugar the tannin was not removed previous to the reduction with the Fehling solution. Since the tannin also reduces Fehling's solution, the results are a fraction of a per cent too high. The results are comparative, however, and that is all that is claimed. In Experiments 1, 2, 3 and 4, the fermentation was carried out under very slightly alkaline conditions, while in 5 and 6 the treated liquor was slightly acidified. The results obtained indicate that the fermentation proceeds much better under slightly acid conditions. The proper conditions may be obtained by adding 1 part of sulfuric acid to 1000 parts of the liquor obtained from the neutralization with lime.

The liquor is easily fermented after treatment; the process appears to effect the complete removal of the sulfur compounds which act as anti-ferments. No special yeast is required as is the case in some of the proposed processes of securing alcohol from sulfite liquor. Ordinary brewers' yeast was used with good success in all the experiments which have been tried. The fermentation takes place rapidly and, under the conditions here reported, it is complete in

to fish. Experiments were tried placing gold fish in the diluted liquor; the fish seemed not to be injured by the liquor. Similar experiments made using the untreated liquor caused the death of the fish in a few seconds. Although the treated liquor is detoxicated, it must still be considered a source of stream pollution because of the large amount of organic matter present. Further experiments have not been made to ascertain if the liquor remaining after the fermentation can be utilized profitably.

It was practically impossible with an experimental plant of the size used in the work here reported to get at the cost of producing alcohol on a large plant basis. Careful and conservative estimates indicate, however, that the production of alcohol by the above described process is an economic possibility. The experiments made showed that approximately 5 cents worth of sulfur was recovered for each gallon of alcohol produced.

Several other methods have been proposed for the manufacture of ethyl alcohol from waste sulfite liquor. Of these, the one which compares most favorably is the Ekström<sup>1</sup> process. It is now being used in Sweden and at one large plant in this country. In

<sup>1</sup> For references to patents see *Chem. Abs.*, 8 (1914), 1669.



this process the sulfites are partially removed by precipitation as the calcium salt. The liquor is then concentrated and fermented by a special sulfur-resisting yeast. The method here given, however, appears to have several advantages over the Ekström process.

On the whole, the above described process appears to be sound. The reactions brought about are definite, simple and easily controlled.

#### CONCLUSIONS

1—A simple and easily controlled process has been proposed for the economic production of alcohol from waste sulfite liquor.

2—The process also detoxicates the sulfite liquor so as to make it, when diluted in the usual amount, practically harmless to fish.

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### THE USE OF COPPER OXIDE FOR FRACTIONATION COMBUSTION OF HYDROGEN AND CARBON MONOXIDE IN GAS MIXTURES

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The purpose of this paper is to record the authors' experience in using copper oxide for the determination of hydrogen and carbon monoxide in gas mixtures. The method had given us much better satisfaction than methods that demand the use of acid or ammoniacal solutions of cuprous chloride for determining carbon monoxide, or of palladium asbestos, palladium sponge, or colloidal palladium solution for determining hydrogen. It is believed that this method should be more widely used than it is.

In the use of copper oxide the oxygen for the combustion comes from the reagent itself. After it has been used for a time some red cuprous oxide begins to show or even some completely reduced copper. It is then necessary to heat it and pass air over it, when it is again ready for use.

A great advantage of the method over the use of absorbents for carbon monoxide and hydrogen is the elimination of the preparation of solutions and the fact that copper oxide does not become poisoned as at times do some palladium preparations that are used for the hydrogen determination.

Cuprous-chloride solutions for the carbon monoxide determination are somewhat tedious to prepare and have a small absorption capacity. In addition, two solutions have to be used for precise work. Copper oxide, on the other hand, lasts for practically an indefinite number of determinations, and is easily restored to activity when partly reduced by drawing air over it when hot.

Jäger<sup>2</sup> was the first to use copper oxide for the fractional combustion of hydrogen in the presence of methane. He found that hydrogen was completely burned when passed over copper oxide kept at a temperature of 250° C. The tube containing the copper oxide was surrounded by an oven heated with a gas

flame. Jäger recommended that next the methane be burned by heating the tube containing the copper oxide to bright redness. Knorre,<sup>1</sup> in using the method, replaced the soft glass used by Jäger, by one made of transparent quartz. L. Uebbelohde and de Castro<sup>2</sup> also used a quartz tube for holding the copper oxide: the tube was surrounded by an asbestos oven; they used a temperature of 270° C. for burning the hydrogen and copper oxide and a red heat for burning paraffin hydrocarbons.

E. Terres and E. Manguin<sup>3</sup> state that hydrogen is burned completely at 250° to 300° C. They found that dry carbon monoxide by itself in the dry state is only 90 to 94 per cent burned at 300° C.; also that even when hydrogen was mixed with acetylene and ethylene the latter did not burn completely because of the deposition of carbon on the copper oxide. They add further that benzene resembles ethylene as regards completeness of combustion, and that methane begins to burn at 310° C., the temperature being lowered a few degrees, however, by the presence of hydrogen, and is completely burned at a red heat. The oxidation of dry carbon monoxide began at 145° C., and of wet carbon monoxide below 100° C., but was not complete at 310° C. Hydrogen began to oxidize at 160° to 170° C. and at 250° C. the oxidation was complete. Carbon monoxide burned completely, however, in the presence of sufficient hydrogen at 300° C.

J. G. Taplay<sup>4</sup> uses a temperature of 270° C. for hydrogen and 850° C. for the paraffin hydrocarbons. S. H. Worrell<sup>5</sup> confines the copper oxide in a silica tube of 1/4-in. bore and 7 in. long, and heats it with a gas flame. He states that copper oxide passing an 80-mesh sieve should not be used. A temperature of 250 to 260° C. is used by him for burning hydrogen and carbon monoxide, and red heat for methane.

Dennis<sup>6</sup> confines the copper oxide in a soft glass tube and burns the hydrogen and carbon monoxide together at 270° C., but prefers to burn paraffin hydrocarbons, if present in the gas mixture, by means of a platinum spiral in a Dennis combustion pipette. His chief objection to the method of determining methane with copper oxide lies in the fact that prolonged heating of the combustion tube to a high temperature and repeated passage of the gas through it are necessary for the complete oxidation of the methane.<sup>7</sup>

Wibaut<sup>7</sup> mixes cerium oxide with the copper oxide in sufficient quantity to produce a grayish white mixture with the latter. He states that the combustion is made more rapid by this means.

Taylor<sup>8</sup> heats the copper oxide in a glass tube by means of a small electric furnace. The hydrogen and carbon monoxide are burned at a temperature of 275° C. for gases in which the average value of  $n$  in  $C_nH_{2n+2}$  is as high as 1.65, and paraffin hydrocarbons are burned with oxygen by means of a heated platinum

<sup>1</sup> Chem. Ztg., **33** (1909), 717.

<sup>2</sup> J. Gasbel., **54** (1911), 810-814.

<sup>3</sup> Ibid., **58** (1915), 8-11.

<sup>4</sup> J. Gas Lighting, **118** (1912), 217, 285.

<sup>5</sup> Met. Chem. Eng., **11** (1913), 245-247.

<sup>6</sup> L. M. Dennis, "Gas Analyses," **1913**, pp. 198-206.

<sup>7</sup> Chem. Weekblad, **11** (1914), 498.

<sup>8</sup> Jour. Soc. Chem. Ind., **6** (1914), 845.

<sup>1</sup> Published by permission of the Director of the Bureau of Mines.

<sup>2</sup> J. Gasbel., **41** (1898), 764.

spiral. He says the exact temperature that can be used will depend upon the nature of the hydrocarbons present, and that with methane only, 300° C. is probably not too high, but at this temperature there is danger of oxidation of the higher homologs of methane. Tests by Taylor also showed that not only may hydrogen and carbon monoxide be burned in the presence of methane without danger of oxidation of the latter but also in the presence of high concentrations of higher paraffins. He states that the time required for the complete burning of the hydrogen and carbon monoxide does not seem to be a function of the quantities present as much as the nature of the gas mixture. For ordinary illuminating gas he found that the hydrogen is usually completely removed in 10 slow passes over the copper oxide. With some low-temperature coal distillates, not scrubbed, there were required as high as 40 minutes to remove 3 to 5 cc. Taylor concludes that, in general, when the contraction due to the burning of the hydrogen has ceased, the carbon monoxide may be assumed to have been completely oxidized, unless it be present in much greater concentration than the hydrogen, in which case passage through the copper oxide should be continued some minutes longer.

Nemselow<sup>1</sup> uses a temperature of 250° C. He found that silver oxide could also be used, although it is not as practical.

#### EXPERIMENTAL

The apparatus with which the authors performed their work is shown in Fig. 1. The burette *a* has a capacity of 100 cc. and is graduated in 0.1 cc.; an attachment, *j*, *n*, compensates for outside changes of temperature and pressure during the course of the analysis; *h* and *i* are three-way stop-cocks; *b* contains caustic potash solution for the removal of carbon dioxide; *c*, fuming sulfuric acid for removing unsaturated hydrocarbons; *d*, alkaline pyrogallate solution for removing oxygen; *e* is a slow-combustion pipette containing an electrically heated platinum spiral. This coiled spiral is 4½ in. long and No. 30 B. & S. gauge. The glass tubes supporting the spiral are filled with mercury. The latter acts as electrical contacts between the ends of the platinum spiral and the platinum wires sealed into the bottom of each tube. The ends of the platinum spiral are fused to the inside of the open glass tubes at the top. Thus fastened and with the ends of the spiral dipping into the mercury, they always stay in place. A current of about 4 to 5 amperes at 6.2 volts is used to raise the wire to a white heat for burning the paraffin hydrocarbons. Mercury is used in this pipette, also in the burette; *f* is a glass tube (inside diameter, 4 mm.) containing the copper oxide, surrounded by an electrically heated oven, *g*,<sup>2</sup> which is supported by a standpipe, by means of which it can be raised from the copper oxide tube when not in use. Copper oxide that passes a 100-mesh sieve is not used in the tube. One U-tube used by the authors for holding copper oxide contained 0.3 grams and a free space volume of 1.89 cc.

In Fig. 1, *o* and *p* are three-way T stop-cocks, so that the gas can be passed either through the branch *o*, *p* into the pipette *d* or through the copper oxide tube and thence into the pipette *e*. The bulbs *m* and *l* slide up and down on two standpipes (not shown). A simpler burette is shown at *l*, in case it is desired to use water in the burette instead of mercury.

#### USE OF THE APPARATUS SHOWN IN FIG. 1

There follows the method of making an analysis of a gas mixture containing carbon dioxide, unsaturated hydrocarbons (principally ethylene), oxygen, carbon monoxide, methane, ethane, hydrogen and nitrogen.

Before proceeding with the analysis the capillary train and U tube are swept free of oxygen or residual gases from a previous determination by drawing a sample of air into the burette and passing it into the alkaline pyrogallate pipette *d* to remove oxygen. The residual nitrogen is then passed into all the pipettes and through the CuO tube to sweep out other gases

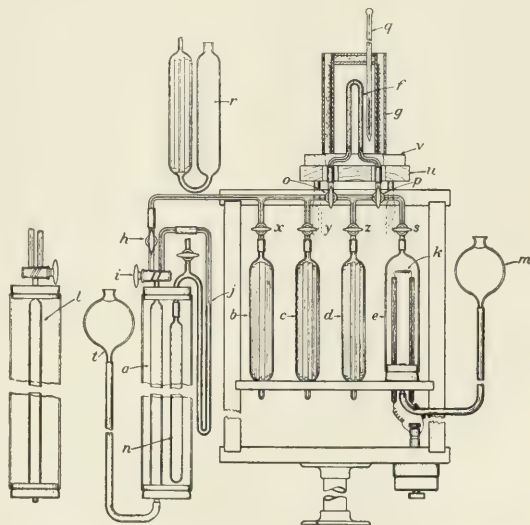


FIG. 1—COMPLETE GAS ANALYSIS APPARATUS INCLUDING COPPER OXIDE TUBE

(usually oxygen) that may have been contained therein. Instead of extracting nitrogen from the air for this purpose each time, a supply of nitrogen may be kept on hand. The electric current is then turned through the oven. Preliminary trials will have shown the current strength demanded. The ovens in use by the authors require about 2.4 amperes at 30 volts. Connection is made through regulating resistances to the 220 volt lighting circuit of the building through a lamp bank rheostat. The current is switched on at the beginning of an analysis so that the oven will be heated to the desired temperature (275° to 300° C.) by the time the analyst is ready to make the fractional combustion analysis.

Some of the gas mixture is then drawn into the burette, measured and passed into the pipettes *b*, *c* and *d*, for the removal of carbon dioxide, illuminants and oxygen. After the percentage of these constituents

<sup>1</sup> *Z. anal. Chem.*, **48** (1909), 232-272.

<sup>2</sup> Similar to the one used by Taylor (*loc. cit.*).



has been recorded, the stop-cocks *o*, *p* and *s* are turned so that communication is made between the burette and the pipette *e*, through the copper oxide tube. By this time the latter will have reached the desired temperature. The furnace is next lowered over the copper oxide tube and the gas mixture slowly passed back and forward through it between the burette and slow-combustion pipette *e* until no further diminution in volume is noted by reading the gas volume in the burette. The authors have found that a maximum of about 15 minutes is required to burn completely the carbon monoxide and hydrogen in various gas mixtures. Carbon monoxide burns readily in the presence of hydrogen, but much more slowly when burned alone. After combustion is complete the electric oven is raised from the copper-oxide tube and the latter allowed to cool. The authors hasten the cooling by playing a blast of cold air from a compressed air pipe on the tube: this operation requires about 5 minutes. A safe way is to make a second reading of the gas volume after a few minutes' time to make sure that no further contraction, due to cooling, takes place. Next the carbon dioxide is removed by passing the gas mixture into pipette *b* (the KOH pipette). Gas in the train and copper-oxide tube containing carbon dioxide is swept into the KOH pipette by raising and lowering the level bulb *m*, with stop-cocks *s*, *p*, *o* and *x* open.

After the hydrogen and carbon monoxide have been determined, the residual gas is passed into the KOH pipette *b* for storage and the stop-cock closed. Enough oxygen to burn the paraffin hydrocarbons is

TABLE I—ANALYSIS (BY CuO METHOD) OF GAS FROM COAL DISTILLATION

	No. 1 cc.	No. 2 cc.	Percentage No. 1	Percentage No. 2
Volume of sample taken.....	40.2	41.5	..	..
Volume after KOH absorption.....	39.6	40.9	..	..
Carbon dioxide (CO) absorbed.....	0.6	0.6	1.5	1.5
Volume after fuming sulfuric acid absorption.....	39.3	40.7	..	..
ILLUMINANTS, etc., absorbed.....	0.3	0.2	0.7	0.5
Volume after alkaline pyrogallate absorption.....	39.3	40.7	..	..
Oxygen absorbed (O <sub>2</sub> ) absorbed.....	0.0	0.0	0.0	0.0
Volume after CuO burning.....	26.1	27.0	..	..
Hydrogen in sample (H <sub>2</sub> ).....	13.2	13.7	32.8	33.0
Volume after KOH absorption.....	23.8	24.6	..	..
Carbon monoxide in sample (CO).....	2.3	2.4	5.7	5.8
Volume taken for slow combustion.....	23.8	24.6	..	..
Oxygen added.....	92.7	92.2	..	..
Total volume.....	116.5	116.8	..	..
Volume after burning.....	69.1	68.0	..	..
Contraction due to burning.....	47.4	48.8	..	..
Volume after KOH absorption.....	45.2	46.3	..	..
Carbon dioxide absorbed.....	23.9	24.7	..	..
Methane in sample (CH <sub>4</sub> ).....	23.3	23.9	58.0	57.6
Ethane in sample (C <sub>2</sub> H <sub>6</sub> ).....	0.3	0.4	0.7	1.0
Nitrogen in sample (by difference).....	..	..	0.6	0.6

then drawn into the burette, measured and passed into the slow-combustion pipette *e* (not through the U-tube *f*), and the platinum spiral therein heated to almost a white heat. Next the residual gas is withdrawn from the pipette *b* into the burette and from there slowly passed, at the rate of about 10 cc. per minute, into the pipette *e*. Slow combustion between the oxygen and combustible residual gas therein takes place as fast as the oxygen enters and an accumulation of the mixture necessary for an explosion cannot take place.<sup>1</sup> Only enough of the residual gas should be taken for the final combustion analysis so that there will be an excess of oxygen for the com-

<sup>1</sup> To protect the operator from possible accident, the combustion pipette *e* should be surrounded with a wire gauze.

bustion. In case of doubt a final determination of oxygen by means of the alkaline pyrogallate solution in pipette *d* can be made. After combustion is complete the resulting contraction and carbon dioxide are measured and the gas mixture again passed into the slow-combustion pipette and burned again. There always results further slight contraction and a small amount of carbon dioxide.

Table I gives the observed data of the analysis of a sample of gas collected from coal distillation at high pressures and temperatures.<sup>1</sup>

Table II shows analyses of two samples of gas. In one case the carbon monoxide and hydrogen were determined by burning them with copper oxide, and in the other case the carbon monoxide was absorbed by means of ammoniacal cuprous chloride solution and the hydrogen by colloidal palladium solution.<sup>2</sup>

TABLE II—PERCENTAGE ANALYSES OF A SAMPLE OF GAS BY TWO METHODS

	SAMPLE 1		SAMPLE 2	
	Colloidal palladium and cuprous chloride	CuO Method	Colloidal palladium and cuprous chloride	CuO Method
CO <sub>2</sub> .....	0.2	0.4	0.0	0.0
C <sub>2</sub> H <sub>4</sub> , etc.....	44.6	44.6	12.7	12.5
O <sub>2</sub> .....	1.7	1.6	0.2	0.2
CO.....	0.8	0.9	1.0	0.8
H <sub>2</sub> .....	7.7	6.7	42.3	42.2
CH <sub>4</sub> .....	26.4	26.4	41.2	41.1
C <sub>2</sub> H <sub>6</sub> .....	11.4	11.2	0.0	0.0
N <sub>2</sub> .....	7.2	8.2	2.6	3.2

Table III shows two analyses of the same sample. One was made by burning the hydrogen and carbon monoxide over copper oxide with the apparatus shown in Fig. I. The other was made by burning the carbon monoxide, hydrogen and methane together (triple combustion) and a slow-combustion pipette of a Hal-dane gas-analysis apparatus. With the latter, gas volumes as small as 0.002 cc. could be measured.

TABLE III—PERCENTAGE ANALYSES BY COPPER OXIDE AND BY TRIPLE COMBUSTION

ANALYSIS BY	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub> , etc.	O <sub>2</sub>	H <sub>2</sub>	CO	CH <sub>4</sub>	N <sub>2</sub>
Copper oxide.....	3.9	0.0	15.5	0.0	0.3	0.9	79.4
Triple combustion.....	3.90	0.00	15.46	0.02	0.17	0.84	79.61

Next a gas mixture was prepared containing 49 per cent each of hydrogen, carbon monoxide and methane, and 88 per cent air. Analysis No. 1 shows the results obtained by burning the hydrogen and carbon monoxide at a temperature of 290° C. and methane at a temperature of 800° C. The copper-oxide tube was made of quartz. Analysis No. 2 shows the results obtained by absorbing the carbon monoxide with cuprous chloride, the hydrogen by colloidal palladium, and the methane in a slow-combustion pipette with a hot platinum spiral.

TABLE IV—PERCENTAGE ANALYSES OF A SAMPLE OF GAS BY TWO DIFFERENT METHODS

No.	ANALYSES BY	CO	H <sub>2</sub>	CH <sub>4</sub>
1	Copper oxide.....	3.8	3.6	4.2
2	Cuprous chloride, colloidal palladium and hot spiral.....	4.1	4.0	4.0

Next a mixture of hydrogen (50 per cent) and natural gas<sup>3</sup> (50 per cent) was prepared. No. 1 analysis was made by burning the hydrogen with copper oxide and the methane with a hot platinum spiral (slow combustion).

<sup>1</sup> The copper oxide was heated to 290° C. in this and other analyses that follow in determining hydrogen and carbon monoxide. Temperatures ranging from 275° to 300° were found to work satisfactorily.

<sup>2</sup> THIS JOURNAL, 6 (1914), 992.

<sup>3</sup> Containing 84.7 per cent CH<sub>4</sub>, 9.4 per cent C<sub>2</sub>H<sub>6</sub>, 3.0 per cent C<sub>2</sub>H<sub>4</sub>, 1.3 per cent C<sub>2</sub>H<sub>2</sub>, 1.6 per cent N<sub>2</sub>.

No. 2 was made by absorbing the hydrogen with colloidal palladium solution and burning the methane with a hot platinum spiral.

TABLE V—PERCENTAGE ANALYSES OF A MIXTURE OF NATURAL GAS AND HYDROGEN BY TWO DIFFERENT METHODS

No.	ANALYSES BY	H <sub>2</sub>	Natural gas
1	Copper oxide and slow combustion.....	50.7	48.3
2	Colloidal palladium and slow combustion....	50.2	48.1

The above analyses showed that the paraffin hydrocarbons higher than methane were not oxidized, at least in any significant amount, by the copper oxide.

Lastly, there is shown work upon the analysis of the artificially mixed coal and water gas of Pittsburgh. The first analysis was made by burning the carbon monoxide and hydrogen with copper oxide at about 290° C. and paraffin hydrocarbons in the slow-combustion pipette with a hot platinum spiral. The second analysis was made by using copper oxide at about 290° C. to burn the carbon monoxide, a solution of colloidal palladium to absorb the hydrogen, and a hot platinum spiral to burn the paraffin hydrocarbons. The third analysis was made by burning carbon monoxide and hydrogen at about 290° C. with copper oxide and by burning the paraffin hydrocarbons at a red heat with copper oxide.

TABLE VI—PERCENTAGE ANALYSES OF THE ARTIFICIAL ILLUMINATING GAS OF PITTSBURGH

No.	CO <sub>2</sub>	Illuminants	O <sub>2</sub>	CO	H <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	N <sub>2</sub>	TOTAL
1.....	2.5	7.4	0.4	11.5	43.6	30.6	2.1	1.9	100.0
2.....	2.6	7.0	0.4	11.7	43.9	30.7	2.2	1.5	100.0
3.....	2.4	7.5	0.4	11.5	43.4	30.4	2.2	2.2	100.0

#### SUMMARY

I.—The authors' experience with the copper-oxide method, devised by Jäger for the fractional combustion of hydrogen and carbon monoxide, is described.

II.—A gas-analysis apparatus, embodying a copper-oxide tube somewhat different in form from others on the market, but containing no new principle, is also described.

III.—A temperature of the copper oxide of between 275° and 300° is adapted for burning hydrogen and carbon monoxide in a wide variety of mixtures. Most previous experimenters have adopted temperatures in this range.

LABORATORY GAS INVESTIGATIONS  
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#### A NEW ACCURATE METHOD OF GAS ANALYSIS

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Figs. I and II show the apparatus used for estimating the quantities of carbon dioxide, illuminants, oxygen, carbon monoxide, methane, ethane, hydrogen and nitrogen in gaseous mixtures.

B, B<sub>1</sub> are 100 cc. burettes graduated the entire length on 0.1 cubic centimeter. C, C<sub>1</sub> are water jackets for the burettes. D is a three-way glass Geissler cock of 2 mm. bore. E, E<sub>1</sub> are bent capillary tubes of 1 mm. bore. F is a three-way Geissler cock, G is a two-way cock having a T capillary fused to F. H is a bent 1.5 mm. bore capillary, whose orifice, H<sub>1</sub>, is melted to measure 0.3 mm. I is a piece of glass tubing having walls of sufficient strength, and an internal diameter of 1.75 cm. drawn down to a

capillary of 1.5 mm. internal diameter. J is the brass body holding the combustion tube. K is a three-way glass cock of 2 mm. bore. N is a two-way glass cock of 5 mm. bore. P is a glass-covered pipette stand whose height is adjustable. Q is a set screw for adjustment of P. J, the brass body holding the combustion tube, has two small holes, a little smaller than 1.5 mm. diameter, drilled from the posterior side into 1/3 of the body J. Into these are fitted the two legs of a platinum combustion tube of 1.5 mm. outside and 0.5 mm. inside diameter. The small holes are 1 cm. apart. The platinum tube is about 10 to 11 cm. long and is bent to form a U, the two legs of which run parallel about 1 cm. apart. Into the forepart of the body two large holes, about 8 mm. in diameter, are drilled, whose centers meet the centers of the 1.5 mm. holes drilled from the rear.

The brass body has grooves milled in large enough to have a water circulation to keep the rubber tubing cool, which holds the bent glass capillaries of 1.5 mm. bore fitting tightly into the larger holes A, A. These

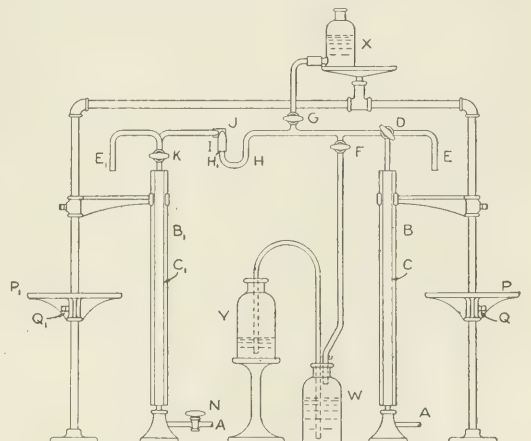


FIG. I—ARRANGEMENT OF APPARATUS

W, a 4 liter bottle for storing oxygen over water, is connected to bottle Y of the same size placed above it to keep the oxygen under pressure

glass capillaries are bent so that the combustion tube protrudes in the rear of the apparatus. Around the brass body is soldered a piece of sheet copper to form a cup for water. The platinum tube is then soldered in, gas-tight.

If mercury is used as the confining fluid in burette B, the platinum tube is either brazed or silvered in, gas-tight. The ends of the platinum tube are tapered so that tight joints are secured by forcing the ends into the brass body.

A small piece of asbestos paper is fitted onto the platinum capillary to prevent the unused heat from softening the solder.

A Meker or Bausch and Lomb high temperature burner is used to heat the tube and is adjusted to position with an iron clamp fastened to the apparatus support. All rubber connections should be made with the best heavy-walled rubber tubing which should be of small enough size to give a tight joint.

All glass capillaries should fit shoulder to shoulder



when connections are made, and all rubber connections should be wired by iron wire 1 mm. in diameter, at the edge of the tubing. All joints that are to be rigid should be stiffened by wrapping a piece of sheet copper of suitable size around the rubber within the space of the two iron wires which hold the tubing tight at the edge and then wiring this sheet on tightly with three iron wires, 1 mm. in diameter.

#### ASSEMBLY OF APPARATUS

D is fastened to the body of burette B with rubber tubing, wired and stiffened. K is fastened in like manner to B<sub>1</sub>. B is then put into C, the rubber stoppers put into place at the ends of C. E and E<sub>1</sub> are fastened to D and K with rubber tubing and wired. The burette B is fastened to the right side of apparatus' support with a universal clamp. The burette B<sub>1</sub> is fastened to the left side in the same way. F and G are connected to D, wired and stiffened. H is fitted tightly into I at H<sub>1</sub> with a piece of rubber tubing. I is connected to J with rubber tubing. J is connected to K in like manner. P and P<sub>1</sub> are then adjusted. N is connected to B<sub>1</sub>, wired, stiffened and fastened to table by wiring it to a large cork nailed to the table.

N is then connected with 36 inches of heavy-walled mercury rubber tubing, wired, and connected to the mercury aspirator bottle which connection is also wired. The lower 18 in. of this tubing should be

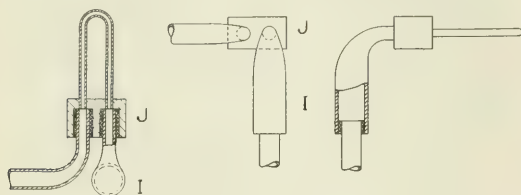


FIG. II.—DETAIL OF CAPILLARY AND TRAP

wrapped with good adhesive tape to prevent the mercury from bulging through the tubing when the aspirator bottle is raised. All stoppers are wired to the cocks. The mercury aspirator bottle is then filled with mercury.

A is connected and wired to 40 in. of smooth bore heavy-walled, best grade rubber tubing, which is then connected to a 500 cc. aspirator bottle which is filled with one part of HCl (sp. gr. 1.2) to 10 parts distilled water. The water jackets are filled with distilled water.

If preferred, manometers and compensating tubes may be added to the burette; otherwise compared Centigrade thermometers should be inserted in the water jackets through the top rubber stoppers.

Mercury should not be allowed to get into the platinum capillary nor should explosive mixtures be run through too fast when the joints are soldered, as this will destroy the solder joints.

For accuracy it is preferred to use mercury in burette B also.

A small amount of water on the surface of the mercury may be allowed, provided the burettes are cali-

brated for mercury and the water meniscus for the amount of water on the mercury surface.

#### REAGENTS USED

(1)—One part of purified stick potash to one part pure water by weight: 150 cc. of this solution are poured into a stoppered, single Hempel pipette filled with clean iron turnings to increase the absorbing surface of the potash.

(2) Nordhausen sulfuric acid, or where preferable, saturated bromine water.

(3)—Yellow phosphorus cast into 5 mm. sticks set upright in a stoppered, single Hempel pipette covered by 150 cc. of pure distilled water.

The Hempel pipette body is painted black. A 1/2-inch strip extending lengthwise on the front side of the phosphorus bulb and the capillary are left unpainted so that the action of the phosphorus may be observed.

(4)—A stoppered, double Hempel pipette filled completely with straight 1.5 mm. copper wires and covered by 125 cc. of the following solution: one part by weight of ammonium hydroxide (sp. gr. 0.90) to four parts by weight of pure distilled water. A large excess of ammonium chloride is then added to this diluted ammonium hydroxide and a saturated solution is made at about 80° F. After being sure the solution is saturated, the excess of ammonium chloride is allowed to settle and the clear solution decanted into a clean flask, stoppered, and kept for use. This copper pipette is the best absorbing agent for oxygen but can not be used when carbon monoxide or dioxide is present. Saturated ammonium chloride in ammonium hydroxide (sp. gr. 0.90) should not be used as the nitrogen of the theoretically ionized NH<sub>4</sub> is, to a certain extent, oxidized to free nitrogen when a 99% oxygen is analyzed. Weaker solutions of ammonium chloride should likewise be avoided.

Phosphorus, according to G. Lunge's 1914 publication, is the best reagent for absorbing oxygen from illuminating or heating gases. This assertion has been proven to be correct.

Low concentrations of oxygen, up to 5 per cent oxygen, mixed with gases such as hydrogen, water gas, coal gas, etc., were separated by treatment with phosphorus and in no case was a perceptible excess contraction noticed. On the other hand, high concentrations of oxygen, 98.6% pure, with hydrogen and other combustible gases, when treated with phosphorus, showed excess contraction due to chemical combination with some of the hydrogen or other gas with the oxygen.

With high concentrations of oxygen the phosphorus melted, trapping gas. Even air, when allowed to come into contact with the phosphorus, gradually melted the phosphorus, necessitating the recasting of the phosphorus. Hence for low concentrations of oxygen, when carbon monoxide is present, phosphorus was considered the best reagent to be used.

The oxygen is absorbed very rapidly. As soon as the white phosphorus pentoxide fumes have nearly

settled or if the pentoxide fumes are washed into solution giving the small amount of oxygen diffused in the gas the opportunity of coming in contact with the moist phosphorus, as the pentoxide fumes retard the movement of the molecules of the gas, the absorption is complete. Further treatment of the gas with phosphorus causes no contraction.

Phosphorus gives valuable indication of the complete absorption of the unsaturated hydrocarbons by the fuming sulfuric acid or bromine water. A phosphorus pipette lasts much longer than a pyrogallate pipette and one pipette can be used for all of the gases while when using alkaline pyrogallol it is necessary to have a separate pipette for each kind of gas analyzed.

Phosphorus is much speedier in action than pyrogallate; besides, continuously accurate results are obtained by its use, which can not be said of pyrogallol. Pyrogallol prepared as directed by R. P. Anderson<sup>1</sup> is also very unpleasant to handle.

Fuming sulfuric acid should always be fresh enough so that the reaction between the oxygen and phosphorus is not interfered with, due to presence of remaining hydrocarbons.

For concentrations of oxygen higher than 5 per cent and where carbon monoxide or dioxide is not present, the best method for absorbing oxygen is by copper with the ammonium chloride solution as directed previously. Such a pipette lasts a very long time. We have used one daily for about two months without renewing any part of it and it does not at present show any signs of becoming exhausted. It must be remembered to use the ammonium chloride solution as specified.

The results obtained by this method agree exactly with those secured by combustion.

Samples of air analyzed gave a value of about 20.87 per cent oxygen, and samples of commercial oxygen analyzed checked among themselves to the hundredths of one per cent when measurements were performed accurately and these results checked with the oxygen determined by combustion over a large number of determinations.

The pipette should have as much copper surface as possible; therefore the copper wires should be thin and straight and should fill the entire length of the pipette body as otherwise the absorption of oxygen is not as rapid as is possible.

The copper wires should be very clean and bright before putting them into the pipette and the last bulb of the pipette should have a little of the ammonium chloride solution in it also. The copper going into solution by chemical change seems to be precipitated back onto the metallic copper as the metal, to some extent. When making an absorption of oxygen by copper it should be remembered that the absorption takes place on the moist surface of the copper; consequently the aim should be to wash gently over the copper with the ammonium chloride solution so that the blue compound is dissolved, giving a fresh

copper surface, and not to shake the pipette to have the liquid absorb the oxygen.

When using a mercury burette care should be taken that no mercury comes in contact with the copper surface as it readily amalgamates at the surface of the copper. The salts of mercury also precipitate on the surface of the copper as metallic mercury and this spoils the pipette.

#### APPLICATION OF THE METHOD TO ANALYSIS

Exactly 100 cc. of the sample of gas to be analyzed are drawn into the water burette. The capillary is then washed by turning cock G, and to seal the gas in the burette, acidulated water is then allowed to completely fill all of the capillaries and trap I up to the edge of the cock K. The potash pipette is then connected to the capillary E, and the gas in the burette aspirated back and forth three times. This procedure removes all of the carbon dioxide. The residue is measured and the reading recorded. The difference between 100 cc. and this reading gives the per cent of carbon dioxide present in the sample.

The potash pipette is disconnected, the capillary washed, the gas in the burette put under slight pressure, the thumb is placed on the end of capillary E, cock D is opened and the water in the capillary allowed to run almost to the end of E. Cock D is then closed and the fuming sulfuric acid pipette attached to E. Not more than 0.02 cc. of air should be introduced at this point, if the pinching up of the sulfuric acid in the pipette capillary and the connection is made carefully. The gas is aspirated back and forth two times, the acid drawn back to the same mark in capillary and cock D is closed. A quick, smooth pull with one hand and with the thumb and finger of the other hand pinching the rubber tube connecting pipette with E prevents the acid from getting into the rubber connection. The other thumb is quickly slipped over the end of E, preventing diffusion of the small amount of gas in the capillary with the air.

Water from a wash bottle is now blown into the rubber connection of the potash pipette and this pipette quickly connected to E, at the same time withdrawing the thumb. To take out the sulfuric fumes, the gas is passed back and forth four times. The reading is taken and recorded. The difference between this and the previous reading gives the per cent of illuminants (unsaturated hydrocarbons, benzene vapor, etc.). If all of the illuminants are not withdrawn by two passages through the sulfuric pipette they should be removed by passing through one more time.

Next remove the oxygen with phosphorus. Allow the gas to remain in contact with the moist phosphorus until most of the fumes disappear. The gas is then drawn into the burette, measured and the amount recorded. The difference between this and the previous reading gives the per cent of oxygen in the mixture.

A gas holder is made by connecting two 500 cc. aspirator bottles with rubber tubing, which is wired on. A 1-hole rounded rubber stopper is fitted to

<sup>1</sup> THIS JOURNAL, 7 (1915), 587.



the neck of one of the aspirator bottles and a piece of capillary glass tubing inserted. The end of this capillary is then closed with a piece of rubber tubing and a pinch-cock just as the pipettes for the reagents. Enough acidulated water (distilled) is added to this holder to completely displace the air in the bottle having the capillary. The other bottle is fitted with a tube and rubber stopper to blow the water out of the capillary.

The rubber stopper for the capillary bottle should be rounded into an inverted basin-like depression so that the air may be quickly and completely displaced. This is done by heating a heavy copper wire to redness and moulding the stopper to the proper shape. The stopper is then rather soft and unfit for use, but it should be hardened by immersing it in a little fuming sulfuric acid.

The residue of gas left after determining the oxygen is transferred to this holder, a measured excess of oxygen is then added by opening cock F and allowing the oxygen to flow into the water burette. After measuring, the oxygen is transferred to the holder and the entire gaseous mixture shaken, at the same time pinching the rubber connection between the two aspirator bottles to prevent air from entering or gas from leaving the holder. Mercury might be used in this holder having a very slight amount of acidulated water on its surface.

After thoroughly mixing the gas and oxygen, 100 cc. of the mixture or a close approximation to 100 cc. are drawn into the water burette and the amount accurately measured. The mercury burette is then adjusted so as to contain 15 or 20 cc. of air. Water fills all of the capillaries, including the trap I up to cock K.

A 250 cc. aspirator bottle can be made a part of burette B, using a small rubber stopper, then the entire mixture may be burned instead of 100 cc. in one operation.

After recording all of the measurements the water in the trap I is forced into the water burette by putting the measured amount of air in the mercury burette under pressure and opening cocks D and K so that the flow is into the water burette. As soon as the water reaches the orifice  $H_1$  cock D is closed, the mercury in the burette leveled, and cock N closed. Cock K is kept open. The burner heating the platinum capillary is then lighted. It should give a flame hot enough to melt to a globule the end of a piece of copper wire 1 mm. in diameter in 5 to 8 seconds. A Bausch and Lomb high temperature burner or a Méker burner should be used. After the platinum tube becomes heated to a bright red, D is opened, the aspirator bottle on the water burette is raised slowly so that the water remaining in the capillaries is not forced through the heated tube, and then put on the high shelf.

The small amount of water, not more than 0.1 cc., which is forced into the trap, prevents the explosion of the mixture of gases from traveling back into the burette, which, if it should occur, would wreck the apparatus.

Cock N is now slightly opened and the explosive mixture of gases allowed to bubble through the water in trap I at a moderate rate and as soon as all of the gas has passed through the water seal, the water is allowed to rise until the beginning of the heated portion of the tube is reached.

Cock N should be closed as soon as water flows through the orifice  $H_1$ . Cock D should next be closed when the heated portion of the combustion tube is reached. The heating is then stopped and water thrown on the hot tube from a wash bottle to cool the tube rapidly. Cock D is opened and the water allowed to come to the edge of cock K, which is then closed.

This residue of gas, after combustion, is measured and the amount recorded. The potash pipette is now connected to  $E_1$  and the gas aspirated back and forth four times. The amount of gas left is measured and recorded and the pipette disconnected. The pressure on the gas is now slightly decreased and 1 cc. of acidulated water drawn into the mercury burette. This is done to prevent mercury from fouling the copper in the copper pipette. The copper pipette is connected to E and the residue of gas completely transferred thereto. In order to absorb oxygen completely in this step it is not necessary to disconnect the copper pipette to shake it. It is only necessary to see that the copper wires have a clean coppery color by washing over them a time or so gently with the solution in the pipette. As soon as the clean copper color is seen the oxygen is completely absorbed, the absorption being very rapid.

After drawing the residue of gas into the burette, it is measured, then passed into a dilute solution of sulfuric acid to see whether any ammonia fumes are taken out. This last residue is then measured and the amount recorded.

It is necessary to heat the platinum combustion tube to the degree mentioned, as otherwise the paraffins will not be completely decomposed.

Mercury should not be run into or through the combustion tube. The burettes should be calibrated and the proper meniscus used. One passage through the properly heated tube decomposes all of the gases quantitatively. Cock K and burette B should be thoroughly washed out with acidulated water by opening N and drawing through 1 part of sulfuric acid to 4 parts water. Cock K is completely revolved several times while drawing the acidulated water into the burette. The formula used for calculating the combustion results is easily remembered. Representing the oxygen used in the chemical combination by  $O_2$ , the contraction by C, we have:

$$\begin{aligned} H_2 &= C - O_2 \\ CH_4 &= \frac{3O_2 - (C + CO_2 \text{ formed})}{3} \\ CO &= CO_2 \text{ formed minus } CH_4 \end{aligned}$$

The nitrogen is found by difference. It can also be calculated by the residual nitrogen. Both methods give the same results.

When a part of the mixture of gas and oxygen is

taken for combustion as directed above, a proportion must be made between the amount of the mixture used for combustion and the total amount on hand. The following example taken from practice illustrates the method of writing down the measurements and making the computations.

ANALYSES BY H. L. DAHM  
Sample of water gas July 3, 1915

Burette reading cc.	Per cent
5.4	CO <sub>2</sub> 5.4
20.2	C <sub>n</sub> H <sub>2n</sub> 14.8
20.8	O <sub>2</sub> 0.6
	CH <sub>4</sub> 17.86
Residue for combustion.... 79.2	CO 25.94
	H <sub>2</sub> 31.56
	N <sub>2</sub> 3.84
	100.00
Residue of gas for combustion.....	79.2 cc.
Amount of oxygen taken.....	77.2 cc.
Total mixture.....	156.4 cc.
Amount of mixture taken for combustion....	100.00 cc.
53.6 cc. reading after combustion	
-15.0 cc. air in mercury burette	
38.6 cc. measurement of the residue of the 100 cc. of gas taken for combustion	
100.00 cc. taken for combustion	
-38.6 cc. residue after combustion	
61.4 cc. contraction for 100 cc. of the mixture	
53.6 cc. reading of gas after combustion plus the 15.0 cc. of air	
-25.6 cc. reading of residue after using potash pipette	
28.0 cc. equals the CO <sub>2</sub> formed in 100 cc. of the mixture	
25.6 cc. reading after using potash pipette	
-15.0 cc. reading after using copper pipette	
10.6 cc. of O <sub>2</sub> left which did not take part in the combustion.	
This amount also contains the oxygen in 15.0 cc. of air used	
10.6	
-3.1 amount of O <sub>2</sub> in 15.0 cc. air	
7.5 cc. equals the oxygen not taking part in the chemical combustion of 100 cc.	
Compute the contraction, the carbon dioxide formed, and the excess oxygen for the 156.4 cc. of the mixture, to get the proper figures for the entire mixture, by using the proportions 156.4 : 100.0 cc.	
61.4 × $\frac{156.4}{100.0}$ = 96.03, contraction for total gas	
28.0 × $\frac{156.4}{100.0}$ = 43.8, CO <sub>2</sub> for total gas	
7.5 × $\frac{156.4}{100.0}$ = 11.73, excess oxygen for total gas	
77.2 cc. of O <sub>2</sub> left which did not take part in the combustion.	
This oxygen contains 1.3 per cent nitrogen.	
77.2 × 0.013 = 1.0 cc. of nitrogen in 77.2 cc. O <sub>2</sub>	
-1.0 cc. nitrogen	
76.2 cc. pure oxygen added	
-11.73 cc. excess oxygen, left after combustion	
64.47 cc. equals the oxygen used to combine chemically with the gas	
96.03 - 64.47 (oxygen used) = 31.56 per cent hydrogen	
3 × 64.47 (oxygen used) = 193.41 minus	
96.03 + 43.8 (CO <sub>2</sub> formed) = -139.83	
53.58 = 17.86 per cent CH <sub>4</sub>	
43.8 (CO <sub>2</sub> formed) - 17.86 (CH <sub>4</sub> ) = 25.94 per cent CO.	
Nitrogen is found by computing as follows: In the 15.0 cc. of air used we have 11.9 cc. N <sub>2</sub> . The residue of nitrogen after burning the 100.0 cc. of the mixture plus the nitrogen of the air after taking out all the oxygen equals 15.0 cc.	
15.0 cc.	
-11.9 cc. N <sub>2</sub> in the air used	
3.1 cc. N <sub>2</sub> in 100 cc. of mixture	
In total mixture 156.4 we will have	
3.1 × $\frac{156.4}{100}$ = 4.84 cc. N <sub>2</sub> due to the nitrogen in the original gas	
plus the nitrogen in the commercial oxygen used. In this case the nitrogen as calculated previously equals 1.0 cc. in the commercial oxygen added	
4.84	
-1.0	
3.84 cc., amount of nitrogen in the original gas	

When it is desirable to measure the total contraction—that is, the contraction due to the formation of the H<sub>2</sub>O + CO<sub>2</sub>—the following formulae may be used:

Representing the total contraction by C and the oxygen used in the chemical combination of the gases by O<sub>2</sub> we have:

$$\begin{aligned} \text{CH}_4 &= \frac{3\text{O}_2 - \text{C}}{3} \\ \text{CO} &= \text{CO}_2 - \text{CH}_4 \\ \text{H}_2 &= \text{C} - (\text{O}_2 + \text{CO}_2) \\ \text{Nitrogen is figured by difference} \end{aligned}$$

Should we use these formulae, the figures of the previous water gas analysis would appear as follows:

Burette reading	Per cent
5.4	CO <sub>2</sub> 5.4
20.2	Illuminants 14.8
20.8	O <sub>2</sub> 0.6
Residue of gas..... 79.2 cc.	CH <sub>4</sub> 17.86
Impure oxygen added. 77.2 cc.	CO 25.94
Total mixture 156.4 cc.	H <sub>2</sub> 31.55
	N 3.85
	100.00
53.6 cc. residue after combustion	
-25.6 cc. residue after using potash	
28.0 cc. CO <sub>2</sub> formed in 100 cc. of mixture	
100.0 cc. of mixture taken for combustion	
+15.0 cc. air	
115.0 cc.	
-25.6 cc. residue after using potash	
89.4 cc. total contraction for 100 cc.	
25.6 cc. residue after using potash	
-15.0 cc. residue after using Cu pipette	
10.6 cc. unused oxygen plus oxygen in 15.0 cc. air	
-3.1 cc. oxygen in 15.0 cc. air.	
7.5 cc. unused oxygen in 100 cc. of mixture	
28.0 × $\frac{156.4}{100}$ = 43.80 = total CO <sub>2</sub> = CO <sub>2</sub>	
89.4 × $\frac{156.4}{100}$ = 139.82 = total contraction = C	
7.5 × $\frac{156.4}{100}$ = 11.73 = total unused oxygen	
77.2 cc. = impure oxygen added	
-1.0 cc. N <sub>2</sub> = 1.3 per cent nitrogen in impure oxygen	
76.2 cc. = pure oxygen added	
-11.73 cc. unused oxygen	
64.47 cc. = used oxygen = O <sub>2</sub>	
CH <sub>4</sub> = $\frac{3\text{O}_2 - \text{C}}{3}$ = $\frac{64.47 \times 3 - 139.82}{3}$	
53.59	
3 = 17.86 per cent CH <sub>4</sub>	
CO = CO <sub>2</sub> - CH <sub>4</sub> = 43.80	
-17.86	
25.94 per cent CO	
H <sub>2</sub> = C - (O + CO <sub>2</sub> ) = $\frac{64.47}{3} - \frac{139.82}{3}$	
+43.80 -108.27	
108.27	
31.55 per cent H <sub>2</sub>	

Using this method, a complete analysis can be made in twenty minutes, as I have repeatedly made an analysis in this time.

A convenient way of cleaning phosphorus is by adding a 3 per cent solution of hydrogen peroxide, if possible free from acetanilide, to the pipette and allowing it to remain until phosphorus assumes the yellow waxy color.

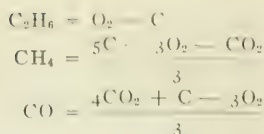
When the ethane is to be estimated the hydrogen is absorbed in a colloidal palladium solution or in a palladium tube as directed in G. Lunge's (1914) "Technical Gas Analysis."

Another wash bottle containing pure water is attached to the apparatus along the side of the wash bottle containing the dilute hydrochloric acid.

After absorbing the hydrogen the residue consisting of carbon monoxide, methane, ethane and nitrogen is transferred to the gas holder and excess of oxygen added and the gases burned as before.

The theoretical formulae for calculating the constituents of the mixture, when O<sub>2</sub> equals the oxygen used in the chemical action, C equals the observed contraction, and CO<sub>2</sub> equals the observed carbon dioxide formed, are





It is usually necessary to remove the carbon monoxide before the absorption of hydrogen.

The mercury can be cleaned by putting it into a two or three liter bottle with some dilute nitric acid and shaking it until the mercury is finally divided. Repeat this operation with pure water.

When mercury is used in burette B, a glass cock exactly the same as is used at the bottom of burette B<sub>1</sub> is attached to B. The mercury surface should be leveled at the lowest part of the meniscus showing as a sort of bright line.

Burrell and Seibert in Bureau of Mines *Technical Paper 54* (1913) again call attention to certain cases of gas analysis where corrections in calculating results are to be made due to certain of the gases not obeying the ideal gas laws.

Below is a new easier method of calculating corrected results and proven by simple stoichiometry to give at least as accurate results as the method given in Burrell and Seibert's paper.

When carbon monoxide, methane and ethane are estimated together, and the factors for the partial pressures of the carbon dioxide formed for each constituent are used, as is necessary in Burrell and Seibert's calculation, the sum of all of the separate parts of corrected carbon dioxide does not equal the total corrected carbon dioxide calculated by dividing the total measured carbon dioxide by its partial pressure factor.

Theoretically, according to Avogadro's hypothesis and Gay-Lussac's law, etc., the molecules in one volume of methane combine with the molecules in two volumes of oxygen to form the molecules in one volume of carbon dioxide and the molecules in two volumes of water vapor.

This water vapor should condense at the ordinary temperature and pressure if the original gases were saturated with moisture.

Therefore, 1000 cc. of methane should combine with 2000 cc. of oxygen to form 1000 cc. of carbon dioxide.

By observation it had been found that the number of molecules in 1000 cc. of methane combine with the molecules in  $2002 \frac{2}{999}$  cc. of oxygen to form the molecules in  $995 \frac{995}{999}$  cc. of carbon dioxide at the ordinary temperature and pressure.

If this amount of carbon dioxide is corrected by dividing by the quotient obtained by dividing the theoretical by the observed specific gravity of carbon dioxide at 20° and 760 mm., the corrected amount will equal the ideal amount of methane  $1001 \frac{1}{999}$  cc.

and if this last amount is multiplied by the quotient of the theoretical, divided by the observed gravity of methane, as shown in Burrell and Seibert's paper, the product will be the actual amount of methane measured.

Now if the methane is to be calculated from the contraction the measured amount of methane must be divided by its pressure factor and the carbon dioxide formed also must be corrected in the same way. Divide the corrected contraction by 2 and the quotient will be the ideal volume of methane. Multiply this quotient by the pressure factor for methane and the product equals the measured volume of methane.

This method of reasoning can be extended to more complicated formulae.

Therefore, if the original amount of gas present as measured or calculated from the theoretical formulae be divided by the factors for the separate gases and the measured volume increased by the difference between the calculated amount and the measured amount, also if the carbon dioxide as measured is corrected by dividing by its pressure factor, the ideal quantities of all of the gases present can be calculated by the usual theoretical formulae by using the corrected values for the contractions and the carbon dioxide.

An oil gas gave these combustion measurements: C = 130.69 cc., O<sub>2</sub> = 117.78 cc., CO<sub>2</sub> = 55.51 cc.

By the usual theoretical formulae the methane equals 55.71 per cent, the carbon monoxide —0.20 per cent, the hydrogen equals 12.91 per cent, and the nitrogen equals 0.28 per cent. The total was 68.7 per cent of the original 100 cc. taken for analysis.

The carbon dioxide partial pressure equaled 50.3 per cent and the partial pressure of the methane was 84.7 per cent. From Burrell and Seibert's paper the molecular volume factor for the carbon dioxide is 0.99717 and for methane 0.99915. Divide 55.51 cc. by 0.99717; the quotient, 55.668, is the corrected volume of carbon dioxide. Divide 55.71 cc., the calculated amount of methane, by 0.99915; the quotient, 55.758 cc., is the corrected volume of CH<sub>4</sub> if 55.71 cc. was the measured volume of methane. This is not the case here; the idea is to get the increase of the corrected over the theoretically calculated methane; add this difference to the total volume of gas for combustion in order to arrive at the corrected figures for the contraction.

This difference is 0.048 and can be added to the uncorrected contraction provided the difference between the corrected and measured carbon dioxide is subtracted, as this last difference is 0.158 cc., the corrected contraction is 130.58 cc. The corrected carbon dioxide is 55.668 cc. The oxygen used is 117.78 cc.

By the ordinary theoretical formulae the calculations are completed and give the following values:

Methane	55.6 per cent
Hydrogen	12.8 per cent
Nitrogen	0.3 per cent

From the foregoing deductions, the molecular volume factors and the specific gravity of the pure gases can be determined by the ordinary combustion

method as described in this paper provided pure samples can be obtained as directed in Bureau of Mines *Technical Paper*, 104 (1915) by Burrell, Seibert and Robertson.

For accurate work in these determinations larger measuring instruments should be used.

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## RAPID METHOD FOR THE ANALYSIS OF RED LEAD AND ORANGE MINERAL

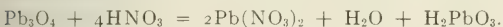
By JOHN A. SCHAEFFER

Received August 4, 1915

In estimating the chemical value of red lead and orange mineral, it is essential that the true red lead,  $Pb_3O_4$ , content or the lead dioxide,  $PbO_2$ , content be determined. Where a large consumption of these products or their purchase on specifications necessitates determination of these constituents at all times the methods in use at present are rather long and involved.

The following method has been perfected for this analysis and gives accurate results in a most rapid manner.

The method depends upon the initial decomposition of the true red lead,  $Pb_3O_4$ , with nitric acid, according to the following reaction:<sup>1</sup>



The  $H_2PbO_3$  or  $PbO_2$  is then decomposed with hydrogen peroxide as follows:<sup>2</sup>



The excess of standard hydrogen peroxide used is then titrated with a standard potassium permanganate solution.

In carrying out the analysis, one gram of the red lead or orange mineral is treated with 15 cc. of nitric acid, having a specific gravity of 1.2. The mixture is then stirred until the first reaction given is complete, as evidenced by an entire disappearance of all red color. There is then added from a calibrated burette or pipette exactly 10 cc. of dilute hydrogen peroxide, made up of a mixture of 1 part of 3 per cent hydrogen peroxide solution to 3.5 parts of water. It has been found that a 10 cc. automatic pipette, with a three-way stop-cock, is excellent for delivering a definite volume of hydrogen peroxide solution at all times. After the addition of the hydrogen peroxide solution, the resultant mixture is stirred until almost complete decomposition of the lead peroxide has been effected, as shown by the second reaction. The decomposition is completed by the addition of a little hot water and stirring. The contents of the beaker, after complete decomposition and solution of the lead peroxide, are diluted with hot water to about 250 cc. volume and titrated directly with a standard potassium permanganate solution having an iron value of 0.005. The solution is titrated to a faint pink permanganate color.

A blank titration is then made on exactly the same

volume of the hydrogen peroxide solution and nitric acid in the same manner.

The difference between the number of cc. of potassium permanganate solution required for the blank titration and the number of cc. required for the red lead titration is the amount required for the hydrogen peroxide

	34.2
34.1	
	34.0
33.9	
	33.8
33.7	
	33.6
33.5	
	33.4
33.3	
	33.2
33.1	
	33.0
32.9	
	32.8
32.7	100.00
99.69	
	99.38
99.07	
	98.77
98.46	
	98.16
97.85	
	97.55
97.24	
	96.94
96.63	
	96.32
96.01	
	95.71
95.40	
	95.10
94.79	
	94.49
94.18	
	93.88
93.57	
	93.26
92.96	
	92.66
92.35	
	92.04
91.74	
	91.43

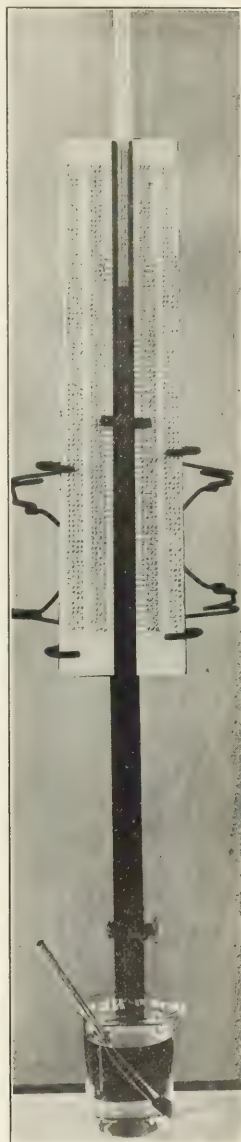


FIG. 1

necessary for the complete decomposition of the lead peroxide. This difference multiplied by 3.058 gives the percentage of red lead according to the following proportion:

$$2Fe : Pb_3O_4 = 0.005 : X, \text{ or, } 112 : 685 = 0.005 : X$$

whence,  $X = 3.058.$

<sup>1</sup> Treadwell and Hall, "Analytical Chemistry," Vol. II, p. 623.

<sup>2</sup> *Ibid.*, Vol. I, p. 53.



To determine the lead peroxide present the difference is multiplied by 1.067, according to the following proportion:

$2\text{Fe} : \text{PbO}_2 = 0.005 : X$ , or,  $112 : 239.0 = 0.005 : X$   
whence,  $X = 1.067$ .

These calculations have been arranged in a series so devised as to permit the direct reading of the red lead percentage. The basis of the calculations depends on the fact that each cc. of potassium permanganate solution (iron value, 0.005) is equivalent to 3.058 per cent of true red lead; or, each 0.1 cc. is equivalent to 0.3058 per cent true red lead on a one gram sample.

A red lead or orange mineral having a 100 per cent true red lead content requires 32.7 cc. potassium permanganate solution of the above strength.

The calculation, therefore, arranges itself as follows: Each 0.1 cc. on the selected burette represents 0.3058 per cent true red lead. The number 32.7, being equivalent to 100 per cent, occupies an analogous position on the chart. A representative portion of the series is shown alongside Fig. I. The series is continued upward in steps of 0.1 and downward in steps of 0.30 and 0.31 to such points as are required for the red lead usually examined.

Fig. I is an illustration of the apparatus in use; calculations have been continued upward to 40.0, or to that point where the hydrogen peroxide solution used is of such strength that 10 cc. of the hydrogen peroxide solution require 40 cc. of the potassium permanganate solution. Calculations have been continued downward to 9.48 per cent true red lead content.

In using the series the chart is attached to the burette by a screw clamp. A blank determination is first made on the hydrogen peroxide solution and the value found is placed opposite zero on the burette. In the analysis of the red lead the value is then read off directly. As a hypothetical case we will use hydrogen peroxide solution with a blank titration of 34.1 cc. In the analysis of the red lead or orange mineral 4.2 cc. of potassium permanganate solution are required for a final titration value. The calculation shows the difference between the two readings to be 29.9 cc. or multiplied by 3.058 equals a true red lead percentage of 91.43 per cent. Comparing this with the series of calculations we find 4.2 cc. from the value 34.1 to be 91.43 per cent.

Should it be preferred to determine directly the lead peroxide content, the calculation will be based on the value 0.1067 for each 0.1 cc. on the potassium permanganate burette. It is understood that the division must be made to correspond with each 0.1 cc. on the burette. It is always advisable to make several blank determinations each day where this analysis is constantly carried out, or when only occasionally used a blank titration should be made before the final analysis. The strength of the hydrogen peroxide solution will vary from time to time when a stock solution is kept on hand, but the permanence of the potassium permanganate solution renders the method accurate over a long period of time.

## CHROMIUM OXIDE ANALYSIS

By ALLAN J. FIELD

Received August 13, 1915

The chief difficulty in chromium oxide analysis is in the fusion. Sodium peroxide affords the quickest and most complete fusion but has the disadvantage of attacking nickel, copper and platinum crucibles. As nickel crucibles contain iron they cannot be used if iron is to be determined in the chromium oxide.

The method of heating the crucible as suggested by Treadwell-Hall<sup>1</sup> has given very good results. He recommends using a porcelain crucible which is placed inside a larger porcelain crucible and heated for fifteen or twenty minutes over a small flame. The fusion is dissolved out with water and evaporated down to dryness to remove the last traces of peroxide.

The author has found the following modifications to afford decided advantages. Instead of using a porcelain crucible, which interferes with the silica determination, a platinum crucible is used. The sodium peroxide has very little action on the platinum crucible when it is placed inside of a porcelain crucible and heated with a low flame. After making twenty determinations there was a loss of only 0.019 g. in the weight of the platinum crucible, which loss took place principally in the cleaning of the crucible after each determination.

Another modification is that it is not necessary to evaporate the solution to dryness to decompose all peroxide as 20 minutes' boiling decomposes it entirely; in fact after 10 minutes' boiling no peroxide could be found.

(To detect peroxide the following test was worked out: To 5 cc. of a 1 per cent solution of sulfanilic acid add one drop of the sodium chromate solution, which should be neutral, then 2 drops of a 5 per cent oxalic acid solution. If peroxide is present a pink color develops immediately. This is a very delicate test and will show minute quantities.)

For the determination of chromium the following volumetric method has given excellent results: One-half g. of the finely powdered chromium oxide is mixed intimately with 3 g. of sodium peroxide in a platinum crucible. The crucible is placed inside of a larger porcelain crucible and heated with a low flame so that the mixture just melts. After heating in this manner for 20 minutes all the chromium is converted into soluble sodium chromate. The fusion is dissolved out with water and the solution boiled for 15 or 20 minutes. If there is any iron it will be insoluble and should be filtered off before proceeding further. The solution is made neutral with hydrochloric acid and diluted to 250 cc. in a graduated flask. An aliquot portion of 100 cc. is taken out into a liter Erlenmeyer flask, 10 cc. conc. hydrochloric acid are added and the solution diluted to about 300 cc. with water. About 3 g. of potassium iodide are added and the liberated iodine is titrated with *N*/10 sodium thiosulfate.

The gravimetric determination of chromium as oxide does not give very accurate results probably due,

according to G. Rothaug,<sup>1</sup> to the precipitate absorbing atmospheric oxygen during ignition with the formation of chromic chromate ( $\text{Cr}_2\text{O}_3 \cdot 3\text{CrO}_3$ ). If ignition takes place in a current of hydrogen, accuracy will be secured.

In the absence of sulfates the author used the following method to check up the volumetric method and obtained results agreeing very closely. The sample is fused as in the volumetric method, then dissolved out and made neutral with acetic acid, 0.5 cc. glacial acid is added in excess and the solution diluted to 400 cc. The chromate is precipitated at the boiling temperature with a dilute solution of barium acetate. The barium acetate should be added by drops so as to avoid carrying down some of the barium acetate with the barium chromate. After the precipitate settles it is filtered off on a Gooch crucible, washed with dilute alcohol and dried.

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## THE SOLUTION OF THE CERIUM GROUP OXIDES BY CERTAIN ACIDS

By W. S. CHASE

Received September 13, 1915

As is well known, the oxides of the trivalent rare earth metals are moderately strong bases, resembling the alkaline earth oxides in that respect. With this fact in mind, one would expect that the addition of a dilute mineral acid to a mixture of cerium group oxides would effect the quick solution of the more basic earths with but slight action on the least basic. If this did occur, the result would be the complete separation of  $\text{CeO}_2$ , which is the least basic of all the rare earth oxides and very resistant to acids. Such a separation, which indeed would constitute a rapid and easy method for the extraction of cerium, might be expected when it is considered that the other oxides present are, for the most part, among the more basic of the rare earth oxides.<sup>2</sup>

Unfortunately, the addition of dilute or even concentrated acid does not produce the expected result, and this must be due to the influence of the  $\text{CeO}_2$ . This substance is practically insoluble even in hot concentrated acids, except sulfuric acid. It possesses the power of combining with the other rare earth oxides, and to this combination is undoubtedly due the failure of acids to react with the mixture of oxides in the manner that might be expected. Another result of this combination is that the  $\text{CeO}_2$ , when thus combined, dissolves readily in acids in which it is otherwise insoluble provided its value in the mixture does not exceed 55 per cent. Therefore, on treating the mixed oxides with acid the basic earths do not rapidly dissolve and the  $\text{CeO}_2$  remain untouched, but, instead, the entire mixture goes into solution at a moderately rapid rate. This behavior is rather remarkable in view of the fact that  $\text{CeO}_2$  itself is practically insoluble, and that the other oxides by themselves will dissolve instantly in a small excess of very dilute acid.

The rate of solution of the mixed oxides can be very

greatly increased by the addition of some substance that will reduce cerium to the cerous condition. Hydrogen peroxide answers this purpose admirably, for not only is the reaction very rapid and complete but there is the added advantage that no other salt is introduced into the solution (as is the case for example when KI or  $\text{FeCl}_2$ , etc., are used).

### EXPERIMENTAL

The rare earth residue obtained after the extraction of thorium from monazite sand was the material used in this work. This residue consists essentially of the oxides of the cerium metals though possibly small quantities of the yttrium elements may be present. No attempt was made to separate the latter as they were not in sufficient quantity to be detrimental in any way. The principal constituent of the mixed oxides was, of course,  $\text{CeO}_2$ , with a value of 52.70 per cent, the others in order of importance being  $\text{Nd}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Pr}_4\text{O}_7$  and  $\text{Sa}_2\text{O}_3$ .

The composition of the ordinary commercial residue is quite constant, the  $\text{CeO}_2$  value for instance fluctuating between 50 and 60 per cent, and in most cases being around the mean of those values. The color of the mixed oxides varies from reddish brown to chocolate, depending on the composition of the sample, ignition temperature,<sup>1</sup> etc. Their solubilities in sulfuric, hydrochloric, nitric and acetic acid of different concentrations were studied, as was also the use of  $\text{H}_2\text{O}_2$  as a reducing agent for  $\text{CeO}_2$ .

The theoretical quantity of acid required to react with 1 g. of sample was calculated on the basis of  $\text{RO}_2 = 55$  per cent,  $\text{R}_2\text{O}_3 = 45$  per cent (about the average composition of the residues handled in this laboratory) and the following figures were thus obtained:

Acid	Sulfuric	Nitric	Hydrochloric	Acetic
Approximate strength.....	96%	70%	38%	99.5%
Cc. per 1-g. sample.....	0.58	1.33	1.7	1.2

**SULFURIC ACID**—As is well known, with a large excess of acid and evaporation to strong fuming, complete solution is obtained. The  $\text{CeO}_2$  dissolves with but slight reduction, so that the solution is of a yellow or yellowish red color due to the ceric sulfate. However, this process is rather tedious, and as it is desirable that the fuming operation be avoided, if possible, the action of  $\text{H}_2\text{O}_2$  along with dilute  $\text{H}_2\text{SO}_4$  was tried.

A few experiments sufficed to show that with a moderate excess of acid diluted as much as 1:10 or more, and a similar excess of  $\text{H}_2\text{O}_2$ , solution is rapid and thorough. For example, 1 cc. each of acid and 30 per cent  $\text{H}_2\text{O}_2$  and 10 cc. of water were added to 1 g. of the oxides and the mixture heated for 3 minutes, by which time solution was complete. This experiment indicates that these oxides are dissolved by dilute  $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$  much more rapidly than by concentrated  $\text{H}_2\text{SO}_4$  alone, and further the fuming nuisance is also avoided.

**NITRIC ACID**—The mixed earths dissolve fairly readily in this acid, which is most efficient when concentrated. However, when diluted, even as much as

<sup>1</sup> Z. anorg. Chem., **84** (1913), 165-189.

<sup>2</sup> Levy, "The Rare Earths," pp. 117, 118.

<sup>1</sup> Levy, "The Rare Earths," p. 119.



1:2, it still acts fairly satisfactorily though somewhat slowly. When the acid alone is employed it is always necessary that a considerable excess be taken, but the quantity of the latter naturally decreases as the size of the sample increases. With the smaller samples, in order to avoid the use of a very great excess of acid, the same should be diluted, which serves to increase the volume enough so that all the acid is not boiled off before complete solution can occur. These points are indicated by the following data:

Sample used Grams	Nitric Acid Parts	Acid water Parts	Used Times theoretical	Total cc. of liquid at start	Minutes required for solution (approximate)
1	1	2	6	24	7
3	1	3	4	48	20
8	1	3	3	60	20
1	1	0	8	10.5	4
5	1	0	6	40	10

The use of  $H_2O_2$ , however, produces results greatly superior, in every way, to those obtained with the nitric acid alone, but especially so in regard to speed of reaction and excess of acid. Solution occurs so quickly and completely that even small samples can be readily dissolved in a slight excess of acid, it being unnecessary to have a considerable volume of liquid at the start, on account of the rapidity of the reaction. The following results indicate the advantages pertaining to the use of  $H_2O_2$ . Practically the same results could be obtained with considerably more dilute acid.

Sample used Grams	SOLUTION Parts $HNO_3$	MIXTURE Parts water	Cc. $H_2O_2$	Total cc. of liquid at start	Minutes required for solution (approximate)
1	1	2	0.5	5	1
3	1	1	1.5	10	1

**HYDROCHLORIC ACID**—The action of this acid about parallels that of nitric, or if anything, it is somewhat more efficient, for although concentrated hydrochloric is only about one-half as strong as concentrated nitric acid, it acts with equal speed. Owing to its lesser concentration a larger volume is required for the same equivalent of acid than with nitric, and it was found that owing to this, a smaller excess of hydrochloric could be used for a given sample than is necessary when nitric is employed; *e. g.*, a 5 g. sample which was readily dissolved by 4 times the theoretical amount of hydrochloric acid, required 6 times the theoretical quantity of nitric acid to effect its solution.

This behavior with hydrochloric acid was quite unexpected, the writer having always been under the impression that these oxides were practically insoluble in it except in the presence of a reducing agent. The chloride ion apparently acts in the latter rôle, free chlorine being given off during the reaction.  $H_2O_2$  acts with hydrochloric acid in exactly the same manner as with nitric.

**ACETIC ACID**—The acid used contained 99.50 per cent  $HC_2H_3O_2$  and proved to be a very unsatisfactory solvent for these oxides. Its action is extremely slow, so that long boiling, with the consequent necessity of a large excess of acid, is necessary in order to obtain the solution of even a moderate amount of material: *e. g.*, a 1-g. sample was treated with 20 times the required quantity of acid, the mixture heated to boiling, then placed on the steam bath and frequently

shaken; after half an hour the residue was filtered off, the filtrate precipitated with oxalic acid, and the oxalates ignited to oxides; this oxide did not exceed more than about 0.05 g. in weight.

Very peculiarly  $H_2O_2$  does not seem to facilitate solution in this case, repeated experiments using large excesses of the peroxide giving no better results than that above noted. As suggested by Dr. W. C. Moore, of the Research Laboratory, this behavior may be due to some reaction taking place between the hydrogen peroxide and the acetic acid itself.

#### SUMMARY

I—This investigation has shown that the cerium group oxides are fairly readily dissolved by sulfuric, nitric or hydrochloric acid, and especially so when the concentrated acids are used, although in the case of the latter two, considerable dilution still permits of satisfactory results being obtained. However, it is necessary to use a considerable excess of the respective acid, and more particularly so if the sample is small and it is required to dissolve it in concentrated acid.

II—Acetic acid was shown to be a very unsatisfactory solvent.

III—The use of hydrogen peroxide makes rapid dissolving of the oxides by a very small excess of sulfuric, nitric or hydrochloric acid, possible even in quite dilute solution. With acetic acid, however, the use of hydrogen peroxide does not produce this favorable result.

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#### A METHOD FOR THE DETERMINATION OF ALCOHOL IN THE PRESENCE OF PHENOL<sup>1</sup>

By J. EHRLICH

Received October 27, 1915

It has been repeatedly observed in this laboratory that the usual method of determining alcohol in the presence of phenol by means of distillation from strongly alkaline solution is by no means exact. Notwithstanding the presence of a large excess of alkali, a bromine test on the distillate invariably indicates that a portion of the alkaline phenate always undergoes hydrolysis, allowing phenol to be carried over.

Inasmuch as tribromophenol or sodium tribromphenate would be expected to have a much higher dissociation constant than phenol or sodium phenate because of the brominated nucleus, it was thought that the conversion of the latter into the former would result in decreased hydrolysis and hence obviate the difficulty referred to above. The method proved to be practicable.

Aqueous solutions (8.6 and 20.0 per cent by volume) of ethyl alcohol were prepared, an accurately standardized bottle pycnometer being used for the determination of specific gravity. Throughout the work solutions were measured and the alcoholic distillates weighed at 25° C. The 50 cc. receiving flask and the 25 cc. and 50 cc. pipettes were found to be relatively correct at 25° C.

<sup>1</sup> Published by permission of the Secretary of Agriculture.

When employing the scheme outlined below the following results were obtained:

No.	8.6% alcohol Cc.	Phenol added Grams	Alcohol found Per cent
1	50	1	8.6
2	50	3	8.6
3	50	10	8.6

No.	20.0% alcohol Cc.	Phenol added Grams	Alcohol found Per cent
4	50	1	20.0
5	50	3	20.0
6	50	10	20.0

In testing the method the phenol was dissolved in 50 cc. strong NaOH solution in the distilling flask to which the known alcohol solution was then added.

#### METHOD

Pipette 50 cc. of sample into a 300 cc. flask containing 30 cc. water. Make strongly alkaline with an excess of strong NaOH solution so that the final volume is about 100 cc. and the odor of phenol is absent. Add glass beads and distil into a 50 cc. graduated flask containing 1 or 2 cc. water. The end of the condenser or adapter should almost touch the surface of the distillate in the receiver, especially at the beginning of a distillation. A drawn-out thistle tube is serviceable in this connection. The flask is lowered as distillation proceeds.

When nearly 50 cc. of distillate have been collected, remove the receiver, dilute with water to mark, shake thoroughly and pipette 25 cc. into another 300 cc. flask containing 30 cc. water. Precipitate the phenol as its tribrom-derivative by adding bromine water, drop by drop, to slight excess while rotating flask. Without delay add normal "hypo" solution (a few drops will be sufficient) to decolorize (*i. e.*, to remove the free bromine excess) and finally add enough strong NaOH solution to dissolve the white tribromphenol into its phenate, and then a decided excess of alkali. The final volume will be less than 100 cc. After the addition of glass beads distil into the 50 cc. flask as before, dilute to mark and determine density by weighing. The percentage of alcohol in this last distillate multiplied by 2 gives the required figure.

For high concentrations of alcohol a 100 cc. receiving flask may be substituted in the above method and 50 cc. of distillate treated and redistilled. For high concentrations of phenol the method is directly applicable since the amount of phenol which passes over during the first distillation is small. If the original phenol content is low, the first distillation may be omitted. In this case the 50 cc. sample plus 30 cc. water in the 300 cc. flask is treated directly with bromine water to slight excess as shown by color; then add "hypo," alkali, etc., as above and distil into a 50 or 100 cc. flask according to alcohol concentration. Samples high in phenol cannot be treated directly in this manner because the bulky precipitate of tribromphenol prevents thorough mixing while adding the bromine water, making it impossible to perceive when an excess of bromine is present.

The hydrobromic acid formed by the action of bromine on the phenol is neutralized and retained by the alkali.

#### CONCLUSION

The method is seen to be not only accurate in result but extremely simple in manipulation, no filtration or separation being required. The results obtained

demonstrate that a low concentration of bromine acting during a short period of time has no appreciable effect on aqueous ethyl alcohol at room temperature.

The behavior of methyl alcohol when present in phenolic ethyl alcohol mixtures will be investigated in the same way.

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#### THE ANALYSIS OF MAPLE PRODUCTS, VI<sup>1</sup>

##### A Volumetric Lead Subacetate Test for Purity of Maple Syrup

By J. F. SNELL, N. C. MACFARLANE AND G. J. VAN ZOEREN

Received August 20, 1915

The fact that lead subacetate produces a heavy precipitate in genuine maple syrup has been utilized in various ways for the detection of adulteration.<sup>2</sup> In the method here communicated a more dilute solution of this reagent than is employed in any of the older methods is gradually added to the diluted syrup from a burette and the end-point of the titration is determined by means of measurements of electrical resistance in the manner suggested by van Suchtelen and Itano.<sup>3</sup> The method in detail is as follows:

#### SOLUTION

A filtered solution of Horne's lead subacetate of specific gravity 1.033.<sup>4</sup> This solution is to be kept in a bottle connected with a burette and protected from atmospheric carbon dioxide by a soda-lime tube.

#### METHOD

Dilute the syrup with water, boil until the temperature reaches 219° F., and filter through cotton wool. After cooling, dilute 10 cc. to 100 cc. with distilled water and measure 60 cc. of the diluted syrup into a 100 cc. beaker.

Measure the electrical resistance using a dip electrode.<sup>5</sup> Maintaining the temperature constant, add 1 cc. of the lead subacetate solution from the burette, stir well and again measure the electrical resistance. Continue the addition of the subacetate in this manner, 1 cc. at a time, until 10 cc. have been added. Plot the resistances found against the quantities of subacetate solution used. If the syrup is genuine the results of the plot will be two intersecting straight lines. In the 70 genuine maple syrups,<sup>6</sup> to which the

<sup>1</sup> Presented at the 51st Meeting of the American Chemical Society at Seattle, August 31-September 2, 1915. Previous papers of this series: *THIS JOURNAL*, **5** (1913), 740, 993; **6** (1914), 216, 301; **8** (1916), 144. An account of the preliminary experiments leading to the volumetric test is given in Paper V, *THIS JOURNAL*, **8** (1916), 144.

<sup>2</sup> Hortvet, *J. Am. Chem. Soc.*, **26** (1904), 1543; Bureau of Chem., U. S. Dept. Agric., *Circ.* **23** (1903); Jones, Vermont Agr. Expt. Sta., *18th Ann. Rept.*, **1904-5**, p. 322; Thos. MacFarlane, Laboratory Inland Revenue Dept., Ottawa, *Bull.* **120** (1906); Winton and Kreider, *J. Am. Chem. Soc.*, **28** (1906), 1204; McGill and Valin, Laboratory Inland Revenue Dept., Ottawa, *Bull.* **140** (1907); **228** (1911); Ross, Bureau of Chem., U. S. Dept. Agric., *Circ.* **53** (1910); Department of Inland Revenue, Ottawa, *C. G. 994*.

<sup>3</sup> van Suchtelen and Itano, *J. Am. Chem. Soc.*, **36** (1914), 1793.

<sup>4</sup> We make a cold, saturated solution of the subacetate, dilute to approximately the correct density, filter and adjust to exactly 1.033, as measured by a hydrometer.

<sup>5</sup> A suitable form of electrode is described in a paper by Van Zoeren, published in the *Journal of the American Chemical Society*, March, 1916. The rest of the apparatus used by us for the measurements of electrical resistance is described in Paper I of this series (*THIS JOURNAL*, **5** (1913), 740).

<sup>6</sup> These syrups were all collected from the makers in the Province of Quebec, 62 in the season of 1915 and 8 in that of 1914.



method has been applied, the intersections have all fallen between 4.8 and 6.6 cc.

**SPECIMEN PLOT**—The accompanying diagram is a typical specimen of the plots obtained with a pure syrup and with mixtures of the same syrup of equal density made from commercial white sugar.

**THE EFFECT OF TEMPERATURE** Measurements at 20°, 25° and 30° C. with five of the syrups indicate that the particular temperature at which the measurement is made is of no consequence as long as the temperature remains constant during the measurements. The resistances were uniformly higher the lower the temperature but the intersection points did not change.

#### EFFECT OF ADULTERATION WITH SUCROSE SYRUP

Table I gives the results of determinations of, respectively, (1) the "volumetric lead number," *viz.*, the abscissa of the point of intersection of the two straight lines, and (2) the Canadian lead number, upon 20 syrups (10 of which were dark-colored, late-run prod-

TABLE I VOLUMETRIC AND CANADIAN LEAD NUMBERS OF 20 PURE MAPLE SYRUPS AND THEIR MIXTURES WITH CANE SUGAR SYRUP OF EQUAL DENSITY

No.	1—VOLUMETRIC LEAD NUMBERS				2—CANADIAN LEAD NUMBERS			
	100%	90%	80%	70%	100%	80%	70%	60%
1	4.8	4.9	4.8	C	5.35	2.85	2.72	2.23
2	4.9	5.9	9.7	C	1.94	1.40	1.02	...
3	4.9	5.8	4.8	C	2.43	1.44	1.17	...
4	6.0	6.2	5.0	C	2.58	1.68	1.35	...
5	6.1	5.3	4.9	C	1.96	1.14	0.84	...
6	5.4	5.6	4.7	5.4	3.25	1.96	1.53	...
7	5.8	6.0	5.5	C	2.23	1.45	1.11	...
8	5.6	5.1	5.0	C	2.67	1.85	1.10	...
15	6.0	5.3	5.7	C	1.82	1.38	0.99	...
19	6.0	5.3	4.8	C	2.29	1.14	0.99	...
31	5.8	5.8	5.3	C	4.27	2.80	2.38	1.6
32	5.8	6.0	5.9	C	4.44	2.53	2.06	1.5
33	6.0	6.2	5.5	C	3.90	2.46	2.01	1.31
34	5.4	5.5	5.2	C	1.72	1.03	0.59	...
35	5.4	4.8	4.8	C	4.11	2.54	2.23	1.79
36	6.2	6.4	5.1	C	2.56	1.72	1.18	...
37	5.4	5.1	5.0	C	2.21	1.58	0.96	...
38	5.9	5.9	C	4.5	4.76	1.96	1.29	...
39	6.0	5.7	5.9	C	3.70	2.59	2.15	1.65
40	5.3	6.0	5.9	5.5	2.54	1.95	1.31	...

	VOLUMETRIC	CANADIAN
Maximum for pure syrup.....	6.6	5.35
Minimum for pure syrup.....	4.8	1.72
Difference.....	1.8	3.63
Mean for pure syrup.....	5.64	3.04
Variation, per cent of mean.....	31.9	113
Variation, per cent of minimum.....	37.5	211

ucts) and upon mixtures of these with a syrup of equal density made from commercial granulated sugar. In the table a smooth curve on the plot is represented by the letter "C." Such a curve is given by all but 2 of the mixtures containing 60 per cent of maple syrup and by all but 3 of those containing 70 per cent. The two exceptional 60 per cent mixtures give intersections outside the limits (4.8 to 6.6 cc.) found in genuine syrups.

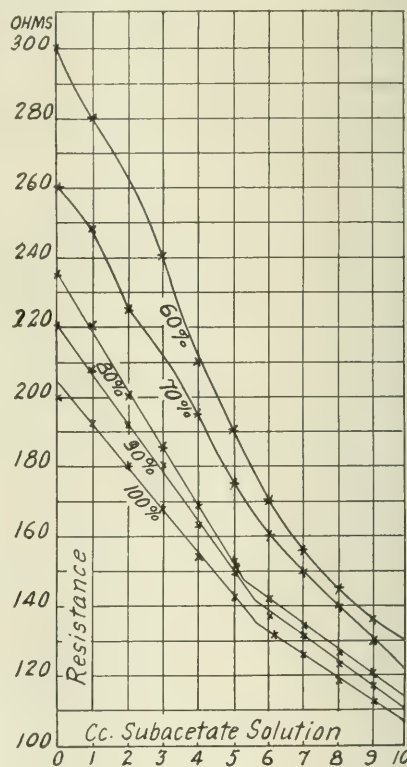
The Canadian standard (minimum) for Canadian lead number is 1.7. Two of the 62 per cent and 6 of the 70 per cent mixtures attain to this standard.

The results of Snell and Scott<sup>1</sup> show (as well as can be shown by the study of so small a number of syrups) that the Canadian lead method has this advantage over all the other current tests, that its value falls off more rapidly than in proportion to the adulteration with cane sugar syrup. The basis of comparison employed by Snell and Scott in their paper appears scarcely applicable to the volumetric lead subacetate test, inasmuch as the 90 per cent mixture frequently,

and the 80 per cent mixture occasionally, gives a higher intersection point than the pure syrup itself. If, however, we assume as a provisional standard for the volumetric lead number the minimum value found in our 70 syrups (*i. e.*, 4.8) it is clear that this test condemns all the 60 and all but 3 of the 70 per cent mixtures, whereas the Canadian lead test, as we have seen, passes 2 of the 60 and 6 of the 70 per cent mixtures and it seems probable from Snell and Scott's work that the other tests, had they been applied, would have made a still poorer showing.

#### RANGE OF VARIATION IN GENUINE SYRUPS

The range of variation of the volumetric lead number among the 70 syrups (4.8 to 6.6) amounts to only 37.5 per cent of the minimum or 31.9 per cent of the



TYPICAL PLOTS FOR A PURE MAPLE SYRUP AND FOR MIXTURES CONTAINING 90 TO 60 PER CENT OF THE SAME WITH CANE SUGAR SYRUP OF EQUAL DENSITY. VARIATIONS IN ELECTRICAL RESISTANCE AS LEAD SUBACETATE SOLUTION IS ADDED

mean (5.64). In the same syrups the conductivity value shows a range of 97 per cent of the minimum or 74 per cent of the mean (125). The volumetric lead number, therefore, appears to have a narrower range than the conductivity value, which, as will be seen by reference to Table V of Paper III, excels all the older analytical values in this respect.

In 28 of the 70 syrups (8 of the season of 1914 and 20 of the season of 1915) the Canadian lead number has been determined. In these 28 samples the three values determined compare as follows:

<sup>1</sup> Paper II of this series, *THIS JOURNAL*, 5 (1913), 993.

	Conductivity Value	Canadian Lead No.	Volumetric Lead No.
Maximum.....	189	7.55	6.6
Minimum.....	108	1.72	4.8
Difference.....	81	5.83	1.8
Mean.....	134	3.22	5.77
Range, per cent of mean.....	60	181	31
Range, per cent of minimum.....	75	339	37.5

**MEASUREMENTS ON NON-MAPLE SYRUPS**—We have applied the method to 5 of the non-maple and compound maple syrups referred to in Paper I, *viz.*, Nos. 7 and 13 of Table VIII—a golden syrup and a syrup made from a pale brown commercial sugar—the latter of which had given a conductivity value within the limits for maple syrup—and Nos. 11, 31 and 33 of Table IX. All five of these syrups gave smooth curve plots.

A compound syrup, a syrup sold as pure but known to be adulterated, and 5 syrups made from raw cane sugars by dissolving in water, boiling to 219° F., and filtering, gave smooth curves. Two other syrups made from raw cane sugars and a sample of raw beet sugar gave breaks at 3.4, 4.1 and 4.2, respectively,—all outside the limits for maple syrups. Two of these syrups had conductivity values (143 and 210) within the limits found in maple syrups. In 3 samples of cane molasses no material change in the electrical resistance (which, of course, was much lower than with maple syrup) was produced by the addition of the 10 cc. of lead subacetate solution.

**TIME REQUIRED FOR THE TEST**—The time required to reboil, filter and cool the syrup and to make the test is about half an hour. The time consumed in the test itself is less than 5 minutes.

#### SUMMARY

I—The volumetric lead subacetate test consists in diluting the syrup to 10 times its original volume and titrating with lead subacetate solution of sp. gr. 1.033, obtaining the end-point by measurements of electrical resistance.

II—The volumetric lead number is the abscissa of the point of intersection of two straight lines on the plot of volumes as abscissae with resistances as ordinates.

III—Seventy genuine Quebec 1914 and 1915 syrups gave volumetric lead numbers ranging from 4.8 to 10.6—a range of 37.5 per cent of the minimum, as compared with 97 per cent for the conductivity value. In 28 of these syrups, the ranges of volumetric lead number, conductivity value and Canadian lead number were, respectively, 37.5, 75 and 339 per cent of the minima.

IV—Seventeen out of 20 syrups containing 30 per cent of sucrose syrup gave smooth curve plots: 18 out of 20 containing 40 per cent sucrose syrup gave smooth curves and the remaining two gave intersections outside the limits for genuine syrups.

V—Of 18 adulterated and non-maple syrups, 12 gave smooth curve plots, 3 gave intersections outside the limits found in genuine syrups and in the remaining (cane molasses) the electrical resistance remained constant.

#### CONCLUSION

If future work by ourselves and others corroborates our experience of its reliability, we believe that, com-

bining as it does the merits of rapidity, narrow range of values in genuine maple syrup and rapid falling off or early disappearance as the syrup is adulterated with cane sugar syrup, this test will prove the most useful single test for purity of maple products yet proposed.

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#### COMPARISON OF LIME REQUIREMENT METHODS

By J. W. AMES AND C. J. SCHOLLENBERGER

Received September 17, 1915

The results presented have been obtained in the soil investigations pertaining to the effects of lime treatment being conducted at the Ohio Experiment Station. An estimation of the lime requirement in relation to effectiveness of applications of lime under different conditions of fertilizer treatment has been made, using several of the methods proposed for this determination.

**METHODS**—The methods used included the Veitch, Hopkins, Hutchinson-MacLennan,<sup>1</sup> MacIntire<sup>2</sup> and Vacuum<sup>3</sup> methods. The Veitch and the Hopkins, which are two of the more generally used methods, are entirely different in principle. The Hutchinson-MacLennan method and that proposed by MacIntire, two of the more recent of the numerous methods which have been published, are somewhat similar, a solution of calcium bicarbonate being the carrier of base in the two latter-mentioned methods. In the Hutchinson method the soil is kept in contact with the bicarbonate solution for 3 hours and a portion of the filtrate is titrated against *N/10* acid, using methyl orange<sup>4</sup> as indicator, to obtain a figure for the amount of calcium absorbed. The MacIntire method differs in that the bicarbonate solution is evaporated in contact with the soil to a thin paste; after transferring to a suitable flask, the excess of calcium carbonate is determined by addition of acid and estimation of liberated carbon dioxide.

**SOILS**—These five methods were compared on soils from a number of variously treated plots from one of the fertility sections of the Wooster farm, located on silt loam soil which is largely derived from sandstones and shales. So far as its history is known, it contains no natural supply of calcium carbonate, and each year it becomes increasingly difficult to secure a satisfactory growth of clover, unless lime is applied. The west half of the plots had been treated with 1875 lbs. per acre of calcium oxide in 1903, and 2000 lbs. of limestone in 1909. The composition of the lime materials applied was such that the equivalent of 5700 lbs. of calcium carbonate had been applied to the limed halves of the plots previous to the time samples were taken from the plots, which was 3 years after the last treatment with lime.

From determinations of calcium carbonate which

<sup>1</sup> *Chem. News*, **110**, No. 2854, Aug. 7, 1914.

<sup>2</sup> *Am. Fert.*, **41**, No. 11, Nov. 28, 1914.

<sup>3</sup> This method was proposed by E. W. Gaither, formerly of this laboratory, and is essentially a modification of the Tacke procedure for estimation of degree of acidity of peat soils. Instead of boiling the mixture of soil and calcium carbonate at 100°, the soil was heated in contact with finely divided calcium carbonate under reduced pressure as in the Marr (*Jour. Agr. Science*, **3**, Part 2, p. 155) procedure for determination of soil carbonates; the carbon dioxide liberated by decomposition of the calcium carbonate by the soil is taken as a measure of the lime requirement.



are available for several of the differently fertilized plots on which lime requirement determinations were made, it is evident that the greater portion of the lime applied has disappeared or no longer exists in the carbonate form.

QUANTITIES OF CALCIUM CARBONATE PRESENT IN THE LIMED HALVES

Plot	FERTILIZER	Lbs. per acre
0	None	150
2	Acid phosphate	225
3	Muriate potash	450
5	Sodium nitrate	875
11	Complete	300
24	Complete, including ammonium sulfate as carrier of nitrogen	None
26	Complete, including bone meal as carrier of phosphorus	250
29	Complete, including basic slag as carrier of phosphorus	300

When tested with litmus paper, all of the soils—the limed soils containing a small amount of lime carbonate residual from application made, as well as the unlimed soils—gave a decided acid reaction. The amounts of  $\text{CaCO}_3$  required for 2,000,000 lbs. (approximately) per acre 6 in. of soil are stated in Table I.

TABLE I—LBS.  $\text{CaCO}_3$  INDICATED FOR 2,000,000 LBS. SOIL

Plot	FERTILIZER	Hopkins	Veitch	MacIntire	Hutchinson	Vacuum
0	None	3440	2000	3550	2925	7300
0	None + Lime	100	Alk.	2250	1700	4900
2	Acid Phosphate	2640	2000	3850	2700	7800
3	Acid Phosphate + Lime	80	Alk.	2400	975	3800
3	Muriate Potash	3240	2000	3550	3025	...
3	Muriate Potash + Lime	200	Alk.	2650	1600	...
5	Sodium Nitrate	3640	1200	3550	2550	6200
5	Sodium Nitrate + Lime	120	Alk.	2500	1250	4225
11	Acid Phos. + Mur. Pot. + Sod. Nitr.	3080	1800	3850	2825	7100
11	Acid Phos. + Mur. Pot. + Sod. Nitr. + Lime	80	Alk.	2500	1375	5900
24	Acid Phos. + Mur. Pot. + Amm. Sulf.	4240	3000	4000	2700	8300
24	Acid Phos. + Mur. Pot. + Amm. Sulf. + Lime	260	200	2850	1475	5700
26	Bone Meal + Mur. Pot. + Sod. Nitr.	2940	2000	3700	2250	7350
26	Bone Meal + Mur. Pot. + Sod. Nitr. + Lime	360	Alk.	2900	1325	4050
29	Basic Slag + Mur. Pot. + Sod. Nitr.	2560	1200	3600	2250	6600
29	Basic Slag + Mur. Pot. + Sod. Nitr. + Lime	150	Alk.	2100	1075	4050
18	Manure	2760	2600	4200	3100	8500
18	Manure + Lime	120	Alk.	2950	1950	5200

The fact that no residual carbonate is present in the soil, and the poor growth of clover on the plot which received ammonium sulfate as the nitrogen carrier, is in accord with the lime requirement indicated by the Veitch and Hopkins methods, since the figures for the unlimed end of this plot are higher than those obtained for any of the other plots, by either of these methods, while the MacIntire, Hutchinson and Vacuum methods each show the highest lime requirement in the case of the manure-treated plot.

A comparison of the figures for the soils where three different carriers of phosphorus (acid phosphate, bone meal and basic slag) have been used, shows a higher lime requirement for the acid phosphate-treated soil by the Hopkins, MacIntire and Hutchinson methods. The Veitch and Vacuum methods give slightly higher results for the bone meal plot, while the Hutchinson method gives the same figure for both the bone meal and basic slag plots. With this one exception, all the methods indicate a lower requirement for the basic slag plot. The figures by those methods which show a lower requirement for the basic slag and bone plots agree with the growth of clover on the unlimed ends of these plots, since a more satisfactory stand of clover is secured on these plots than on the plot where acid phosphate is the carrier of phosphorus.

The variations shown by several of the methods

indicate the possible usefulness of some of these methods for comparative purposes where different soil treatments have been made. For the soils which have been limed, but with amounts which were evidently too small, since the growth of clover on the limed halves of the plots indicates that they will be benefited by additional quantities, the MacIntire, Hutchinson and Vacuum methods have, no doubt, given a better indication of the optimum quantity of lime necessary to make conditions satisfactory for the growth of leguminous plants.

If either the Hopkins or the Veitch test were used to obtain a figure for the limed soil's requirement, the results would lead to erroneous conclusions, because the Veitch method indicates that the limed halves of all the plots are alkaline, excepting the one where ammonium sulfate has been used; and the Hopkins test has shown a very small requirement for the limed halves of the plots, the largest amount of calcium carbonate required, according to this test, being 360 lbs. per acre. The results obtained by the Hutchinson, MacIntire and Vacuum methods are much higher than those by either the Hopkins or Veitch test for the soil which has been limed.

While the figures obtained for the unlimed soil by the several methods do not exhibit the wide variation that is found for the limed soil by the Veitch and Hopkins methods as compared with the other methods, there are appreciable differences indicated. Excepting the ammonium sulfate-treated plot, the results for the unlimed soil are uniformly lower by the Veitch test. In some instances there is a very close agreement between the Hopkins and MacIntire results, although in the majority of cases the Hopkins and Hutchinson methods agree more closely. The results by the Veitch method for Plots 24 and 26, which have received different carriers of phosphorus and nitrogen, correspond to those secured by the Hutchinson method. In the case of the manure-treated soil, the results by the Veitch and Hopkins methods are practically the same.

The Vacuum method shows a much larger amount of lime required than is indicated by the other methods, and it may be that for non-calcareous soils the figures closely approximate the actual amount of calcium carbonate required. However, for many soils naturally supplied with calcium carbonate and which gave an alkaline reaction with litmus, results by this method indicate a further need of lime, the amount required in many cases being considerably in excess of the amount of calcium carbonate present. This would seem to indicate that the results obtained for lime requirement are probably too high and that the method would not be applicable to soils in general.

In Table II the differences between the results obtained for the limed and unlimed soil of the several fertilized plots is expressed in percentages of the figures for the unlimed soil. Considering to what extent the soils lime requirement has been satisfied following the lime treatment, the results obtained by the Hopkins and Veitch methods exhibit a marked uniformity, although the lime requirement for the un-

limed soil by the Hopkins test is considerably in excess of the amount shown by the Veitch test. The figures show that the decrease in lime requirement as measured by either the Hopkins or Veitch test is quite uniform for all the plots.

TABLE II—PERCENTAGES OF THE ORIGINAL LIME REQUIREMENT SATISFIED BY LIME TREATMENT

SOIL TREATMENT	Hopkins	Veitch	MacIntire	Hutchinson	Vacuum
None.....	97	100	36	41	32
Acid phosphate.....	97	100	37	60	51
Muriate of Potash.....	94	100	25	47	..
Sodium Nitrate.....	96	100	29	50	31
Acid Phos. + Mur. Pot. + Sod. Nitr.....	97	100	35	51	17
Acid Phos. + Mur. Pot. + Amm. Sulf.....	94	93	28	45	31
Bone Meal + Mur. Pot. + Sod. Nitr.....	87	100	21	41	45
Basic Slag + Mur. Pot. + Sod. Nitr.....	94	100	41	52	38
Maunre.....	95	100	29	37	39

The MacIntire and Hutchinson methods exhibit a variation between the soils variously fertilized, the figures by the MacIntire procedure for the majority of the soils showing that a smaller percentage of the lime requirement has been satisfied by the lime treatment previously given the plots.

#### CHANGES IN LIME REQUIREMENT DURING 16 YEARS

A comparison of the lime requirement figures for soil sampled in 1896 and again in 1912 is of interest in relation to changes which have taken place in soil during a period of 16 years. By inspection of results grouped in Table III, it will be noted that, as measured by the Hopkins method, the requirement of the unlimed soil at the earlier period is markedly lower than that obtained by the other methods, while the same soil at the latter date of sampling has a higher requirement by the Hopkins method than by the other methods, excepting the Vacuum method, and in one case the MacIntire method.

The Veitch results being lower at the latter sampling as compared with the earlier sampling are just the reverse of those by all the other methods which have indicated a decidedly increased lime requirement for the soil after a period of 16 years. Although all the methods excepting the Veitch show an increase

TABLE III—COMPARISON OF LIME REQUIREMENT OF SAME SOIL SAMPLED IN 1896 AND 1912

FERTILIZER	Sampled	Hop- kins	Veitch	Mac- Intire	Hutch- inson	Vac- uum
Ammonium Sulfate.....	1896	750	4000	3000	1750	5500
Ammonium Sulfate.....	1912	4240	3000	4000	2700	8300
Ammonium Sulfate + Lime.....	1912	260	200	2850	1475	5700
None.....	1896	625	4000	2700	1575	6100
None.....	1912	3440	2000	3550	2925	7300
None.....	1912	100	Alk.	2250	1700	4900

in the lime requirement for the soil at the latter date as compared with the earlier sampling, the Hopkins method indicates a much greater increase than the other methods. In direct contrast to the lower results by the Veitch method for the soil at the later date compared with results by the same method for the first sampling, is the fact that for the soil when first sampled, the Veitch method gave higher indications than the Hopkins, MacIntire or Hutchinson methods.

It should be stated that the determinations on the soil collected in 1896 and that in 1912 were made by each of the methods used, at the same time, so that the differences found cannot be attributed to factors introduced by variations in the procedure employed.

Many changes have taken place in the soil during 16 years. Following the deeper plowing and better cultivation the soil has received since the 1896 sampling, the physical condition of the soil and its organic content will have been affected to an extent sufficient to cause the variations observed in the lime requirement of the old and new soil by the several methods.

#### INFLUENCE OF VARIATIONS IN METHOD ON RESULTS

It may be pointed out that these methods for the determination of a "Lime Requirement" are empirical in nature, and comparatively slight variations in procedure affect the results obtained markedly. Thus, the Veitch method is much affected by the degree of clarity of the extract—the clearer the extract the lower the lime requirement, and a method of filtration removing every trace of suspended clay might possibly show a zero requirement in a great number of cases where the usual procedure indicates a considerable lime requirement. On the other hand, all soils do not settle to the same extent when allowed to stand over night, and a comparatively small amount of suspended clay will prevent any appearance of a pink color on boiling, although calcium hydroxide solution in quite measurable quantity is added directly to the boiling solution. For this reason, it was thought best to employ filtration.

Ten grams of soil were weighed into a porcelain dish, wet with sufficient water to give about 50 cc. of liquid after the standard lime water had been added and evaporated on the steam bath as rapidly as possible, stirring once or twice before the mass is dry. It was then washed into a 100 cc. Jena flask with 100 cc. water, shaken occasionally for 15 to 30 minutes, and allowed to stand over night. The contents of the flask were shaken and poured onto an S. & S. 18 cm. folded filter; the first 30 or 40 cc. were rejected, the next 50 cc. collected, a few drops of phenolphthalein added, and immediately boiled down to about 5 cc. in a Jena beaker. A distinct pink color was taken to indicate alkalinity, but in cases where the color was only faint, the result was recorded as doubtful and the experiment repeated.

The Hopkins method will not give the same indications if another salt is substituted for KNO<sub>3</sub>. In this work, 100 g. air-dry soil were shaken with 250 cc. N KNO<sub>3</sub> for 3 hours, using a shaking machine, then filtered immediately, 125 cc. pipetted off, boiled and titrated with N/10 NaOH, using phenolphthalein. The factor 2.5 was used.

The method proposed by MacIntire is quite sensitive in this respect; the directions call for evaporation "to a thin paste," but higher results are obtained

TABLE IV—LIME REQUIREMENT BY MACINTIRE METHOD. LBS. CaCO<sub>3</sub> PER 2,000,000 LBS. SOIL

C. in 100 cc.	TREATMENT	CaCO <sub>3</sub>
10	Evaporated to thin paste immediately.....	7500
10	Evaporated to dryness immediately.....	8200
10	To thin paste immediately, to dryness next morning.....	8900
10	Let stand over night, to dryness next morning.....	8100
20	Evaporated to thin paste immediately.....	5750
20	Evaporated to dryness immediately.....	6300

if the evaporation is carried to dryness. The results also vary with the time required for the evaporation, even when it is carried to the same stage (see Table IV).



It should be noted that the soil used in this experiment had a rather high requirement, and that if the requirement as determined when using 10 g. soil to 100 cc. of solution was the correct figure, 20 g. of the soil should be more than sufficient to exhaust 100 cc. of the  $\text{Ca}(\text{HCO}_3)_2$  solution. As a matter of fact, only about three-fourths of the total amount of  $\text{CaCO}_3$  was decomposed by the 20 g. charge. The soils under investigation showed a requirement of about one-third the total calcium carbonate in 100 cc. bicarbonate solution when 20 g. of soil were used; the evaporations were carried to dryness as rapidly as possible, and stirred several times meanwhile. The residual  $\text{CO}_2$  was determined by the Marr method.

The Hutchinson method seems to be affected to some extent by allowing the soil and  $\text{Ca}(\text{HCO}_3)_2$  solution to remain in contact for a period longer than 3 hours. Thus, a determination in which 40 g. soil was shaken with 200 cc.  $\text{Ca}(\text{HCO}_3)_2$  solution for 3 hours indicated a calcium absorption of 3025 lbs. per acre; 100 g. of the same soil shaken with 500 cc. of the same bicarbonate solution for 3 hours, then allowed to stand over night, on titration showed a requirement of 3600 lbs. per acre. The soil used for this experiment was from plot treated with muriate of potash. The bicarbonate extract of the soil showed but a faint trace of chlorine, no potassium, but traces of sodium and magnesium. The calcium in the bicarbonate extract by permanganate titration was only about 0.4 cc. lower than the figure obtained by direct titration with acid, both being on the  $N/10$  basis. This shows that with the Hutchinson method interchange of bases plays but a very subordinate part and the chief factor is absorption. The method will sometimes show a lime requirement in the case of a soil which contains a great excess of carbonate.

For this work, 20 g. soil to 200 cc. solution was the rule, the air in the bottle was displaced by  $\text{CO}_2$ , the bottle securely stoppered, shaken for 3 hours, immediately filtered, and 100 cc. of the filtrate titrated with  $N/10$   $\text{HCl}$ , using methyl orange; 100 cc. of the original solution was titrated in the same way.

The Vacuum method, it will be noticed, invariably shows the highest figures for the lime requirement; this is doubtless because the conditions of the method are such that the decomposition of  $\text{CaCO}_3$  by the soil can proceed to a maximum without hindrance.

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### THE ACTIVITY AND AVAILABILITY OF INSOLUBLE NITROGEN IN FERTILIZERS AS SHOWN BY CHEMICAL AND VEGETATION TESTS<sup>1</sup>

By F. R. PEMBER AND BURT L. HARTWELL

Received July 30, 1915

Since 1908 the Agricultural Experiment Station of the Rhode Island State College has conducted vegetation tests in pots under greenhouse conditions to ascertain the availability of the water-insoluble

nitrogen of certain brands of commercial fertilizers collected in the state, and in various nitrogenous substances, such as Kanona tankage, rape meal, castor pomace, etc.

Until the season of 1910, this station had employed no means, except the vegetation test, for differentiating between the organic nitrogen of one brand of commercial fertilizer and that of another. In March, 1910, the directors of the New York, New Jersey and New England Stations adopted the alkaline permanganate method<sup>1</sup> as a means of distinguishing between the more or less active forms of the water-insoluble organic nitrogen of mixed fertilizers.

The Rhode Island Station, having already secured results by the vegetation method showing a wide variation in the availability of the water-insoluble nitrogen of certain commercial fertilizers, submitted to Mr. C. H. Jones, for activity tests by the alkaline permanganate method, some of the same nitrogenous materials as were used in the vegetation tests and he, without knowing the vegetation results, secured a close agreement.<sup>2</sup>

#### I—EFFECT OF SEASON ON PLANT GROWTH

In carrying on vegetation tests at different seasons of the year, it was felt that the season and different soil conditions might have a very important influence upon the relative growth of a plant or different kinds of plants. With this in view two experiments were conducted: the first from November 11, 1910, to February 15, 1911, and the second from February 23, 1911, to May 30, 1911; thus 96 days elapsed between planting and harvesting. In both experiments, 6-inch galvanized iron pots were used, each containing 1 lb. of soil and 6.5 lbs. of a medium fine, fresh-water beach sand. Oat and rye plants were grown in pots having the same mixture of sand and soil, and oats alone were grown in a mixture of the same sand and a different soil: otherwise the treatment of all the pots was the same, with the exception of the nitrogenous material which was added to furnish 0.1 g. of nitrogen per pot except where the amount of blood was doubled. All of the pots received 3 g. of potassium sulfate and 8 g. of acid phosphate. The mixture of sand and soil was changed in each pot for the second experiment so that the two were identical in every way except for the season of year in which they were conducted.

It will be seen from the weights of the dry tops as given in Table I that the plants growing from February 23rd to May 30th made a greater growth in every instance than those growing from November 11th to February 15th under late fall and early winter conditions. The per cent of nitrogen in the dry tops of the first experiment was enough larger, however, than that in those of the second experiment to make the total amount of nitrogen recovered in the tops much alike in the two experiments having the same treatment.

<sup>1</sup> Report on Nitrogen, C. H. Jones, Referee, Association of Official Agricultural Chemists. Proceedings of the Twenty-seventh Annual Convention, 1910.

<sup>2</sup> "The Availability of Insoluble Nitrogen in Certain Commercial Fertilizers," B. L. Hartwell and F. R. Pember, THIS JOURNAL, 8 (1911), 584.

<sup>1</sup> Contribution 217 of the Agricultural Experiment Station of the Rhode Island State College.

Plants having the double amount of blood showed a marked increase in yield and nitrogen recovered over those having half as much, while plants having their nitrogen in the form of garbage tannage, or fertilizer No. 2 were unable to recover in their tops any more nitrogen than those receiving no nitrogen in the manures.

The rye plants were unable to make as great a growth as the oats under the same condition, but the relative

growth in all of the pots. The average weight from the no-nitrogen pots was 36.2 g. of dry tops as compared with 49.2 g. from those receiving blood, or a difference of 13 g.

Since there was very little lack of nitrogen in the soil, as shown by the oat crop, and as the millet had the benefit of any nitrogenous residues left by the oats, together with a like nitrogen application as in the first experiment, the weights of the two crops are taken

TABLE I—SHOWING THE RELATIVE AVAILABILITIES OF NITROGEN FOR DIFFERENT PERIODS, CROPS AND SOILS

SOURCE OF NITROGEN	Dry Topp			N in Dry			Dry Topp			Availability	Dry Topp			N in Dry			Dry Topp			Availability	Dry Topp			N in Dry			Dry Topp			Availability		
	Grams	I	II	Per cent	I	II	Grams	I	II		Grams	I	II	Per cent	I	II	Grams	I	II		Grams	I	II	Per cent	I	II	Grams	I	II			
Zone	8.39	9.39	0.89	0.86	0.0746	0.0807				0	0	0	6.64	8.84	0.84	0.69	0.0557	0.0678				4.35	6.20	1.23	0.77	0.0335	0.0477			0	0	0
Seed	16.6	10.92	0.88	0.76	0.0894	0.0839							9.50	9.94	0.90	0.77	0.0632	0.0731				4.35	6.57	1.26	0.86	0.0567	0.0573					
10	10.52	13.73	0.85	0.76	0.0894	0.1043	80	80	80	10.74	13.14	0.86	0.74	0.0923	0.0972	80	80	80	6.91	13.13	0.82	0.68	0.0382	0.0887	80	80	80					
8	8.92	13.65	1.10	0.86	0.0981	0.1173							10.39	13.87	0.95	0.74	0.0987	0.1026				6.91	8.13	1.40	0.88	0.0967	0.0715					
blood	13.18	16.15	0.99	0.83	0.1304	0.1340	289	109					14.86	17.76	0.88	0.74	0.1307	0.1314	170	169		9.18	11.11	1.30	0.87	0.1193	0.0966	155	173			
(doubled)	13.80	13.78	0.92	0.99	0.1269	0.1364							14.76	17.82	0.90	0.77	0.1328	0.1372				8.31	10.60	1.42	0.94	0.1180	0.0996					
garbage	8.49	10.66	0.91	0.77	0.0772	0.0820							6.59	9.50	0.87	0.73	0.0733	0.0693	0	6	359	5.59	5.69	1.37	0.89	0.0491	0.0506	-20	-26			
tankage	8.65	10.40	0.89	0.79	0.0769	0.0821				16	8		6.95	10.37	0.88	0.73	0.0611	0.0757				4.16	5.72	1.25	0.85	0.0520	0.0486					
No. 1	10.44	12.64	0.89	0.75	0.0929	0.0948				93	56		9.26	12.47	0.82	0.70	0.0759	0.0837	44	50		4.99	7.79	1.35	0.86	0.0637	0.0721	28	28			
fertilizer	7.62	9.26	1.08	0.79	0.0822	0.0731	-41	-47					5.97	9.70	0.94	0.79	0.0561	0.0766	-14	13		3.75	6.88	1.31	0.85	0.0491	0.0584	-17	9			
No. 2	7.45	10.43	0.96	0.80	0.0715	0.0834							6.26	10.92	0.95	0.74	0.0594	0.0808				4.13	6.38	1.28	0.89	0.0528	0.0567					

growth in comparison with 80, as representing the increase in yield of the plants receiving the smaller amount of blood over those to which no nitrogen was added, was much the same in all.

II—STANDARD OF COMPARISON FOR NITROGEN  
AVAILABILITY TESTS

The results in Table II are from vegetation tests conducted in 8-in. Wagner pots containing about 2 lbs. of an air-dry, light, sandy loam soil, which, previous to liming in preparation for the experiment, had been deficient in available nitrogen under field conditions. The water-insoluble nitrogen used, aside from that in the blood, came from brands of commercial fertilizers sold in New England in 1910, which by the alkaline permanganate method showed a wide range in activities.

The oats grew from November 11, 1910, to March 6, 1911. The same pots were replanted June 10th with Japanese millet, which grew until August 25th.

TABLE II—POT TESTS ON SOIL DEFICIENT IN NITROGEN

SOURCE OF NITROGEN	AIR-DRY TOPS Weight in Grams						Availability for Oats and Millet	Activity by Alkali Permanganate Methods
	Oats			Millet				
None.....	42.0	48.5	44.0	37.5	35.5	35.5	0	..
Fertilizer 517.....	53.5	48.0	..	37.5	47.5	..	50	70
Fertilizer A 2.....	56.5	54.0	..	42.0	43.0	..	65	39
Fertilizer 10.....	51.0	47.0	..	41.5	36.0	..	27	30
Fertilizer C14.....	57.0	50.0	..	40.0	41.0	..	51	34
Fertilizer G 3.....	49.5	54.0	..	44.0	41.0	..	52	37
Dried Blood.....	50.0	52.0	54.5	48.0	50.5	49.0	80	..
Dried Blood and Extra Phos- phorus.....	53.0	53.0	..	44.0	46.5	..	..	..
Dried Blood, doubled.....	55.0	57.0	..	61.0	61.0	..	..	..
Sulfate of Soda.....	61.0	54.0	..	49.0	52.0	..	..	..

Before each planting all of the pots received optimum amounts of potassium and phosphorus in sulfate of potash, Thomas slag and acid phosphate. The accompanying nitrogen application was 0.1 g. of nitrogen per pot. The soil proved to be only slightly deficient in nitrogen with the first crop, oats, for the average weight of dry tops from the no-nitrogen pots was 44.8 g., and from those receiving blood, 52.2 g., a difference of only 7.4 g. The millet made a fair

together in calculating the relative availability of the water-insoluble nitrogen in the various fertilizers. This is based arbitrarily on 80 as representing the increase in growth caused by the dried blood (when nitrate of soda is used as the standard of comparison the increase caused by it is usually considered as 100).

It will be seen readily that by this method of expressing the availability of the water-insoluble nitrogen in the various nitrogenous substances, the greater the difference in growth between the plants receiving no nitrogen and those receiving dried blood, the less the effect of small differences in growth will be upon the degree of availability. When the difference is just 80 g., then a variation of 10 g. in growth would change the availability only 10 points while with a difference of only 40 g., a variation of 10 g. in yield would change the availability 20 points.

As might be expected, considering that the plants were grown in soil in which there was no marked deficiency of nitrogen, the activity values (per cent of the insoluble nitrogen which is "active" or is liberated by the alkaline permanganate method from the water-insoluble nitrogen) for the fertilizers were not in close accord with the vegetation results.

### III—VEGETATION TESTS OF FERTILIZERS SOLD IN RHODE ISLAND

Vegetation experiments have been conducted during the last four winters, using one or more brands of commercial fertilizer from most of the different companies doing business in the state of Rhode Island, to test the availability of the water-insoluble nitrogen as compared with nitrogen in blood, and also to show to what extent the availability as shown by the oat crop agreed with the activity obtained by the alkaline permanganate or neutral permanganate method. Most of the fertilizers chosen for the tests were those containing at least 0.75 per cent water-insoluble nitrogen having an activity of less than 65 by the alkaline permanganate method. The fertilizers were ground fine enough to pass through a 1 mm. sieve and washed free of water-soluble nitrogen. The washing at first



was by decantation but finally all of the material was placed on the filter and washed until 15 cc. of distilled water per gram of the original material had been used. After the washed material had been

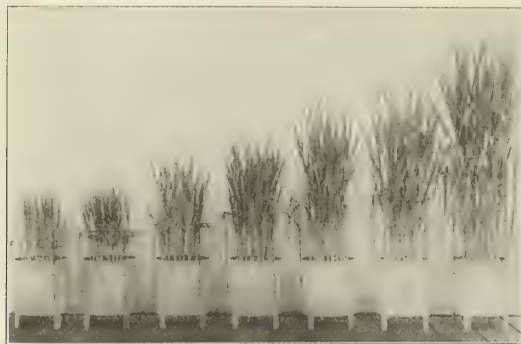


FIG. 1.—GROWTH OF OATS WITHOUT NITROGEN, AND WITH EQUAL AMOUNTS OF NITROGEN IN THE INSOLUBLE PART OF CERTAIN FERTILIZERS AND IN OTHER UNEXTRACTED MATERIALS

allowed to dry at a low temperature, it was resifted and analyzed for nitrogen. Dried blood, the same as used for the standard, was subjected to the same grinding and washings as the fertilizers; another sample of blood was also included for comparison with the first. Two pots having aluminum nitride were included in the experiment.

Eight-inch Wagner pots were used for these tests. The soil medium was composed of about 15 lbs. of fine, dry sand, and 3 lbs. of dry soil which under field conditions was deficient in nitrogen. Optimum amounts of potassium and phosphorus were provided in sulfate and muriate of potash, potassium magnesium carbonate, acid phosphate and Thomas slag. For the first three winters each pot received 20 g. of well-rotted, finely chopped hay. In 1911 the sand and soil were inoculated with 250 cc. of a garden soil extract and the nitrogen application was 0.3 g. per pot.

Oats were planted in all of the pots December 27, 1911, and harvested April 9, 1912, just as the best plants were ready to put out heads. Fig. 1 shows the general condition of the plants the week before they were harvested.

The results of the tests appear in Table III. In selecting the 1911 brands for repetition in 1912, those showing in most cases a rather marked difference between the availability as determined by the oat plant and the activity by the alkaline permanganate method, were chosen. The 1912 crop was allowed to mature and produce grain.

It will be seen by Table III that the relative availability as shown by the two vegetation tests agrees quite closely; that the addition of the extra phosphorus was not needed and that the nitrogen in the water-extracted blood was just as available as that in the unextracted. Aluminum nitride proved to be utterly worthless.

The relative amounts of nitrogen determined in the dry tops correspond very closely with the relative

availability obtained from the weights of the dry tops. The amount of nitrogen in the dry tops of the 1912 oats grown with fertilizer No. 17 was found to be 0.9594 g., representing a relative availability of 63. In securing the relative availability based upon the nitrogen in the 1912 oat plants, the amounts given in Table V for the plants receiving blood and no nitrogen respectively were used.

For purposes of comparison an availability for the oat plant of less than 45 as related to one of 80 for dried blood is in the present paper considered as representing inferior water-insoluble nitrogen. Likewise an activity of less than 80 by the neutral, and less than 55 by the alkaline method is herein considered as indicating inferior material. With these bases of comparison it will be seen in Table III that 7 of the 18 fertilizers were shown by the oat plant to have inferior insoluble nitrogen, of which 4 were also detected by the alkaline method and 5 by the neutral method. The alkaline method rated fertilizer 51 as poor with an activity of 50 while the availability was only 46; and the neutral method rated fertilizer 53 as poor, with an activity of 79 while the availability was 49.

TABLE III.—VEGETATION TESTS ON FERTILIZERS SOLD IN RHODE ISLAND

SOURCE OF NITROGEN	Weight of Air-Dry Oat-Tops Grams	Dry Nitrogen in Tops Gram	Relative Amount of Nitrogen Recovered	Repeats (1912) Dry Tops Grams	Availability of Nitrogen for Oats		Activity by Permanganate Methods	
					1911	1912	Alkaline	Neutral
None	6.5	7.06	0.1016	0	0	0	69	86
Fertilizer 85	21	21	...	...	66	...	71	92
Fertilizer 36	21	23	...	...	70	...	79	87
Fertilizer 988	15	16.5	0.2125	40	60.5	61.5	42	52
Fertilizer 34	26.5	23.5	...	...	93	88	84	97
Fertilizer 936	23	22.5	...	...	74	...	77	90
Fertilizer 75	19	19.5	0.2902	60	...	...	88	72
Fertilizer 958	16.5	17.5	...	...	58	...	66	83
Fertilizer 67	16	18.5	...	...	49	...	67	80
Fertilizer 26	15	15.5	0.2532	51	...	40	65	83
Fertilizer 17	17	21	...	...	70	67	57	63
Fertilizer 982	11.5	12	...	...	40	41	24	20
Fertilizer 997	8.5	8	0.102	12	33	34.5	8	9
Fertilizer 72	13	13	...	...	...	...	29	52
Fertilizer 28	14	13	...	...	...	...	32	50
Fertilizer 51	17	15	0.2198	42	60.5	55.5	44	47
Fertilizer 77	13.5	11.5	...	...	27	...	49	70
Fertilizer 50	8	9.5	0.1176	14	35.5	34.5	10	11
Fertilizer 53	18	16.5	...	...	49	...	60	79
Aluminum Nitride	5.5	7	...	...	—	...	...	...
Dried Blood	25.5	23	24	...	80	...	80	...
Dried Blood+extra Phosphorus	25	24	...	...	...	81	...	...
Dried Blood, water-extracted	24	25.5	...	...	...	82	...	...
Dried Blood, triple amount	61.5	60.5	...	...	...	246	...	...
Dried Blood, another sample	30.5	27.5	...	...	...	102	...	...
Nitrate of Soda	43.5	39.5	...	...	...	158	...	...

Table IV gives the activities secured by the alkaline and neutral permanganate methods,<sup>1</sup> and, with certain modifications of the latter by Mr. R. A. Lichtenthaler, on the water-insoluble nitrogen in the commercial fertilizers used in the previous vegetation tests. The modifications of the neutral permanganate method consisted of changes in the reaction of the solution by the addition of  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$  or  $\text{H}_2\text{SO}_4$  and in the time and temperature of digestion. All of the activities obtained by means of the different modifications were lower than those obtained by the unmodified method; in most cases they were much lower.

<sup>1</sup> J. P. Street, "Note on the Neutral Permanganate Method for the Availability of Organic Nitrogen," *THIS JOURNAL*, 4 (1912), 437.

Digesting for 18 hours at 25° C. with Na<sub>2</sub>CO<sub>3</sub> present gave the highest activities of the various modifications but the average of the activities was 19 points lower than those secured by the unmodified method of digesting at the temperature of boiling water for half an hour, while digesting for 30 minutes at 40° C. reduced the average of the activities 26 points, and digesting for 30 minutes at 60° C. without Na<sub>2</sub>CO<sub>3</sub> present reduced the average of the activities 37 points. Substituting CaCO<sub>3</sub> for Na<sub>2</sub>CO<sub>3</sub> and digesting for 30 minutes at 40° C. reduced the average of the activities 32 points, or 6 points lower than where Na<sub>2</sub>CO<sub>3</sub> was used under otherwise like conditions. Acidifying the solutions to N/100 with H<sub>2</sub>SO<sub>4</sub> and digesting for 30 minutes at 40° C. gave the lowest activities of any of the modifications, while digesting for 18 hours at 25° C., otherwise under like conditions, raised the average of the activities more than 10 points.

IV—SECOND TESTS OF TANKAGES, ETC.

After the vegetation results of the water-insoluble nitrogen in certain fertilizers sold in the state in 1911 had been obtained, the manufacturers were informed of such result as concerned them individually, and in certain cases, where the availability was very low, the manufacturer sent a sample of tankage direct from his factory, claiming such sample was the basis of his 1911 goods. These, with tankages collected in the state in 1912, and also samples of castor pomace, rape meal, and Kanona tankage, were subjected to the same treatment as the commercial fertilizers. Blood from the same lot as used in 1911 for the standard was again used, and pots receiving their nitrogen in calcium nitrate and American Calcium Cyanamid were included. The nitrogen application was 0.6 g. per pot except where the extra amount of blood was used. Two of the pots to which dried blood was applied each received 7.22 g. C. P. CaCO<sub>3</sub> to ascertain whether the effect of the Calcium Cyanamid might be attributable in part to its calcium, and two others

pendent upon Kanona tankage for their nitrogen were unable to make a very satisfactory growth, showing an availability of 39 compared with 80 for blood. The 0.6 g. of nitrogen per pot in American Calcium Cyanamid proved quite injurious to the young plants, but they were able to recover sufficiently to make a fair growth.

Accepting the same arbitrary standard as used in the preceding experiment for classifying the water-insoluble nitrogen in fertilizers, we find that of the 18 fertilizers tested by the oat plant as given in Table V, 6 were shown to have inferior insoluble nitrogen. The alkaline method detected 3 of the poor ones and condemned 2 more with availabilities of 54 and 50. The neutral method detected the 6 poor ones, and also condemned 4 more which had availabilities of 81, 74, 54 and 50, respectively.

In conducting the vegetation availability test of the water-insoluble nitrogen in some of the fertilizers collected in 1913, 5 g. of corn meal was added to each pot with the regular fertilizer application and rotted hay, except that two of the pots to which the

TABLE V—SECOND SERIES OF TESTS ON TANKAGES, ETC

the state in 1912, and also samples of castor pomace, rape meal, and Kanona tankage, were subjected to the same treatment as the commercial fertilizers. Blood from the same lot as used in 1911 for the standard was again used, and pots receiving their nitrogen in calcium nitrate and American Calcium Cyanamid were included. The nitrogen application was 0.6 g. per pot except where the extra amount of blood was used. Two of the pots to which dried blood was applied each received 7.22 g. C. P. CaCO <sub>3</sub> to ascertain whether the effect of the Calcium Cyanamid might be attributable in part to its calcium, and two others																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																</
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(a) Tops from one pot.

received a half more than the regular application of potassium and phosphorus. Oats were planted in all of the pots on January 20, 1913, and were allowed to mature seed.

It will be seen in Table V that the plants receiving their nitrogen in ordinary tankage, castor pomace, rape meal or some of the fertilizers were as good, if not better, than those receiving it in blood. The amount of nitrogen in the dry tops was determined in certain cases. Here again the amount of nitrogen found in each case bore about the same relation to the standard as the weight of the dry tops. Plants de-

standard amount of blood was added, received neither the corn meal nor the hay. The addition of corn meal was made after considering the results obtained in the preceding experiment, in which plants having their nitrogen in the form of rape meal or castor pomace made larger growths than with any other form of organic nitrogen used. It seemed probable that the increase in growth was due to the greater amount of carbonaceous material rather than because the nitrogen was in the form of vegetable instead of animal matter.

For some unexplained reason the oat plants having the standard application of blood together with rotted hay and corn meal made the very unsatisfactory growth of 49 grams of dry tops per pot while under like con-



ditions, but without the rotted hay and corn meal, the weight was 67 grams per pot, which is nearly the normal weight for oat plants having that amount of nitrogen in blood when grown under like conditions for the same period, as shown by the preceding and succeeding experiments. Although the plants having extra blood made a good increase over those having the standard amount, namely 82 compared to 49 grams dry tops per pot, the growth was about half the usual amount. Plants receiving their nitrogen in nitrate of soda made a normal growth.

In Table VI are given the weights of the dried tops cut May 11, 1914, and their relative availabilities, also the activities by the alkaline permanganate

TABLE VI—TESTS ON 1913 FERTILIZERS, ETC.

SOURCE OF NITROGEN	Weight of Air-Dry Oat-Tops Grams	Availability of Nitrogen for Oats	Activity by Alkaline Permanganate Method
None.....	24 19.5	0	68
Fertilizer 310.....	60.5 62.5	70	56
Fertilizer 319.....	48 52.5	30	48
Fertilizer 426.....	24 26.5	6	63
Fertilizer 328.....	63.5 55.5	66	55
Fertilizer 329.....	51.5 54.5	55	48
Fertilizer 341.....	38 37	28	52
Fertilizer 350.....	38 31.5	23	53
Fertilizer 355.....	48.5 50	48	59
Fertilizer 356.....	46 50	46	61
Fertilizer 367.....	63.5 58.5	69	75
Fertilizer 371.....	58.5 61	67	57
Fertilizer 373.....	50 48.5	48	66
Fertilizer 382.....	42.4 43.5	37	54
Fertilizer 391.....	41.5 43.5	36	42
Fertilizer 397.....	47 44	42	54
1146 Mass.....	53.5 46.5	50	48
Dried Blood.....	49 49	48	..
Dried Blood + extra Potash and Phosphorus.....	52.5 52.5	54	..
Dried Blood without corn meal or hay.....	67 67.5	80	..
Dried Blood (triple amount).....	85 78.5	106	..
Nitrate of Soda.....	91.5 98.5	129	..

method. Inasmuch as the standard blood plants having rotted hay and corn meal mixed with the soil made such a poor growth, those grown with the same amount of blood but without the rotted hay and corn meal were taken as the standard.

On the bases stated previously, the oat plant condemned 6 of the 16 fertilizers tested as having inferior water-insoluble nitrogen. The alkaline method rated 4 of the 6 as poor, and condemned 2 more with activities of 48 and 54 which had availabilities of 55 and 50. It is interesting to note that the latter had an availability of 49 when tested at the Massachusetts Agricultural Experiment Station.

#### V—TESTS OF 1914 FERTILIZERS, ETC.

In conducting the vegetation test for the availability of the water-insoluble nitrogen in certain of the fertilizers collected in 1914, the use of rotted hay and corn meal was dispensed with, except where used in certain pots to determine their toxic effect, if any. Four of the fertilizers tested in 1913, Nos. 310, 328, 356 and 426, were included, in order to ascertain to what extent the growth of the oat plants was influenced in the last experiment by the addition of rotted hay and corn meal. Dr. R. N. Brackett, Clemson College, S. C., A. O. A. C. referee on nitrogen, kindly furnished us with samples of tartar pomace, Nos. 5 and 6 nitrogenous manures and beet root manure, from the same materials as furnished the different stations in 1914 for nitrogen determinations and activities by the alkaline and neutral permanganate methods.

All of these materials were given the same laboratory treatment as the fertilizers. Two pots were included having oxamide,  $C_2O_2N_2H_4$ , prepared by Dr. John E. Bucher, Brown University; likewise two with soot for use in plant growing, an English importation.

The fertilizing materials with  $CaCO_3$  at the rate of two tons per acre were added to the soil medium December 31, 1913, and the oats planted January 13, 1914. The weights of the dry oat tops and relative availabilities are given in Table VII, also the activities by the alkaline and neutral permanganate methods. The activities for the material received from Dr. Brackett were obtained by averaging those reported from the different stations. Fig. II shows the growth of oats without nitrogen and with an equal amount of nitrogen in blood and in the water-insoluble part of the A. O. A. C. material.

It will be seen by the weights of the dry tops that the addition of the extra potassium and phosphorus to the standard blood pots did not change the growth



FIG. II.—GROWTH OF OATS WITHOUT NITROGEN AND WITH AN EQUAL AMOUNT OF NITROGEN IN BLOOD AND IN THE INSOLUBLE PART OF OTHER MATERIALS

of the plants, while the addition of rotted hay increased the growth of the dry tops about 10 g. per pot, and rotted hay and corn meal nearly as much. Where a triple amount of the corn meal (15 g.) was used without any rotted hay, the growth was depressed about 10 g. per pot. Furthermore, by comparing the weights of the dry tops for fertilizers Nos. 310, 328, 356 and 426 in Table VII with those in Table VI it appears that with only one exception, fertilizer No. 328, the combined weights of the dry tops for the two pots were a little larger in the first trial. It is interesting to note that oxamide, which is insoluble in water, ranks between blood and nitrate of soda as a source of nitrogen for the oat plant.

On the bases previously stated, it will be seen in Table VII that of the 20 fertilizers tested by the oat plant, 11 were found to contain inferior insoluble nitrogen. Of these the alkaline method detected 6 and failed on 2 more by only two points or less either way.

neutral method detected 8 of the 11 poor ones and 1 good one as poor. The oat plant showed the nitrogen in the material from Dr. Brackett to be of inferior quality: the alkaline method rated 3 having inferior nitrogen, while the neutral method condemned but 1.

TABLE VII—TESTS OF 1914 FERTILIZERS, ETC.

SOURCE OF NITROGEN	Weight of Air-Dry Oat-Tops Grams	Availability of N	Activity by Permanganate Methods Alk.	Neut.
ilizer 506.....	12.5 10	0	56	76
ilizer 512.....	41 48	43	70	87
ilizer 513.....	35 32	29	50	73
ilizer 525.....	20 21	12	63	89
ilizer 536.....	47 51.5	49	55	86
ilizer 547.....	60 59.5	63	70	86
ilizer 548.....	73.5 69	70	10	74
ilizer 575.....	37.5 42.5	37	55	89
ilizer 584.....	43 47	44	55	88
ilizer 591.....	63 59	64	58	88
ilizer 592.....	41.5 44	41	50	74
ilizer 598.....	19 20.5	11	40	74
ilizer 605.....	57.5 54	51	65	88
ilizer 606.....	32 34	28	50	65
ilizer 310.....	57.5 59.5	61	68	89
ilizer 426.....	23.5 22.5	15	48	77
ilizer 328.....	63 64.5	68	63	64
ilizer 356.....	42.0 48.5	44	59	78
ar Pomace.....	11.5 13	1	35	60
5 Nitrogenous Manure.....	28 35	26	57	86
6 Nitrogenous Manure.....	16 16	6	49	80
Root Manure.....	11.5 10.5	0	23	85
.....	57 52	56	..	..
inde. $\text{CO}_2\text{N}_2\text{H}_4$ .....	91.5 91.5	104	..	..
d Blood.....	70 76.5	80	..	..
d Blood + extra Potassium Phosphorus.....	72 74	80	..	..
d Blood + Rotted Hay.....	83 84	93	..	..
d Blood + Rotted Hay + 5 Corn Meal.....	81.5 82	91	..	..
d Blood + 15 g. Corn Meal.....	63 65.5	68	..	..
d Blood (triple amount).....	161 158	191	..	..
ate of Soda.....	100 105	118	..	..

## SUMMARY

—Rye and oat plants grown during late fall and early winter conditions did not make as large a growth as those grown after midwinter for the same period under otherwise the same conditions, but the amount of nitrogen removed in the tops of the plants was much the same in both experiments.

—Although the rye plants did not make as large a growth as the oat plants, the relative growth was much the same with those having like treatment.

—Plants having their nitrogen added in the form of garbage tankage or aluminum nitride made no larger growth than those to which no nitrogen was added.

—Nitrogen in water-extracted blood proved just as available to the oat plant as that in the unwashed blood.

—Plants securing their water-insoluble nitrogen from animal tankage made fully as large a growth as those receiving it in blood.

—The water-insoluble nitrogen in castor pomace and rape meal proved excellent sources of nitrogen for the growth of oat plants while Kanona tankage proved to be quite an inferior source of nitrogen.

—An application of 0.6 g. nitrogen in Cyanamid (5 lbs. of nitrogen per acre) proved toxic to the young plants but they were able to overcome the toxicity and make a fair growth.

—All the water-insoluble nitrogen in the material received from Dr. Brackett, A. O. A. C. referee on fertilizers, proved to be of inferior value when subjected to the plant test.

—The nitrogen in soot had an availability of 56 compared with that in blood at 80.

10—Nitrogen in oxamide produced plant growth about equal to the average produced by that in blood and in nitrate of soda.

11—Lower activities, secured by modifications of the neutral permanganate method, in general agree no better with the availabilities than those secured by the unmodified method.

12—Of the 56 fertilizers tested, not only by the oat plant but also by the alkaline and neutral permanganate methods, 24 were found to contain water-insoluble nitrogen having an availability of less than 45 as compared with blood nitrogen at 80; of these, 13 were actually classed as inferior by having an activity of less than 55 by the alkaline permanganate method, and 3 more were practically so classed, their activities being only one to two points higher: 2 having availabilities of only 54 and 50 were condemned by activities of 51 and 41. None was condemned by the alkaline method which proved to have a high availability.

13—The neutral method, on the basis of activities of less than 80, detected 19 of the 24 inferior ones and three more having availabilities of only 54, 50 and 49, but unfortunately condemned three with the satisfactory availabilities of 81, 74 and 68.

14—Concerning the A. O. A. C. inferior nitrogenous material, distributed for cooperative work in 1914, the inferiority of 3 of the 4 samples was detected by the alkaline method, whereas only 1 of them was detected by the neutral method.

15—It will be seen that about the same percentage of the inferior samples was detected by the two methods, but that the neutral method condemned some samples which proved to have satisfactory availabilities according to the vegetation tests.

16—The percentage of the insoluble nitrogen attacked by the potassium permanganate solution agrees much closer with the relative availability by vegetation test, in case of the alkaline than of the neutral method.

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## A PROPOSED NEW METHOD FOR CITRATE-INSOLUBLE PHOSPHORIC ACID

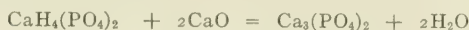
By CHAS. H. HUNT

Received September 24, 1915

There is, perhaps, no other point in the chemistry of fertilizers which has called forth so much discussion and difference of opinion as the method for the determination of citrate-soluble or reverted phosphoric acid by means of neutral ammonium citrate. The present arbitrary method for this determination is unsatisfactory and also unscientific, since the same substance frequently gives different results in the hands of different analysts. If a method could be found that would measure the amount of citrate-insoluble  $\text{P}_2\text{O}_5$  and, indirectly, the amount of citrate-soluble  $\text{P}_2\text{O}_5$ , in which there are not so many factors that influence the results, it would be of great aid to the fertilizer chemist. It is believed that the method proposed below will, in a way, help solve the problem.



It has been known for some time that lime,<sup>1</sup> limestone and other forms of calcium<sup>2</sup> added as a filler or as an essential ingredient in fertilizers, decreases the available  $P_2O_5$ , or, in other words, increases the citrate-insoluble  $P_2O_5$ , and also, that the rate of increase in the amount of citrate-insoluble  $P_2O_5$  is proportional to the amount of added calcium. This fact has been further confirmed in this laboratory. It is believed that the explanation for this is that the calcium, in whatever form it may be, reacts with the mono- and dicalcium phosphate, in the ammonium citrate medium, and changes them into the tricalcium phosphate, a form which is supposed to be insoluble in neutral ammonium citrate, according to the following equations:



Whether a similar reaction takes place in those fertilizers containing no added lime or other forms of calcium the writer is not able to say just now, but it has been noticed that there is a fairly constant ratio between the amount of calcium oxide, determined as such, both in those fertilizers that do and those that do not contain added calcium compounds, and the citrate-insoluble  $P_2O_5$ , as is shown in Table I. The proposed method is based upon some of these facts.

TABLE I

FERTILIZER	Per cent citrate-insoluble $P_2O_5$	Per cent calcium oxide	Ratio citrate-insoluble $P_2O_5$ to calcium oxide
Tankage.....	8.55	20.00	1 : 2.34
Tankage.....	4.85	11.72	1 : 2.41
Tankage.....	4.83	11.50	1 : 2.38
Bone meal.....	16.65	31.80	1 : 1.91
Fish fertilizer.....	1.80	4.06	1 : 2.25
Complete(a).....	10.80	27.34	1 : 2.53
Complete(a).....	6.25	13.78	1 : 2.20
Complete(a).....	8.45	19.35	1 : 2.29

(a) Contains added calcium compounds.

## METHOD

The fertilizer is digested as in the Official method<sup>3</sup> for total phosphoric acid and made up to a definite volume. An aliquot is then taken and an excess of ammonia is added whereupon a white precipitate of tricalcium phosphate is formed.<sup>4</sup> It is then filtered and washed thoroughly with water. The precipitate is dissolved on the filter paper with nitric acid and the phosphoric acid determined in the filtrate according to the volumetric optional method.<sup>5</sup>

From this investigation it has been found that the phosphoric acid is in excess of the calcium that is necessary to combine with it to form tricalcium phosphate, or that all of the phosphoric acid is not precipitated with ammonia. Now the amount of tricalcium phosphate precipitated with ammonia depends upon the amount of calcium present in the fertilizer. Also the amount of citrate-insoluble  $P_2O_5$  depends upon the amount of calcium as has already been pointed out. Now if the amount of calcium governs these two factors then there must be some

definite ratio between the factors themselves. This ratio is shown in Table II.

TABLE II

FERTILIZER	Per cent $P_2O_5$ precipitated with ammonia	Per cent(a) citrate-insoluble $P_2O_5$	Ratio of citrate-insoluble $P_2O_5$ to $P_2O_5$ precipitated with ammonia
Meat and bone.....	22.45	17.39	1 : 1.29
Concentrated fertilizer.....	19.75	10.80	1 : 1.82
Vegetable.....	19.00	13.02	1 : 1.46
Meat and bone.....	15.35	9.10	1 : 1.68
Rose lawn.....	20.90	12.60	1 : 1.68
Lawn fertilizer.....	14.15	9.43	1 : 1.67
Concentrated.....	13.60	9.06	1 : 1.52
Bone meal.....	22.35	16.03	1 : 1.39
Bone meal.....	19.70	14.07	1 : 1.40
Blood and bone.....	14.90	10.04	1 : 1.48
Fish fertilizer.....	8.85	6.47	1 : 1.37

(a) Determined by Official method.

It is seen that the ratio between the citrate-insoluble  $P_2O_5$  and that precipitated with ammonia is about 1 : 1.50. Hence, by dividing the amount precipitated with ammonia by 1.50 we obtain a figure which is approximately equal to the citrate-insoluble  $P_2O_5$  as obtained by the Official method. This ratio varies in some cases. The proposed method does not seem applicable to superphosphates, perhaps due

TABLE III

No.	Fertilizer	Per cent N	Per cent total $P_2O_5$	Per cent water-soluble $P_2O_5$	Per cent citrate-insoluble $P_2O_5$	Per cent $P_2O_5$ New method	Diff.
1413	Bone meal.....	2.98	23.63	17.39	14.96	—2.43	
1595	Bone meal.....	3.02	26.20	18.07	15.36	—2.71	
1518	Bone meal.....	9.94	33.75	27.40	21.53	—5.88	
1540	Bone meal.....	3.73	23.29	15.50	12.70	—2.80	
1530	Bone meal.....	4.08	24.60	16.03	14.90	—1.13	
1281	Bone meal.....	3.94	19.80	14.07	13.13	—0.94	
1314	Bone meal.....	3.98	23.85	16.65	12.27	—4.38	
1619	Bone meal.....	4.06	20.10	11.40	13.26	+1.86	
1716	Bone meal.....	3.66	26.20	18.55	17.06	—1.49	
1730	Bone meal.....	4.07	20.20	15.15	13.00	—2.15	
1774	Bone meal.....	2.63	25.85	15.25	17.00	+1.75	
1791	Bone meal.....	4.31	24.22	16.60	15.70	—0.90	
1669	Bone meal.....	3.85	21.98	13.55	14.40	+0.85	
1687	Bone meal.....	4.08	22.69	16.57	14.80	—1.77	
1511	Tankage.....	4.37	16.10	8.55	10.63	+2.08	
1545	Tankage.....	7.23	10.20	4.85	6.63	+1.78	
1515	Tankage.....	7.07	11.27	4.83	5.63	+0.80	
1668	Tankage.....	7.05	5.19	1.90	2.24	+0.34	
1672	Tankage.....	5.58	16.48	5.29	8.13	+2.84	
1673	Tankage.....	5.27	13.86	9.20	9.10	—0.10	
1676	Tankage.....	7.13	7.20	2.70	4.26	+1.56	
1688	Tankage.....	8.47	3.23	0.79	0.53	—0.26	
1731	Tankage.....	4.72	14.20	8.30	9.56	+1.26	
1767	Tankage.....	7.93	15.13	7.80	9.66	+1.86	
1788	Tankage.....	7.98	13.38	12.35	13.17	+0.83	
1267	Bone and blood.....	4.05	14.98	10.04	9.93	—0.11	
1596	Meat and bone.....	6.48	15.90	9.10	10.23	+1.13	
1728	Meat and bone.....	2.64	24.80	16.90	16.13	—0.77	
1737	Meat and bone.....	7.18	12.65	8.25	8.46	+0.21	
1475	Fish guano.....	13.60	4.50	1.80	1.40	—0.40	
1278	Fish guano.....	7.11	8.97	6.47	5.90	—0.57	
1772	Fish guano.....	9.34	6.15	2.23	3.60	+1.37	
1670	Sheep guano.....	3.77	1.93	0.62	0.82	+0.20	
1671	Sheep guano.....	4.48	3.83	1.37	1.38	+0.01	
1522	Complete fertilizer.....	2.95	15.30	0.18	11.35	9.70	+1.65
1523	Complete fertilizer.....	2.70	20.93	2.95	10.80	13.16	+2.36
1516	Complete fertilizer.....	2.44	19.08	0.08	13.02	12.66	+0.36
1581	Complete fertilizer.....	3.90	11.85	3.10	6.25	7.76	+1.51
1576	Complete fertilizer.....	5.61	21.65	12.60	13.93	1.33	+0.33
1564	Complete fertilizer.....	3.02	13.60	2.45	8.50	8.85	+0.35
1541	Complete fertilizer.....	4.45	14.35	0.71	8.45	9.83	+1.38
1542	Complete fertilizer.....	3.99	14.10	1.40	8.95	9.06	+0.11
1616	Complete fertilizer.....	3.19	10.60	2.26	6.30	6.13	—0.17
1618	Complete fertilizer.....	1.98	12.40	3.45	6.25	7.60	+1.35
1622	Complete fertilizer.....	2.05	14.35	5.25	6.60	8.93	+2.33
1625	Complete fertilizer.....	3.08	16.40	4.65	8.15	10.50	+2.35
1629	Complete fertilizer.....	4.60	11.75	0.96	6.35	7.17	+0.82
1712	Complete fertilizer.....	7.17	10.70	6.20	6.70	0.50	—0.50
1727	Complete fertilizer.....	3.32	16.10	12.05	10.40	—1.65	
1781	Complete fertilizer.....	3.48	8.25	2.58	4.05	5.17	+1.12

to the fact that a large part of the calcium has been removed as water-soluble  $P_2O_5$ . Also, since the amount of citrate-insoluble  $P_2O_5$  in a fertilizer depends upon the amount of material digested,<sup>1</sup> we can readily account for the low results in the case of those fertilizers containing a large amount of water-soluble  $P_2O_5$ , because the amount of material treated has been con-

<sup>1</sup> Wash. Agric. Exp. Station, Bull. 116.

<sup>2</sup> THIS JOURNAL, 6 (1914), 20; also 8 (1913), 933.

<sup>3</sup> U. S. Dept. Agric., Bull. 107, Rev. Ed., p. 2.

<sup>4</sup> Perkin, "Qualitative Chemical Analyses," p. 86, foot-note. If iron is present it will be precipitated here.

<sup>5</sup> U. S. Dept. Agric., Bull. 107, Rev. Ed., p. 4.

<sup>1</sup> Wiley, "Principles and Practice of Agricultural Anal.," Vol. II, p. 136

derably decreased from the amount supposed to be used in making the determination. If the amount of citrate-insoluble  $P_2O_5$  depends upon the weight of material digested, is it not illogical to determine the amount of citrate-insoluble  $P_2O_5$  on a 2 gram sample in the case of bone meal or tankage and make the same determination on the residue of a 2 gram sample, after the water-soluble  $P_2O_5$  has been removed, which, in many cases is much less than 2 grams, in the analysis of a mixed fertilizer containing superphosphate? Results obtained, on the same sample, by the Official method and the proposed new method are given in Table III. While these results vary somewhat, there is yet a degree of uniformity in the variations. Those obtained by precipitation with ammonia are usually lower than those by the Official method in the case of bone meal and generally higher in the case of tankage and complete fertilizers. The plus and minus errors for all classes of fertilizers reported are nearly equal to each other, which fact seems to suggest the possibility of using a different factor for different types of fertilizers. Again, it is noticeable that the differences between those obtained by the Official and proposed methods are, in most cases, no greater than the variations in those obtained by different analysts working upon the same sample, when the Official method is used.

#### SUMMARY AND CONCLUSIONS

I—Lime, limestone and other calcium compounds, added as a filler or as an essential ingredient increases the citrate-insoluble  $P_2O_5$ .

II—The ratio between the calcium oxide, determined as such, and the citrate-insoluble  $P_2O_5$  is fairly constant both in those that do and those that do not contain added calcium compounds.

III—In the proposed method the fertilizer is digested as for total  $P_2O_5$ . An aliquot is made alkaline with ammonia and the  $P_2O_5$  is determined in the precipitate thus formed.

IV—The ratio between the citrate-insoluble  $P_2O_5$  and the  $P_2O_5$  precipitated with ammonia is about 1:1.50.

V—By dividing the amount of  $P_2O_5$  precipitated with ammonia by 1.50 we obtain a figure which is approximately equal to the citrate-insoluble  $P_2O_5$  determined by the Official method.

VI—The plus and minus errors in the final results nearly balance each other. The fact that the errors for bone meal are nearly the same and that for tankage and complete fertilizers are also nearly the same but of opposite quantity, seems to suggest a possibility of using a different factor for different types of fertilizers.

VII—The difference between the results obtained by the Official and proposed methods are no greater than the differences in the results obtained by different analysts working on the same sample when the Official method is used.

VIII—The proposed method claims to be much simpler and less expensive, doing away with the use and preparation of neutral ammonium citrate.

#### LABORATORY NOTES ON THE STANDARDIZATION OF THE MERCURIALS

By DONALD K. STRICKLAND

Received September 7, 1915

Six methods for the estimation of mercury were submitted for study,<sup>1</sup> by the committee on quantitative methods of the division of pharmaceutical chemistry of the American Chemical Society. These included: (1) the Hempel volumetric method for mercurous chloride, bromide and iodide, involving the use of iodine and sodium thiosulfate solutions; (2) a modification of the method of Rupp, in which the metallic precipitate is redissolved in nitric acid and reprecipitate as mercuric iodate, which at length is determined volumetrically by the use of sodium thiosulfate; (3) an electrolytic method;<sup>2</sup> (4) the well-known Rupp<sup>3</sup> formaldehyde method for mercuric salts; (5) a method in which mercuric arsenate is weighed; and (6) a gravimetric estimation as mercurous chloride. These methods were studied with the object of devising methods which might be used as pharmacopoeial methods, where a standard of purity for mercury salts has been required, without offering an official method of examination.

The methods in use to-day for establishing the standard of purity of these chemicals are no doubt quite uniform and the best methods have long since been established in practice. These were pointed out by C. E. Smith.<sup>4</sup> The Hempel method serves best for the analysis of calomel and mercurous iodide, while mercuric chloride, iodide, and ammoniated mercury are analyzed by the method of Rupp. For oxide of mercury the method most serviceable is that of R. Cohn<sup>5</sup> simplified by Rupp and Kraus,<sup>6</sup> which is found in the German Pharmacopoeia.

Recently the effort has been made, not only to determine the purity of these salts as they enter into the manufacturing processes, but also to standardize the finished products, especially in tablets and pills. L. F. Kebler<sup>7</sup> reported the results obtained upon analysis of 30 samples of calomel and of calomel and sodium bicarbonate tablets, 12 of which (or 40 per cent) varied more than 10 per cent from the claim on the label as to the calomel content. In this they were slightly more inaccurate than the average of the samples of tablets on the American market at that time. It was found in this investigation that 36.7 per cent of all the tablets varied more than 10 per cent from the standard claimed. At the same time, 5 tablets of corrosive sublimate, out of 17 examined, were found to vary 10 per cent or more from the declaration on the label. Two antiseptic mercuric chloride tablets were examined, both of which were inaccurate by more than 10 per cent. In this important contribution to pharmaceutical chemistry there are recommended for the estimation of calomel

<sup>1</sup> *Am. Jour. Pharm.*, **83** (1911), 186.

<sup>2</sup> Smith, "Electro-Analysis," 90-94.

<sup>3</sup> *Ber.*, **39** (1906), 3702.

<sup>4</sup> *Am. Jour. Pharm.*, **83** (1911), 311.

<sup>5</sup> *Ber.*, **34** (1901), 3502.

<sup>6</sup> *Ibid.*, **35** (1902), 2015.

<sup>7</sup> *J. Am. Pharm. Assoc.*, **3** (1914), 1069.



three methods: (1) the Hempel, (2) a gravimetric, and (3) a volumetric method, in which the calomel is decomposed with normal sodium hydroxide and the chloride ion is titrated with silver nitrate by the Volhard method. For the corrosive sublimate tablets there was utilized: (1) the Rupp formaldehyde method, (2) precipitation of mercuric sulfide and (3) a method<sup>1</sup> involving the conversion of mercuric chloride into the undissociated mercuric cyanide and the titration of the hydrochloric acid.

J. W. Marden<sup>2</sup> has pointed out the many difficulties arising in the assay of calomel tablets in control work. In part at least, these difficulties are due to the fact that gum acacia, confection of rose, etc., are used in the process of manufacture. A. W. Bender<sup>3</sup> notes similar difficulties in the assay of mercuric iodide tablets. The general result of these difficulties in the assay of mercurial preparations, so far as tablets and pills are concerned, has given rise to numerous proposed methods for their assay, many of which are based upon the fundamental idea of removing by oxidation<sup>4</sup> the sugar which interferes.

R. M. Chapin<sup>5</sup> in a paper on the assay of mercuric chloride tablets points out the difficulties involved in using the Rupp method in the presence of ammonium chloride and gives a modification of the Rupp method to apply to tablets of the Wilson formula.

In the work of standardizing mercurial preparations a very considerable experience has demonstrated that a perfect calomel tablet is prepared by using lactose as the diluent, a 10 per cent solution of cane sugar in distilled water as granulating material and avoiding all use of gums, confections, etc., so that the finished tablet contains only 0.9 per cent lubricant and 1.5 per cent chalk besides the granulation. Tablets made by this method were assayed for some time by the simple method of Hempel, just as if they consisted of mercurous chloride alone. The recent literature above quoted, which shows discrepancies in results obtained in assaying tablets by the Hempel method, has caused me to analyze in the routine work the same samples of calomel products by three methods, given in detail in the experimental part. Since the first method must be correct, the comparison with the other quicker and more commonly used methods is interesting in indicating the error caused by the presence of lactose. The writer is strongly inclined to the view that a tablet which must be boiled with aqua regia to dissolve the calomel, does not represent a suitable product. The results given in Table III show that, for tablets made as stated above, the Hempel method is accurate, and that the method involving the titration of the chloride ion had a tendency to low results.

We have never had cause to doubt the accuracy of the Hempel method when used on mercury protiodide tablets and pills.

For the determination of mercuric chloride, the

hydrogen sulfide method is used for the tablet of Wilson's formula thus avoiding the difficulty presented by possible secondary reactions between ammonium chloride and formaldehyde. The Rupp method is used for all other mercuric chloride tablets. The tablet made according to the Wilson formula is a compressed tablet and by assaying the granulation before compression a closer approach to the desired strength is possible than in the moulded tablet made according to the Bernay formula. In fact this large moulded tablet of brittle nature is very difficult to bring to the same degree of accuracy as is possible for most other tablets: here accuracy is sacrificed for the sake of speedy solubility.

I took occasion before utilizing the Rupp method for standardizing mercuric iodide products to see if the presence of lactose even to the extent of 25 times the weight of the mercuric iodide present caused any interference with the method, but noted none. Provided the alkalinity of the solution is sufficient and the length of time given to the reduction is ample, the estimation proves to be exquisitely accurate.

There is appended, in the experimental part, the methods used with expediency for the various mercury ointments. Our attention was directed to these by the paper of Smith.<sup>1</sup>

#### EXPERIMENTAL

The methods used for obtaining the results upon calomel tabulated are as follows:

##### I—DETERMINATION OF CALOMEL IN SIMPLE GRANULATIONS, TABLETS AND PILLS

(A)—A quantity of material containing 0.324 g. (5 grains) calomel is treated with warm water during a period of about 30 minutes. Filter the undissolved calomel upon a weighed, previously ignited Gooch crucible, wash with water, finally with alcohol, and dry at 100° C., cool in desiccator, and weigh. Heat the Gooch crucible in a Bunsen flame sufficiently to volatilize completely the calomel. The difference in weight represents calomel. In the case of calomel and sodium bicarbonate tablets, the sodium bicarbonate may be estimated volumetrically in the filtrate.

(B)—A quantity of the granulation or a number of the finished tablets or pills containing 0.324 g. (5 grains)<sup>2</sup> of calomel is placed in a glass stoppered Erlenmeyer flask. Add 1 gram of potassium iodide and 5 to 10 cc. water. Rotate the flask a few times and add 30 cc. of *N*/10 iodine solution. Stopper the flask and shake until the mercury has dissolved. Remove the stopper, rinsing it so that the washings flow into the flask and titrate the excess of iodine with *N*/10 sodium thiosulfate solution, using starch solution as an indicator, until the blue color disappears, and lastly with *N*/10 iodine solution until the blue color returns. 1 cc. *N*/10 iodine = 0.02361 g. calomel.

(C)<sup>3</sup>—The material in amount sufficient to contain 0.324 g. of calomel is first disintegrated with 30 cc.

<sup>1</sup> *Apoth. Ztg.*, **24** (1909), 939.

<sup>2</sup> *Am. Jour. Pharm.*, **86** (1914), 511.

<sup>3</sup> *This Journal*, **7** (1914), 753.

<sup>4</sup> A. W. Bender, *Loc. cit.*, and R. I. Grantham, *J. Am. Pharm. Assoc.*, **4** (1915), 442.

<sup>5</sup> *Am. Jour. Pharm.*, **86** (1914), 1.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> In the case of tablets, etc., containing large quantities such as 1 grain. 20 tablets were weighed and powdered and an aliquot weight equivalent to 5 grains of calomel was taken.

<sup>3</sup> J. W. Marden and O. E. Cushman, *Loc. cit.*

TABLE I—ASSAY OF GRANULATIONS OF CALOMEL AND MILK SUGAR BY THE HEMPEL METHOD

(These data are given as indicating the nature of the results. The method was used on 37 products. The average error of the calomel in granulation is 2.23 per cent, while in the finished tablet the average error is .3 per cent.)

Lot No.	Weight Taken Grams	Calomel per Tablet		Error Per cent Calomel	Calomel in Finished Tablet	Error Per cent Calomel
		Prospective Found	Required			
20134	5.0	0.006433	0.00648	-0.7	.....	...
20229	5.0	0.00663	0.00648	-2.8	.....	...
20271	5.0	0.006632	0.00648	-2.5	.....	...
20329	5.0	0.006499	0.00648	+0.3	.....	...
20480	5.0	0.006455	0.00648	-0.4	0.006575	+1.5
20556	5.0	0.006632	0.00648	-2.5	0.006272	-3.2
20884	5.0	0.00649	0.00648	+0.15	0.00662	+2.2
20889	5.0	0.00628	0.00648	-3.1	0.006358	-1.9
21248	6.5	0.00633	0.00648	-2.3	.....	...
20005	2.5	0.01584	0.0162	-2.2	.....	...
20335	1.5	0.0156	0.0162	-3.7	0.0156	-3.7
20600	2.0	0.01584	0.0162	-2.2	0.01568	-3.2
20833	2.0	0.0161	0.0162	-0.6	0.0161	-0.6
21510	2.0	0.0156	0.0162	-3.7	0.01588	-2.0
20583	6.0	0.003213	0.00324	-0.8	0.00312	-3.7
20415	4.0	0.00783	0.0081	-3.3	0.008133	+0.4
20799	0.5	0.03178	0.0324	-1.9	.....	...
20816	1.0	0.0312	0.0324	-3.7	0.0311	-4.0
20062	0.8	0.0633	0.0648	-2.3	0.06351	-2.0
20254	0.7	0.06163	0.0648	-4.9	0.06374	-1.6
20774	0.5	0.06214	0.0648	-4.1	.....	...
20926	0.5	0.1283	0.1296	-1.0	.....	...

TABLE II—ASSAY OF CALOMEL PILLS BY HEMPEL METHOD

Lot No.	No. of Pills Used	Calomel per Pill		Error Per cent Calomel
		Found	Required	
24736	20	0.01612	0.0162	-0.5
24812	5	0.06559	0.0648	+1.2
25842	50	0.00647	0.00648	-0.1
24828	50	0.006445	0.00648	-0.5
24460	10	0.03152	0.0324	-2.7

AVERAGE ERROR OF CALOMEL IN PILLS..... 1.0

TABLE III—COMPARISON OF RESULTS OBTAINED UPON ASSAYING CALOMEL PREPARATIONS BY GRAVIMETRIC, HEMPEL AND CHLORIDE TITRATION METHODS

Lot No.	METHOD (See text)	CALOMEL PER TABLET		Error Per cent Calomel	Calomel in Tablet	FINAL ERROR Per cent Calomel
		Found	Required			
1845	A	0.0631	0.0648	-2.6	.....	...
	B	0.06186	0.0648	-4.5	0.06384	+1.4
	C	0.06044	0.0648	-6.7	.....	...
1849	A	0.00642	0.00648	-1.0	Not det.	...
	B	0.00640	0.00648	-1.2	Not det.	...
	C	.....	0.00648	.....	.....	...
1854	A	0.00654	0.00648	+0.9	Not det.	...
	B	0.006516	0.00648	+0.5	Not det.	...
	C	0.006044	0.00648	-6.7	Not det.	...
1749	A	0.03153	0.0324	-2.7	.....	...
	B	0.03168	0.0324	-2.2	0.03197	-1.3
	C	0.03017	0.0324	-6.8	.....	...
1835	A	0.1859	0.1944	-4.3	.....	...
	B	0.1866	0.1944	-4.0	0.1816	-6.6
	C	0.1821	0.1944	-6.3	.....	...
1601	A	.....	0.1620	.....	0.1561	-3.6
	B	.....	0.1620	.....	0.157	-3.1
	C	.....	0.1620	.....	0.1428	-11.8
1580	A	.....	0.0162	.....	0.01624	+0.2
	B	.....	0.0162	.....	0.01662	+2.6
	C	.....	0.0162	.....	0.01639	+1.2

ter and made slightly acid to litmus with dilute nitric acid; sodium peroxide is added a little at a time, with stirring, until the metallic mercury separates at about 1 gram of sodium peroxide is added in excess. After warming for a very few minutes, the precipitated mercury is filtered onto a Gooch crucible

and washed with water. The filtrate is rendered acid with nitric acid,  $N/10$  silver nitrate is added in excess, and the excess of silver nitrate is titrated with  $N/10$  ammonium sulfocyanate, using ferric alum as an indicator. 1 cc.  $N/10$   $AgNO_3$  solution = 0.02361 g. calomel.

## II—ASSAY OF CALOMEL AND SODIUM BICARBONATE TABLETS AND GRANULATIONS

(1) DETERMINATION OF SODIUM BICARBONATE—A quantity of the granulation or of the powdered tablets equivalent to 5 to 10 grains of sodium bicarbonate is transferred to a covered beaker and about 10 cc. of water are added. Now add a quantity of standard sulfuric acid solution which is in excess of the required amount.

1 cc.  $N/20$   $H_2SO_4$  = 0.0042 g.  $NaHCO_3$ .

For example, if 10 tablets of 0.5 grain (=0.324 g.)  $NaHCO_3$  is used, then  $0.324/0.0042$  or 77.2  $N/20$  acid is required. Now add a volume in excess of the calculated quantity. After effervescence has stopped, transfer by filtration to a 100 cc. graduated flask and wash the beaker and filter paper containing the insoluble calomel with cold water, finally bringing up to the mark.

The excess of acid is titrated in an aliquot of the filtrate. Methyl orange may be used as an indicator for direct titration. If the filtrate is light pink the solution may be boiled and cooled and quite accurately titrated with phenolphthalein.

(2) DETERMINATION OF CALOMEL—Transfer the filter paper containing the calomel to a glass stoppered Erlenmeyer flask and proceed as described above under determination of calomel (Method B).

## III—ASSAY OF CALOMEL AND BISMUTH SUBNITRATE PRODUCTS

Transfer a quantity of the material sufficient to contain 5 grains of calomel to a glass stoppered Erlenmeyer flask. Add sufficient dilute hydrochloric acid to dissolve the bismuth subnitrate and then filter through a hardened filter, retaining as much of the calomel in the flask as possible. Repeat washing by decantation, using dilute hydrochloric acid to remove the bismuth subnitrate, and finally remove the acid by washing with water. Return the filter paper to the flask and proceed with the determination of calomel as outlined above (Method B).

TABLE IV—ASSAY OF GRANULATIONS AND TABLETS OF CALOMEL AND SODIUM BICARBONATE (HEMPEL METHOD) (Forty assays of these formulae gave the same average error as here recorded)

Lot No.	Grams Taken for Assay	GRAM CALOMEL PER PROSPECTIVE TABLET		Error Per cent Calomel	GRAM SODIUM BICARBONATE PER PROSPECTIVE TABLET		Error Per cent	GRAM ACTUALLY IN FINISHED TABLET		Error Per cent	SODA
		Found	Required		Found	Required		Calomel	Soda		
20681	2.5	0.00644	0.00648	-0.6	0.0637	0.0648	-1.7	0.0064	0.0648	-1.2	0.0
20776	2.5	0.00658	0.00648	-1.5	0.0642	0.0648	-0.9	0.00635	0.06233	-2.0	-3.8
21478	5.0	0.00633	0.00648	-2.3	0.0633	0.0648	-2.3	0.00623	0.0634	-4.0	-2.0
21555	5.0	0.00634	0.00648	-2.1	0.0607	0.0648	-6.3	0.00634	0.06065	-2.2	-6.4
20242	2.5	0.0164	0.0162	+1.2	0.0659	0.0648	+1.7	.....	.....	.....	.....
20277	2.0	0.01564	0.0162	-3.4	0.01644	0.0162	+1.5	0.0157	0.0163	-3.1	+0.6
20272	1.5	0.0151	0.0162	-6.8	0.0640	0.0648	-1.2	0.1626	0.0642	+0.4	-1.0
20584	1.5	0.0156	0.0162	-3.7	0.060	0.0648	-7.4	0.160	0.0637	-1.3(a)	-1.7(a)
20456	1.0	0.0618	0.0162	-4.6	0.0617	0.0648	-4.6	0.0637	0.0648	-1.7(b)	-0.0(b)
20852	1.0	0.0644	0.0162	-0.6	0.0623	0.0648	-4.0	0.0626	0.0652	-3.4	+0.6

Average error in calomel and sodium bicarbonate granulations..... 2.68 3.16

Average error in calomel and sodium bicarbonate tablets or pills..... 2.13 1.80

(a) It was estimated that a correction of 3 per cent of the weight of the tablet should be added to the weight calculated in the tablet manufacturing department.

(b) Was raised 2 per cent. This tablet is made by mixing dry granulations and the mixture is assayed before compression.



TABLE V—ASSAY OF CALOMEL AND BISMUTH TABLETS FOR CALOMEL

Lot No.	No. of Tablets Used	CALOMEL PER TABLET FOUND	CALOMEL PER TABLET REQUIRED	ERROR PER CENT CALOMEL
1905	50	0.00646	0.00648	0.3
20486	25	0.00648	0.00648	0.0
20775	50	0.00627	0.00648	-3.2
21579	50	0.00645	0.00648	-0.5

## IV—DETERMINATION OF MERCURY PROTIODIDE (YELLOW) IN GRANULATIONS, TABLETS AND PILLS

The method of analysis used is practically identical with the method described above for calomel.

$$1 \text{ cc. } N/10 \text{ iodine} = 0.032752 \text{ g. HgI.}$$

TABLE VI—ASSAY OF MERCURY PROTIODIDE PRODUCTS (This method gave similar results with 27 products)

Lot No.	Taken for Assay	Gram HgI per Prospective Tablet or Pills Found	Gram HgI in Finished Tablet or Pill Required	ERROR PER CENT HgI	PER CENT HgI
20015	40 Tablets	0.0081	0.0081	...	+1.0
20353	2.5 Grams	0.01617	0.0162	-0.2	
20361	4.0 Grams	0.01045	0.0108	-3.2	-3.3
20709	0.5 Gram	0.03174	0.0324	-2.0	
21324	3.0 Grams	0.01216	0.01296	-6.2	
24720	20 Pills	0.0162	0.0162	0.01637	+1.0
24536	10 Pills	0.0324	0.0324	0.03183	-1.75
24758	24 Pills	0.0081	0.0081	0.00812	+0.2
24870	20 Pills	0.0162	0.0162	0.01626	+0.4
25232	20 Pills	0.0162	0.0162	0.01588	-1.9
25302	10 Pills	0.0324	0.0324	0.03201	-1.2
25414	40 Pills	0.0081	0.0081	0.00801	-1.1
25464	25 Pills	0.01218	0.01296	0.01262	-2.6

AVERAGE ERROR FOR HgI IN GRANULATIONS..... 2.9  
 AVERAGE ERROR FOR HgI IN TABLETS..... 2.1  
 AVERAGE ERROR FOR HgI IN PILLS..... 1.27

## V—DETERMINATION OF MERCURIC CHLORIDE

(A) METHOD OF RUPP—For hypodermatic tablets, compressed tablets and pills, introduce a quantity equivalent to 2 to 4 grains of mercuric chloride, accurately weighed, into a 250 cc. Erlenmeyer flask, dissolve in 25 cc. water, add 2.5 grams of potassium iodide (dissolved in 5 cc. of water), 30 cc. of *N* sodium hydroxide solution (above the quantity required to make the solution alkaline in the first place), and 3 cc. of a 37 per cent formaldehyde solution. Mix thoroughly and set aside for 15 to 30 minutes with occasional shaking. Render the solution acid with 18 per cent acetic acid and mix. Finally add 25 to 50 cc. of *N/10* iodine solution, stopper the flask and shake vigorously until all the mercury has been dissolved. Titrate the excess of *N/10* iodine solution with *N/10* sodium thiosulfate solution using starch as an indicator.

$$1 \text{ cc. } N/10 \text{ iodine solution} = 0.01385 \text{ g. HgCl}_2.$$

For the assay of antiseptic tablets of the Bernay and Wilson formula, we have used the above method for the

TABLE VII—ASSAY OF MERCURIC CHLORIDE PRODUCTS

Lot No.	Kind of Tablet	Method Used	GRAM MERCURIC CHLORIDE FOUND	GRAM MERCURIC CHLORIDE REQUIRED	ERROR PER CENT HgCl <sub>2</sub>
21225	Bernay (small)	V(A)	0.1135	0.1179	-3.7
21225	Bernay (small)	V(B)	0.1133	0.1179	-3.8
21933	Bernay (small)	V(A)	0.1133	0.1179	-3.8
21933	Bernay (small)	V(B)	0.1190	0.1199	+1.0
21725	Wilson (large)(a)	V(A)	0.4728	0.4730	0.0
21725	Wilson (large)(a)	V(B)	0.4810	0.4730	+1.7
21682	Wilson (large)(a)	V(A)	0.4698	0.4730	-0.7
21682	Wilson (large)(a)	V(B)	0.47705	0.473	+0.8
18706	Wilson (large)(a)	V(A)	0.4842	0.47304	+2.4
18706	Wilson (large)(a)	V(B)	0.46694	0.47304	+1.3
21409	Triturate	V(A)	0.00214	0.00216	-0.9
21936	Bernay (large)	V(A)	0.4622	0.473	-2.2
21936	Bernay (large)	V(B)	0.4736	0.4730	+0.1

(a) Compressed tablet.

## (B) DETERMINATION BY WEIGHING THE SULFIDE

The smaller tablet (Bernay, small) contains 1.82 grains and the larger (Bernay and Wilson) contains 7.3 grains of corrosive sublimate. Of the smaller, dissolve 15 in 500 cc. Take an aliquot of 100 cc. for analysis. Of the larger, take 5 tablets in 500 cc. and remove 100 cc. for analysis. Acidify the solution with dilute hydrochloric acid, precipitate mercuric sulfide with hydrogen sulfide and filter on a weighed Gooch. Wash with water, alcohol (10 cc.) and finally with carbon disulfide until all the free sulfur has been removed. Dry at 100° and weigh. Mercuric sulfide multiplied by 1.1756 = corrosive sublimate. It is seen from Table VII that the methods check but that the mercuric sulfide method has a tendency to give high results.

## VI—DETERMINATION OF MERCURIC IODIDE

The method described under V(A) was successfully used for the determination of mercuric biniodide. Before applying it to various products it was tried out upon known quantities in the presence of varied amounts of sugar of milk. It was found that the sugar did not affect the result. Other factors in the reaction

TABLE VIII—INFLUENCE OF VARIOUS FACTORS ON RUPP METHOD FOR MERCURIC IODIDE

Gram HgI <sub>2</sub> Taken	Grams Lactose Taken	Cc. N Alkali Added	Time Min	Cc. N/10 Iodine Used	Grams HgI <sub>2</sub> Recovered	Error Per cent HgI <sub>2</sub>
0.2	3.5	0.5	10	0.38	0.0086	-95.7
0.2	3.5	0.5	40	0.45	0.0102	-94.9
0.2	3.5	13.0	80	7.99	0.1815	-9.2
0.2	3.5	25.0	10-15	8.69	0.1974	-1.3
0.2	3.0	30.0	10-15	8.7	0.1976	-1.2
0.2	5.0	30.0	40	8.8	0.1999	-0.05
0.1	3.0	30.0	30	4.42	0.1004	+0.4
0.1	5.0	30.0	30	4.39	0.0997	-0.3
0.25	1.0	30.0	30	11.06	0.2512	+0.5
0.2	3.5	30.0	30	8.83	0.2006	+0.3
0.2	4.0	30.0	30	8.75	0.1998	-0.1
0.2	5.0	60.0	10	8.8	0.1999	-0.05
0.2	5.0	60.0	20	8.8	0.1999	-0.05
0.2	5.0	60.0	30	8.82	0.2004	+0.2

TABLE IX—ASSAY OF MERCURY BINIODIDE PRODUCTS BY RUPP PROCESS

Lot No.	Taken for Assay	Grams HgI <sub>2</sub> per Prospective Tablet Found	Grams HgI <sub>2</sub> per Tablet Required	ERROR PER CENT HgI <sub>2</sub>	GRAMS HgI <sub>2</sub> IN FINISHED TABLET OR PILL	ERROR PER CENT HgI <sub>2</sub>
20527	4 grams	0.003104	0.00324	-4.2	0.003205	-1.0(a)
21199	5 grams	0.003882	0.00405	-4.1	0.00387	-4.4
21215	1.25 grams	0.01571	0.0162	-3.0	0.0162	
25196	24 pills	0.00804	0.0081	-0.7	0.00804	-0.7
21476	2.5 grams	0.00804	0.0081	-0.7	0.008122	+0.2

(a) Was raised 2 per cent.

were varied. Thus it was observed that the time which the solution stood after alkali and formaldehyde were added was important. The most important factor, however, is the alkalinity of the solution. Unless there is a considerable excess of alkali, present the mercury is not precipitated quantitatively: 30 minutes is the time required.

$$1 \text{ cc. } N/10 \text{ iodine} = 0.02272 \text{ g. HgI}_2.$$

## VII—VOLUMETRIC DETERMINATION OF MERCURY IN OINTMENTS

(A) OINTMENT OF AMMONIATED MERCURY<sup>1</sup>—Heat about 5 grams of the ointment accurately weighed, in a small flask upon a water bath with 25 cc. of 12.5 per cent hydrochloric acid, for 30 minutes. Pour the acid liquid through a small plug of cotton into a 100 cc. graduated flask. Warm the fat once more with 20 cc. of diluted hydrochloric acid and then twice more with 20 cc. portions of water, and add these

<sup>1</sup> This method is readily adapted to the assay of ammoniated mercury itself.

former product and have occasionally checked it by the following method. The tablet made according to Wilson's formula is also assayed as outlined below.

sings to the solution already in the flask. Make the volume up to 100 cc., mix thoroughly and transfer an aliquot of 25 cc. to a 250 cc. glass stoppered Erlenmeyer flask. Proceed as in the assay of mercuric chloride tablets, using 15 cc. 2 *N* sodium hydroxide solution after first rendering the strongly acid solution alkaline.

1 cc. *N*/10 iodine solution = 0.01257 g. ammoniated mercury.

(B) ASSAY OF MERCURIAL OINTMENT<sup>1</sup>—Heat under a reflux condenser about 2 grams of the ointment accurately weighed into a small flask) with 20 cc. nitric acid until all the mercury has dissolved. Pour the acid solution through a plugget of cotton into a 100 cc. graduated flask, and rinse the fat in the flask with the water bath two or three times more, first with a small quantity of diluted nitric acid and then with 10 cc. portions of water. To this solution, add a 1 per cent potassium permanganate solution until the color is permanently pink or until brown flakes separate. Decolorize with a 3 per cent solution of ferrous sulfate and finally make the volume up to 100 cc. To an aliquot of this solution, add a few drops of ferric alum solution, and add an excess of 10 cc. *N*/10 KSCN solution. Titrate the excess with *N*/10  $\text{FeSO}_4$  solution, and finally complete the titration with 10 cc. *N*/10 KSCN. 1 cc. KSCN solution = 0.01 g. mercury.

(C) OINTMENT OF RED MERCURIC OXIDE<sup>2</sup>—This is assayed by the above method using five grams of the ointment.

1 cc. *N*/10 KSCN = 0.0108 g. mercuric oxide.

(D) OINTMENT OF MERCURIC NITRATE is assayed as above described, using 10 grams.

In conclusion, the author wishes to thank Dr. Frederick W. Heyl at whose suggestion the work of standardizing the preparations of these preparations was taken up.

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KALAMAZOO, MICHIGAN

## ELECTROLYTIC DETERMINATION OF MERCURY IN MERCURY OLEATES

By B. L. MURRAY

Received September 13, 1915

Owing to the greasy nature of the numerous oleates of mercury the determination of mercury in them by the older methods of analysis presents some difficulties. The necessary separation and removal of the oleic acid together with the tedious determination of mercury by the usual precipitation methods may perhaps have deterred some from assaying the oleates heretofore. The tendency has been to take the assay rates mostly on faith. In our experience, however, an effort has been made to get away from routine endeavor to make a new application of the electrolytic determination of mercury, already found so useful and satisfactory on other pharmaceutical products. The method that is given below has been in use

<sup>1</sup> This method is not as practical as the one given in the U. S. P.  
<sup>2</sup> In assaying an ointment of yellow oxide of mercury which contains only 0.8 per cent of the mercurial, it was found necessary first to remove the base with ether. It was then possible to obtain results approximately correct, i. e. 0.75 per cent.

in its present form about two or three years and in our hands proves accurate. One would hardly believe quantitative results could be obtained if the mixture is observed just before the electrolysis. The apparatus, a cathode beaker, contains metallic mercury, toluene, hydrochloric acid 10 per cent, and the oleate of mercury. Upon turning on the electric current, however, and almost as if by magic, this heterogeneous mixture readjusts itself into orderly arrangement, and in a short time the mercury that was combined in the greasy oleate lies shining and bright on the bottom of the cathode beaker ready to be weighed.

METHOD—About 0.7 to 1.0 gram of the oleate is weighed directly into a mercury cathode cup (such as a small beaker, capacity 50 to 75 cc.). To this sample there are added 15 to 20 cc. of 10 per cent hydrochloric acid and 15 cc. of toluene. The cathode cup with its contents is placed within a somewhat larger crystallizing dish or beaker which later can be filled with cold water to keep the temperature of the reaction down as desired. After attaching the anode and making the connections in the customary way, electrolysis of this non-uniform mixture is begun, gradually and slowly increasing the current up to 3 amperes, using about 10 minutes to do it. The current (3 to 3.5 amperes at about 8 volts) is then maintained for about 30 minutes, the anode rotating at about 800 revolutions per minute. As the electrolysis continues, the contents of the cup become heated nearly to the boiling point of some of the constituents, thus melting the mercury oleate. It is essential that the mercury oleate should melt. If the liquid in the cathode cup becomes too hot and appears apt to boil over, it should be cooled down by pouring water into the crystallizing dish or other surrounding vessel, but it should not be cooled down below 60° C. When the mercury is all deposited the cathode cup is washed out by siphonation in the customary way with water, after which the metallic mercury is washed with alcohol, dried with ether and finally weighed.

LABORATORY OF MERCK & COMPANY  
RAHWAY, N. J.

## ELECTROLYTIC DETERMINATION OF BISMUTH IN BISMUTH $\beta$ -NAPHTHOL

By B. L. MURRAY

Received September 13, 1915

Another useful application of the electric current in analytic work has been found in the determination of bismuth in bismuth  $\beta$ -naphthol. Aside from the electrolytic portion it is only necessary to ignite the compound in order to remove organic matter and dissolve the bismuth oxide and metal thus formed in nitric acid. The resulting bismuth nitrate is then electrolyzed.

METHOD—A sample of 0.3 gram is weighed into a porcelain crucible and heated very gently to decomposition of the  $\beta$ -naphthol. The crucible is finally heated to the full red heat of a Meker burner for 3 minutes to burn off the last traces of carbon. The residue resulting is yellow in color and is composed chiefly of bismuth oxide together with a small quantity of metallic bismuth. The crucible is placed in a



small beaker and a mixture of 4 cc. of nitric acid (sp. gr. 1.4) and 5 cc. of water is added, after which it is heated on a steam bath to complete solution. The solution is washed with distilled water into a mercury cathode cup, keeping the volume down to 20 cc. The cathode cup is conveniently made from a 50 cc. Erlenmeyer flask. The 20 cc. solution is then electrolyzed under the following conditions:

CURRENT (maximum), 4.5 amperes at 6 volts.  
REVOLUTIONS PER MINUTE, 1000. TIME, 45 minutes.

The initial application of the current is 1 ampere and this is followed by a gradual increase to 4.5 amperes. Some black masses are seen to form, but rapid rotation of the anode prevents the formation of a large quantity and all disappear. When the black masses have entirely disappeared the rotation of the anode is stopped and the cathode is washed with distilled water by siphonation while the full strength of current is on. The electrolyte should be tested for bismuth with hydrogen sulfide. After 2 to 3 washings with water, followed by alcohol, and then by ether, the mercury cathode is weighed. The increase in the weight of the mercury cathode is due to the bismuth which has been deposited on and amalgamated with the mercury.

LABORATORY OF MERCK & COMPANY  
RAHWAY, N. J.

## ELECTROLYTIC DETERMINATION OF MERCURY IN MERCURY SALICYLATES

By B. I. MURRAY

Received September 13, 1915

A rapid and convenient method of determining mercury in mercury salicylates is herewith presented. It consists in a new application of the already well and favorably known electrolytic deposition of mercury. The method here given as used on salicylates of mercury has been in use about two years and has proved reliable.

About 0.3 gram is weighed into the mercury cathode dish and dissolved in 10 cc. of sodium sulfide solution (sp. gr. about 1.18). To this solution are added 20 cc. of 10 per cent potassium hydroxide solution. The mixture is now electrolyzed using a current of 1 ampere at 7 volts until the mercury is completely deposited, usually about one-half hour being required. The anode should rotate about 500 revolutions per minute. After the deposition the electrolyte is decanted, the mercury is washed with water until free from alkalinity, then with alcohol, finally with ether, and then weighed.

LABORATORY OF MERCK & COMPANY  
RAHWAY, N. J.

# LABORATORY AND PLANT

## DETERMINATION OF SULFUR DIOXIDE AND SULFUR TRIOXIDE IN FLUE GASES

By R. J. NESTELL AND E. ANDERSON

Received January 15, 1916

In carrying on some experimental work recently on the gases issuing from the roasting furnaces at one of the large Arizona copper smelters, a rapid, accurate and convenient method for the quantitative estimation of  $\text{SO}_2$  and  $\text{SO}_3$  was of primary importance. The conditions of the work in hand demanded:

1—That the determination of both sulfur oxides should be made upon the same sample of gas.

2—That the time necessary for such determinations should be as short as possible in order that any change in the composition of the gases given off in consequence of varying conditions in the operation of the furnaces might be rapidly and continuously determined by one or two operators.

3—That the apparatus required should not be too fragile or unwieldy in character but capable of convenient transportation to any point of the smelter construction.

4—That the analytical operations necessary should be of such a nature as to admit of ready performance in the field.

In considering the various methods, applicable to this problem, previously proposed or employed by other workers and of which we have found any record, it was evident that no one of them fulfilled all the requirements of the present case.

A scheme proposed by Hawley<sup>1</sup> for separating  $\text{SO}_3$  from  $\text{SO}_2$  seemed to be the most promising. This

consists of humidizing the gases with  $\text{H}_2\text{O}$  vapor to convert any  $\text{SO}_3$  into the white fog of  $\text{H}_2\text{SO}_4$  and then passing them through a double filter paper held between the large ends of two funnels. This mechanically retains the  $\text{H}_2\text{SO}_4$  and allows the  $\text{SO}_2$  to pass through. The  $\text{H}_2\text{SO}_4$  so caught is then determined by placing the filters in a small beaker with about 50 cc. of water, adding a drop of methyl orange and titrating with standard alkali.

In support of the accuracy of this method Hawley gives the following data of tests made by him in which known amounts of  $\text{H}_2\text{SO}_4$  were heated in a hard glass tube and the fume, mixed with air, passed through the filter and the acid so caught determined:

	1	2	3
Grams $\text{H}_2\text{SO}_4$ taken.....	0.064	0.050	0.034
Grams $\text{H}_2\text{SO}_4$ found.....	0.060	0.047	0.032
Per cent found.....	93.7	94.0	94.1

We have made a series of similar tests in which accurately weighed amounts of  $\text{H}_2\text{SO}_4$  were heated in a V-shaped hard glass tube and the volatilized acid drawn with a current of air through the "Hawley" filter. The  $\text{H}_2\text{SO}_4$  remaining in the tube and also that caught on the filter were then determined. This gave exactly the amount of acid volatilized and recovered. The following data were obtained:

	1	2	3	4	5
Grams $\text{SO}_3$ taken.....	0.572	0.0989	0.0708	0.0230	0.0482
Grams $\text{SO}_3$ found.....	0.564	0.0976	0.0692	0.0228	0.0481
Per cent found.....	98.6	98.7	97.7	99.1	99.8

These figures show a considerably higher efficiency for the method than do Hawley's and demonstrate it to be sufficiently accurate for general application.

To apply this method then to our work it was necessary to provide only for the estimation of the  $\text{SO}_2$

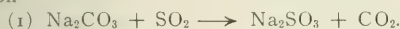
<sup>1</sup> Eng. Min. Jour., Nov. 23, 1912, p. 987.

passing the "Hawley" filter. This might be done by bubbling the gas through a measured excess of standard iodine solution, containing sufficient  $\text{NaHCO}_3$  to neutralize the  $\text{HI}$  and  $\text{H}_2\text{SO}_4$  formed in the reaction between the  $\text{SO}_2$ ,  $\text{I}_2$  and  $\text{H}_2\text{O}$ , and titrating back with  $\text{Na}_2\text{S}_2\text{O}_3$ .

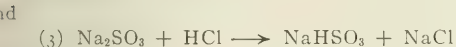
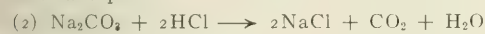
There were certain disadvantages in using this method such as: (1) the necessity of employing two different standard solutions than were required for the  $\text{SO}_2$  estimation; (2) the danger and the necessity of providing against loss of iodine by volatilization on passing hot gases through the solution; (3) the possible presence of reducing gases other than  $\text{SO}_2$ ; (4) the loss of iodine by air oxidation during aspiration (this latter loss is slight).

The iodine method was therefore dismissed from consideration and it was decided to use standard  $\text{Na}_2\text{CO}_3$  as the medium for absorbing the  $\text{SO}_2$ , using a measured excess and titrating back with standard acid. This method presents no difficulties if note is taken of one fact, *viz.*:

The reaction between the  $\text{Na}_2\text{CO}_3$  and the  $\text{SO}_2$ , where the former is in excess, proceeds according to the equation



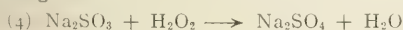
When the solution, then, containing  $\text{Na}_2\text{SO}_3$  and the excess of  $\text{Na}_2\text{CO}_3$ , is titrated with standard acid, using methyl orange as indicator, the two following reactions take place:



$\text{NaHSO}_3$  being neutral to methyl orange, this indicator does not show acidity until the two reactions stated above have been carried to completion. The amount of  $\text{HCl}$  used in this titration is, therefore, not only a measure of the  $\text{Na}_2\text{CO}_3$  remaining unused, but also of the  $\text{NaHSO}_3$  formed in the titration which must be borne in mind when calculating the results.

When, however, a solution of  $\text{Na}_2\text{SO}_3$  is exposed to air, or slightly agitated during titration, and particularly if the air be actually drawn through such a solution, as must be done in these determinations in order to displace all the  $\text{SO}_2$  from the apparatus, some of the  $\text{Na}_2\text{SO}_3$  is oxidized to  $\text{Na}_2\text{SO}_4$ . The sulfate thus formed does not react with the  $\text{HCl}$  in the titration to form an acid salt, and the amount of  $\text{SO}_2$  calculated will be high to that extent.

For this reason all of the  $\text{Na}_2\text{SO}_3$  formed was oxidized, before titration, with  $\text{H}_2\text{O}_2$ —this being first made neutral to methyl orange—the reaction taking place being as follows:



The acid then used in the titration is therefore a measure of the excess sodium carbonate, only, from reaction 1 where the normal salt is formed.

In the usual method of determining the excess of alkali by titration with acid in the presence of the sulfite and with methyl orange as indicator leading to the formation of the acid sulfite, it is evident, from the equation, that each cc. of  $N/10$  alkali consumed

is equivalent to 0.0064 g.  $\text{SO}_2$ , while in the modification we have employed, where the sulfite is first oxidized to sulfate, each cc. of  $N/10$  alkali = 0.0032 g.  $\text{SO}_2$ .

The following tests were made which illustrate clearly the influence of air oxidation above mentioned, a solution of  $\text{SO}_2$  in water being used.

(1)—20 cc. of the  $\text{SO}_2$  solution were titrated with  $N/10$  iodine of which 24.3 cc. were required, showing the  $\text{SO}_2$  content of the solution to be 0.00389 gram per cc.

(2)—20 cc. of the  $\text{SO}_2$  solution were added to a mixture of 25 cc.  $N/10$   $\text{Na}_2\text{CO}_3$  and 5 cc. neutral  $\text{H}_2\text{O}_2$ . Methyl orange was then added and the excess alkali determined with  $N/10$   $\text{HCl}$ . Of this latter 0.65 cc. was required, showing 24.35 cc.  $N/10$   $\text{Na}_2\text{CO}_3$  used up by the  $\text{SO}_2$ . A repetition of this test under parallel conditions gave 24.38 cc. alkali consumed, showing  $\text{SO}_2$  content of the solution to be 0.0039 g. per cc.

(3)—20 cc. of the  $\text{SO}_2$  solution were added to 25 cc.  $N/10$   $\text{Na}_2\text{CO}_3$  and, without the addition of  $\text{H}_2\text{O}_2$  or any further aeration than was caused by mixing the two solutions, titrated with  $N/10$   $\text{HCl}$ : 12.2 cc. of the latter were required, using methyl orange. This shows 12.8 cc. of the  $\text{Na}_2\text{CO}_3$  to have been used up and, as each cc. thereof is equivalent to 0.0064 g.  $\text{SO}_2$ , it would indicate an  $\text{SO}_2$  content of 0.0041 g. per cc. This apparently too high value is readily accounted for by the fact that part of the  $\text{Na}_2\text{SO}_3$  formed in the reaction between the  $\text{SO}_2$  and the  $\text{Na}_2\text{CO}_3$  had been oxidized to  $\text{Na}_2\text{SO}_4$  either previous to or during the titration with the  $N/10$   $\text{HCl}$  and in consequence thereof less  $\text{HCl}$  was required to react with the  $\text{Na}_2\text{SO}_3$  to form  $\text{NaHSO}_3$  thus giving, indirectly, a higher value for the amount of  $\text{Na}_2\text{CO}_3$  consumed.

(4)—20 cc. of the  $\text{SO}_2$  solution were added to 25 cc.  $N/10$   $\text{Na}_2\text{CO}_3$  and then 2000 cc. of air were bubbled through the mixture, requiring 15 minutes for the aspiration. The solution was then titrated with  $N/10$   $\text{HCl}$ , of which only 9.45 cc. were required, indicating an  $\text{SO}_2$  content of 0.00497 g. per cc. Of course the same explanation applies here as in (3) above.

It is evident, therefore, that in titrating the residual alkalinity of solutions containing  $\text{Na}_2\text{SO}_3$ , where the possibility of air oxidation of this compound exists, due precaution must be taken to guard against the error introduced by this factor.

The use of  $\text{H}_2\text{O}_2$  eliminated this difficulty and has been proved to render the method accurate, simple and readily applicable to field work. The addition of the  $\text{H}_2\text{O}_2$  may be made after aspiration is completed and just prior to the titration with standard acid.

For practical work in the field the apparatus shown in Fig. I was employed.

The joints between the several members of the outfit are close and made tight by short lengths of rubber tubing. *B*, *C* and *D* are held in a small, open-top wooden box about 18 in. long, 5 in. wide and 4 in. high with partitions to support and prevent motion of *B* and *D* when carried about. The whole apparatus, without the aspirating bottles, ready for a determination, weighs less than 5 lbs. Two of these outfits can be easily carried under each arm.

In making a test the sampling tube *A* is connected to *B* and inserted at any particular point of the furnace or stack; the aspirator *E* is connected to *D* and aspiration started at the desired rate by loosening the pinch-cock *G*.

Throughout our work 2000 cc. in each case was the



volume of gas aspirated through the apparatus and determined by noting when the water in *F* had reached a mark showing that volume to have passed over.

The tube *A* is then withdrawn from the furnace and, while still attached to *B*, a further volume of 1000 cc. of air aspirated. This was found sufficient to remove completely the last trace of  $\text{SO}_2$  from all parts of the apparatus in front of *D*. *A* is then disconnected, the outside wiped off with a cloth or damp sponge, and the inside thoroughly washed down into a small beaker with distilled water. This point is very important, for it was found that in many cases approximately 50 per cent of the  $\text{SO}_3$  had condensed and been retained in *A*.

The contents of *B* are next added to the washings from *A* and this tube also thoroughly washed out. The two funnels carrying the filters are then disconnected, the filter papers placed in the beaker containing the washings from *A* and *B*, and the funnel

of the aspirated gases is sufficiently high, appreciable amounts of  $\text{SO}_2$  are oxidized to  $\text{SO}_3$  on contact with the hot dust and walls of the tube. If, then, the gases be drawn through slowly this will introduce large errors.

In a number of instances when the gases were aspirated from the hottest hearths of the roasting furnaces, the temperature being between  $600^\circ\text{C}$ . and  $700^\circ\text{C}$ ., the ratio of  $\text{SO}_3$  to  $\text{SO}_2$  found was 1 : 10 when the aspiration rate was 300 cc. per minute, while when the gases were drawn through at 45 cc. per minute the ratio was 1 : 6. With an aspiration of approximately 1000 cc. per second, obtained by allowing the gases to rush into a partially exhausted 2 liter bottle and then drawing this gas through the apparatus, the ratio of  $\text{SO}_3$  to  $\text{SO}_2$  was 1 : 12. With a temperature less than  $450^\circ\text{C}$ . this catalytic action is very slight and can probably be neglected, but with hotter gases it is necessary either to aspirate with sufficient rapidity or to cool the sampling tube by means of a water jacket.

TABLE I—TYPICAL ANALYSES OF FLUE GAS FOR  $\text{SO}_3$  AND  $\text{SO}_2$   
Temperature of flue gases in each case averaged about  $400^\circ\text{C}$ .  
Volume of gas taken, 2000 cc. Pressure, 655 mm.

Tem- pera- ture in aspira- tion bottle	Aspira- tion time Min- utes	Cc. N/10- Na <sub>2</sub> CO <sub>3</sub> for		Gram found		Volume Per cent		Ratio of SO <sub>3</sub> to SO <sub>2</sub>
		SO <sub>2</sub>	SO <sub>3</sub>	SO <sub>2</sub>	SO <sub>3</sub>	SO <sub>2</sub>	SO <sub>3</sub>	
38	5	5.4	78.4	0.0216	0.2508	0.40	5.82	1 : 14.55
60	5	3.5	50.1	0.0140	0.1632	0.28	4.05	1 : 14.45
38	20	4.1	67.8	0.0164	0.2170	0.30	5.02	1 : 16.73
49	15	4.15	48.0	0.0166	0.1539	0.32	3.70	1 : 11.56

Table I shows analyses of gases taken from the outlet flue of a multiple hearth roasting furnace which are typical of a large number in which the method here described was employed.

LABORATORIES WESTERN PRECIPITATION COMPANY  
LOS ANGELES, CALIFORNIA

## BOILING AND CONDENSING POINTS OF ALCOHOL-WATER MIXTURES<sup>1</sup>

By P. N. EVANS

Received December 22, 1915

The boiling points of alcohol-water mixtures depend on the proportions of the constituents, and range from about  $78^\circ\text{C}$ . for pure ethyl alcohol to  $100^\circ\text{C}$ . for pure water. Except at a concentration of 96 per cent alcohol by weight (97.5 per cent by volume) any mixture of alcohol and water when boiled gives off a vapor of different composition from that of the liquid, the vapor being richer or poorer in alcohol than the liquid when the latter contains respectively less or more than about 96 per cent of alcohol. The vapor has, of course, a condensing point identical with the true boiling point of the liquid from which it is given off.

The purpose of the work here reported was to ascertain experimentally the relation between the boiling point (or condensing point) and the composition of both the liquid and vapor phases, that with the information so obtained it might be possible by observation of the corrected boiling point to learn the com-

<sup>1</sup> Abstracted by author from Indiana Academy of Science Report for 1913.

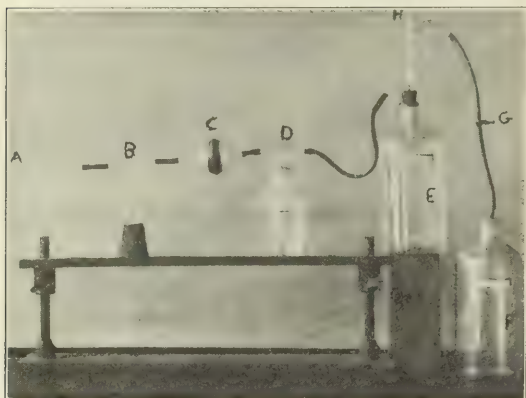


FIG. 1

- A—Hard glass or quartz sampling tube,  $\frac{1}{4}$ " diameter, 3' long.  
B—Humidizing bulb containing just enough water to seal the bend.  
C—Double S. & S. No. 389 or Munkell No. 0 filters held between the large ends of two funnels by a section of rubber tubing such as is used for holding Gooch crucibles.  
D—Double-action Allihn gas wash-bottle containing N/10  $\text{Na}_2\text{CO}_3$  and  $\text{H}_2\text{O}_2$ .  
E, F—Syphon aspirating bottles holding about 3 liters each.  
G—Pinch-cock to regulate flow of syphon water.  
H—Thermometer.

which has been next to *B* also washed and the washings added to the same beaker.

A drop of methyl orange is added to the contents of the beaker and the  $\text{H}_2\text{SO}_4$  present titrated with N/10  $\text{Na}_2\text{CO}_3$ .

To determine the  $\text{SO}_2$  caught, methyl orange is added to *D* and the excess of  $\text{Na}_2\text{CO}_3$  determined by titration with N/10  $\text{HCl}$ . The volume of the N/10  $\text{Na}_2\text{CO}_3$  used up during the aspiration of the gases is a measure of the amount of  $\text{SO}_2$  present.

It was found by repeated trials that the one absorption bottle *D* was sufficient to retain all  $\text{SO}_2$  even when the gases were aspirated at the rate of 2000 cc. in 4 minutes. An important source of error in determinations of this kind is the catalytic action of the walls of the sampling tube and also of dust particles which may collect in the tube. When the temperature

position of the boiling liquid and that of the vapor being evolved at any moment during distillation.

The relation between the boiling point and the composition of the liquid phase was determined for low percentages of alcohol by J. J. Pohl,<sup>1</sup> and for all concentrations by Dupré and Page,<sup>2</sup> and by Gröning,<sup>3</sup> but the results were very discordant. H. W. Wiley<sup>4</sup> gives a rule for calculating the strength of alcohol-water mixtures containing not over 5 per cent of alcohol. W. A. Noyes and R. R. Warfel<sup>5</sup> determined the relation between boiling point and composition over the whole range, with special reference to the minimum boiling point, which they found to be 78.74° for 96 per cent alcohol by weight, and mention is made by them of the determination by J. K. Haywood<sup>6</sup> of boiling points of mixtures containing less than 85 per cent of alcohol. So far as known to the writer the relation between the composition and condensing

stated. The average of the percentages found in the liquid in the flask before and after distillation was taken as that of the liquid phase, and the percentage in the distillate as represented in the vapor phase at the time when the boiling point was observed half-way through the distillation.

The original volume of the liquid in the flask was restored by the addition of 15 cc. of water, and the slightly more dilute mixture so obtained was used for the next experiment. In this way 43 mixtures were examined, ranging from 91 to 0 per cent alcohol.

Corrections were introduced in the temperature readings for the barometric pressure and for the exposed mercury column, as follows: Regnault and Claassen<sup>1</sup> have shown that the effect of such variations of pressure as may be due to atmospheric conditions is practically the same on the boiling point of water

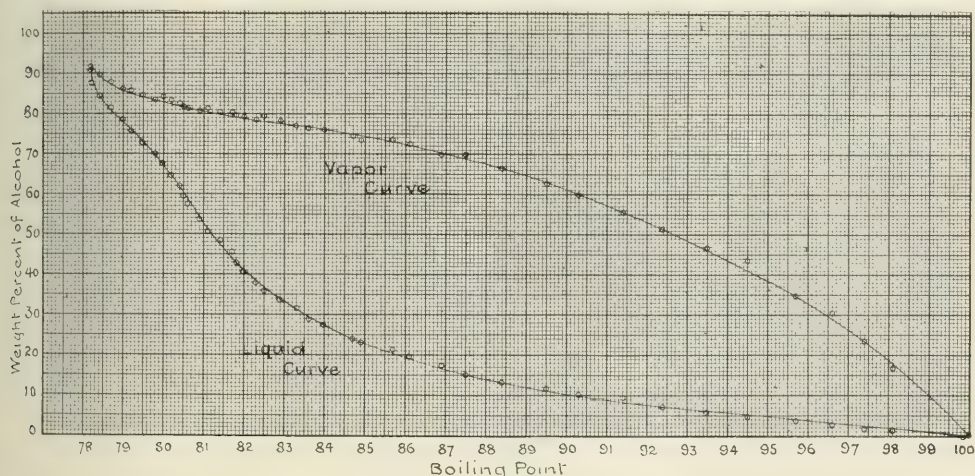


FIG. I

point of the vapor phase has not been previously determined.

#### PROCEDURE

The gravity and temperature of a strong alcohol are determined with a Westphal balance and the weight per cent of alcohol calculated by means of Mendeleff's table.<sup>7</sup> Five hundred cubic centimeters were placed in a one liter distilling flask with an accurate thermometer graduated in tenths of a degree inserted with its bulb just below the side-neck. The liquid was then slowly distilled at a uniform rate of about one drop per second until 15 cc. had passed over, the distilling temperature being read when 75 cc. had collected in the graduated receiver. The per cent of alcohol in the distillate and that in the residue were determined from the gravities as already

and that of alcohol, so it seemed justifiable to use Landolt's correction for these mixtures and add 0.043 to the observed reading for each millimeter below 760 shown by the barometer. The observed temperature reading was also corrected for the exposed mercury column by adding  $N(T - t) 0.000154$ , in which  $N$  is the length of the exposed column in degrees,  $T$  the observed boiling point, and  $t$  the room temperature.

The thermometer used was compared throughout the range of observations with a similar instrument calibrated by the Reichsanstalt. The corrections in no case exceeded 0.1° and were disregarded, as only this degree of accuracy was aimed at. The temperature results are probably accurate within 0.2 degree, and the concentrations within 2 per cent (in most cases within 1 per cent).

#### RESULTS

The results obtained are given in Table I. The relations existing between the boiling point or con-

<sup>1</sup> Jahresber., 1850, p. 455.

<sup>2</sup> Phil. Trans., 1869, p. 591.

<sup>3</sup> Watts' "Dict. Chem.," 1872, I, p. 95.

<sup>4</sup> Jour. Am. Chem. Soc., 18 (1896), 1063.

<sup>5</sup> Ibid., 23 (1901), 463.

<sup>6</sup> J. Phys. Chem., 3 (1899), 318.

<sup>7</sup> Biedermann's "Chem. Kal.," 1914, I, p. 296.

<sup>1</sup> Biedermann's "Chem. Kal.," 1914, II, pp. 112, 113.



TABLE I—VALUES OBTAINED BY EXPERIMENT

No.	Specific gravity before distillation	Temperature during gravity determination	Per cent alcohol before distillation	Specific gravity of residue	Temperature during gravity determination	Per cent alcohol in residue	Average per cent alcohol in liquid	Specific gravity of distillate	Temperature during gravity determination	Per cent alcohol in distillate	Observed temperature of distillation	Barometer reading mm.	Barometer correction in boiling point	Room temperature	Correction for exposed mercury column	Corrected boiling point
1.	0.815	20	91.1	0.812	23	91.1	91.1	0.811	22	91.8	77.2	750	0.4	23	0.6	78.2
2.	0.822	22	87.7	0.821	23	87.7	87.7	0.815	23	90.0	77.2	750	0.4	22	0.6	78.2
3.	0.829	23	84.6	0.829	23	84.6	84.6	0.819	22	89.6	77.4	750	0.4	22	0.6	78.4
4.	0.836	24	81.5	0.838	22	81.5	81.5	0.823	22	88.0	77.6	748	0.5	22	0.6	78.7
5.	0.845	22	78.7	0.843	25	78.8	78.8	0.825	22	86.5	77.7	743	0.7	22	0.6	79.0
6.	0.852	22	75.8	0.851	23	75.8	75.8	0.827	22	85.8	77.8	740	0.8	22	0.6	79.2
7.	0.857	24	72.9	0.860	21	72.9	72.9	0.829	23	84.6	78.1	741	0.8	22	0.6	79.5
8.	0.864	23	70.4	0.866	23	69.6	70.0	0.832	22	83.8	78.4	741	0.8	23	0.6	79.8
9.	0.873	21	67.5	0.873	21	67.5	67.5	0.833	20	84.2	78.6	743	0.7	21	0.6	79.9
10.	0.879	21	65.0	0.880	21	64.6	64.8	0.835	20	83.5	78.9	743	0.7	21	0.6	80.2
11.	0.884	21	62.7	0.885	23	61.4	62.0	0.838	19	82.7	79.1	743	0.7	21	0.6	80.4
12.	0.891	22	59.2	0.893	20	59.2	59.2	0.839	20	81.9	79.5	750	0.4	21	0.6	80.5
13.	0.898	20	57.1	0.899	21	57.5	57.3	0.839	21	81.5	79.6	750	0.4	21	0.6	80.6
14.	0.904	21	54.1	0.904	23	53.2	53.6	0.839	23	80.8	80.2	757	0.1	23	0.6	80.9
15.	0.908	23	51.4	0.910	22	51.0	51.2	0.840	21	81.2	80.3	756	0.2	22	0.6	81.1
16.	0.915	22	48.6	0.916	22	48.2	48.4	0.842	21	80.4	80.5	756	0.2	22	0.6	81.4
17.	0.920	22	46.4	0.923	22	45.0	45.7	0.843	20	80.4	80.8	756	0.2	22	0.6	81.7
18.	0.926	23	43.8	0.928	22	42.5	43.1	0.844	21	79.6	81.0	756	0.2	22	0.6	81.8
19.	0.933	22	40.5	0.932	25	40.0	40.2	0.845	20	79.6	81.2	755	0.2	19	0.6	82.0
20.	0.936	24	38.0	0.938	23	37.5	37.7	0.848	19	78.8	81.5	755	0.2	20	0.6	82.3
21.	0.940	24	36.0	0.942	23	35.5	35.7	0.846	20	79.2	81.6	755	0.2	20	0.7	82.5
22.	0.945	23	33.9	0.947	22	33.3	33.6	0.849	19	78.3	82.0	755	0.2	20	0.7	82.9
23.	0.949	23	31.7	0.950	23	31.1	31.4	0.851	20	77.1	82.4	755	0.2	21	0.7	83.3
24.	0.952	24	30.0	0.955	23	29.1	29.0	0.853	20	76.2	82.7	756	0.2	21	0.7	83.6
25.	0.956	23	27.5	0.956	25	26.9	27.2	0.853	21	75.8	82.5	748	0.5	20	0.7	84.0
26.	0.958	24	26.2	0.961	22	24.7	25.4	0.856	22	74.2	83.4	748	0.5	22	0.8	84.7
27.	0.962	23	23.7	0.964	23	22.3	23.0	0.858	19	73.7	83.7	750	0.4	21	0.8	84.9
28.	0.965	23	21.7	0.966	23	21.0	21.3	0.859	20	73.7	84.3	750	0.4	21	0.8	85.7
29.	0.966	23	21.0	0.969	23	18.9	19.9	0.860	22	72.5	84.8	747	0.5	22	0.8	86.1
30.	0.970	23	17.9	0.972	22	16.7	17.3	0.866	22	70.0	85.5	745	0.6	23	0.8	86.9
31.	0.973	22	15.8	0.974	24	14.4	15.1	0.865	23	70.0	86.2	747	0.5	23	0.8	87.5
32.	0.975	24	13.3	0.977	23	12.3	12.8	0.873	23	66.7	86.9	756	0.6	24	0.9	88.4
33.	0.977	25	12.3	0.979	25	11.0	11.6	0.882	24	62.5	88.1	748	0.5	25	0.9	89.3
34.	0.980	22	11.0	0.982	23	9.3	10.1	0.891	21	60.0	89.1	750	0.4	22	0.9	90.3
35.	0.982	23	11.0	0.984	24	7.9	9.4	0.901	20	55.8	90.1	750	0.4	22	0.9	91.4
36.	0.985	22	7.9	0.987	22	6.4	7.1	0.910	22	51.4	91.1	750	0.4	22	0.9	92.4
37.	0.987	22	6.4	0.989	20	5.0	5.7	0.910	22	46.8	92.2	750	0.4	23	0.9	93.5
38.	0.990	21	4.4	0.991	23	3.9	4.1	0.927	22	43.7	93.3	747	0.5	21	0.9	94.5
39.	0.991	23	3.9	0.992	24	2.8	3.3	0.947	21	33.5	94.3	747	0.5	22	0.9	95.7
40.	0.992	24	2.8	0.994	22	2.2	2.5	0.953	21	30.6	95.2	747	0.5	22	0.9	96.6
41.	0.995	22	1.7	0.996	21	1.1	1.4	0.964	21	23.6	96.0	747	0.5	22	0.9	97.4
42.	0.996	22	1.1	0.996	23	0.9	1.0	0.972	22	16.7	96.8	751	0.4	22	0.9	98.1
43(a)	0.998	25	-0.5	0.999	22	-0.3	-0.4	0.999	21	-0.1	98.7	753	0.3	22	0.9	99.9

(a) This experiment was with water only.

densifying point and the composition of the liquid and vapor phases are shown clearly by the plot in Fig. 1. A convenient table of results estimated from the curves appears in Table II, which enables one to determine quickly the approximate concentration of any alcohol-water mixture by observation of its boiling point, with corrections for barometric pressure and exposed mercury column. It is also possible to tell the approximate composition of both liquid and vapor (or distillate) at any moment during the distillation of a

TABLE II—VALUES ESTIMATED FROM CURVES IN FIG. 1

Boiling point °C.	Weight per cent alcohol in liquid vapor	Boiling point °C.	Weight per cent alcohol in liquid vapor	Boiling point °C.	Weight per cent alcohol in liquid vapor
78.2	91	92	82.0	41	79
78.4	85	89	82.5	36	78
78.6	82	88	83.0	33	78
78.8	80	87	83.5	30	77
79.0	78	86	84.0	27	76
79.2	76	85	84.5	25	75
79.4	74	84	85.0	23	74
79.6	72	84	85.5	21	73
79.8	69	84	86.0	20	72
80.0	67	83	86.5	18	71
80.2	64	83	87.0	17	70
80.4	62	82	87.5	16	69
80.6	59	82	88.0	15	68
80.8	56	81	88.5	13	67
81.0	53	81	89.0	12	65
81.2	50	80	89.5	11	63
81.4	47	80	90.0	10	61
81.6	45	80	90.5	9	59
81.8	43	79	91.0	9	57

mixture. The accuracy is, of course, less than by the usual and more difficult analytical method of distillation and the determination of the gravity of the distillate with a pycnometer.

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## A RAPID PYCNOMETRIC METHOD FOR "GRAVITY SOLIDS" IN CANE-SUGAR FACTORIES

By HERBERT S. WALKER

Received September 13, 1915

Since the introduction into sugar factory control by Deerr<sup>1</sup> of the terms "gravity purity" and "gravity solids," and his demonstration that the determination of total solids by the Brix spindle, while not absolutely accurate except in pure sucrose solutions, when applied to juices, sugars, and molasses at approximately the same dilution (about 15° Brix) yielded, in consequence of consistent error, results fully as valuable for factory control work as the more tedious process of drying to more or less constant weight, this latter method has been entirely abandoned in many factories.

The principal objection to the substitution of densimetric for direct drying methods has been the lack of even relative accuracy in Brix spindle readings; this, as regards accuracy of reading the graduations on the stem of the spindle, has been somewhat improved by several devices suggested in recent years, but there still remain certain inherent errors in the method, due to variable viscosity and surface tension of liquids, which are very difficult to eliminate.

The pycnometer is generally conceded to be an exceedingly accurate means of determining specific gravities, but has thus far found little favor in cane-

<sup>1</sup> Bull. 41, Agr. and Chem. Series, H. S. P. A. Expt. Station.

sugar factories, owing probably to real or fancied difficulty of manipulation and to the extra calculation involved. By means of a few simple modifications, however, a pycnometer determination may be made almost as easily as an ordinary Brix test, and with no calculation other than looking up the Brix on a specific gravity table.

A 100 cc. pycnometer with ground-in thermometer and capillary side arm is used; since all determinations are made at room temperature, the cap of the side arm is thrown away and the arm itself cut off two or three millimeters above the graduation mark, thus facilitating rapid filling to a definite volume.

All calculations could be eliminated by making a pycnometer to contain exactly 100 g. water at a given standard temperature, such as 17.5°, 20°, 27.5° (weighed in air), or 4° (weighed in vacuum), according to the tables one intends to use. The weight of the liquid in the pycnometer would then be 100 times its density as compared with water at that temperature, and if a tare were made to just balance the empty pycnometer, then the weights required to balance the pycnometer filled with sugar solution would indicate the density of that solution without calculation; Brix could then be obtained from the tables, applying the same correction used for Brix spindles in case the determination were not made at exactly standard temperature.

It is, unfortunately, difficult to obtain a pycnometer of exactly a desired capacity; one a little too large may be reduced by grinding in the thermometer with emery powder, a rather tedious though not difficult process; but a bottle of too small capacity is difficult to enlarge with accuracy.

In such cases it is easiest so to regulate the tare that the additional weights required to balance the pycnometer full of water at standard temperature shall be exactly 100 g., irrespective of the true volume of the pycnometer, *i. e.*, if pycnometer contains 101 g. water at standard temperature and weight of tare equals weight of pycnometer, then

$$\text{Pycnometer} + \text{water} = \text{tare} + 101 \text{ g.}$$

Increasing weight of tare by 1 g.,

$$\text{Pycnometer} + \text{water} = \text{tare} + 100 \text{ g.,}$$

and with pure water this pycnometer and tare will always indicate a density by direct weighing of 1.0000.

With dilute sugar solutions, a pycnometer as much as 1 cc. "off" in capacity will give densities with very little error, but when working with more concentrated solutions a small correction must be made to the observed weights, since the 1 cc. excess capacity which, in the case of pure water, was compensated for by the 1 g. heavier tare, will now weigh more than 1 g. In the above case of a 101 cc. pycnometer with tare adjusted for pure water, if it be used with a solution of 1.3000 density, the extra 1 cc. weighs of course 1.30 grams, while only 1 g. has been compensated for by the excess weight of tare.

Knowing the capacity of a pycnometer, it is a simple matter to make a table of corrections to be applied at different densities. Such a table for a pycnometer

containing 101 cc. (a cc. here being considered to be the volume occupied by 1 g. of water at the temperature taken as a standard for the density tables it is desired to use) would be as follows:

Weights used—grams....	100	101	105	110	120	130
Cor. to wts. (subtract)....	0.00	0.01	0.05	0.10	0.20	0.30 g.

According to the amount of change in tare needed to give a weight of 100 g. with pure water, a table such as the above can be easily constructed for any pycnometer; thus, if it contain 100.30 g. water at standard temperature, make tare equal weight of pycnometer + 0.30 g., and the correction table for different densities is the one given above multiplied by 0.30. The following is an example of pycnometer calibration:

Weight of Pycnometer.....	47.40 grams
Weight of Pycnometer + water at 29° C.....	146.93
Weight of water.....	99.53 grams

Assuming that this pycnometer is to be used with 17.5°/17.5° tables, and that the average temperature at which it is to be used approximates that of calibration, the change of volume due to expansion of glass may be neglected and the weight of water contained at 17.5° (or its volume in terms of "17.5° cc.") may be considered to be 99.53 × (density aq. 17.5° ÷ density aq. 29°) or 99.53 × (0.99872/0.99598) = 99.80. If a tare is then made to equal weight of pycnometer minus 0.20 g., or 47.20 g., the weights needed to balance pycnometer full of water at 17.5° will be 100 g., thus giving density direct. The correction for densities greater than 1.0000 will be:

Weights used....	100	101	105	110	115	120	125	130 g.
Correction (add)....	0.00	0.002	0.01	0.02	0.03	0.04	0.05	0.06 g.

After looking up the Brix corresponding to any density, the customary Brix correction for temperature of observation must of course be made.

In case the laboratory temperature prevailing were as high as that just noted, it would perhaps be more convenient to use tables calculated for 17.5°/27.5°, in which case the calculation of tare and correction table would be the following:

Weight water content at 27.5° = $99.53 \times (0.99641/0.99598) = 99.57$ g.										
Weight tare should be $47.40 - 0.43 = 46.97$ g.										
Wts. used..	100	101	102	105	110	115	120	125	130 g.	
Cor. (add)	0.00	0.004	0.009	0.02	0.04	0.06	0.09	0.11	0.13 g.	

Where it is desired to use a pycnometer for juices or solutions of always the same approximate density, the correction for this density may be incorporated in the tare. In case the above pycnometer were to be used solely with solutions of about 15° Brix or 1.06 density, the correction could be added automatically by making tare 0.02 g. lighter than for pure water, *i. e.*, 46.95 g. instead of 46.97 g. Densities around 15° Brix would then be obtained by direct weighing, with absolutely no correction other than that for temperature subsequently applied to the Brix reading.

The calibration of a new pycnometer, including adjustment of a tare (best made from a small bottle weighted with shot) and construction of a correction table, can easily be done in less than an hour; the calibration of a new Brix spindle at three points on the stem, which is just as necessary, takes considerably more time than this.



An ordinary determination of density of a juice or diluted molasses consists simply of filling the pycnometer to the mark and weighing the centigrams on any ordinary sugar balance, which requires from 3 to 5 minutes, hardly more time than is needed for an accurate determination by means of the Brix spindle.

As regards accuracy, an error of more than 0.01 gram in weighing is unusual; this, at 15° Brix, corresponds to 0.023° Brix, or about one-fourth the average error in reading a Brix spindle.

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### SEED ANALYSIS

By NAHUM E. KATZ

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The chemical analysis of cotton seed is of interest and value to oil mill operators only when accompanied by a table showing the available yield of products that may be expected from each ton of seed.

The following formulae are offered as a method for calculating the theoretical yield of products per ton of seed, based on the results of a chemical analysis of the seed. As the derivation of the formulae is rather lengthy, it is omitted.

Let  $a$  = per cent kernels in whole seed  
 $b$  = hulls in whole seed  
 $f$  = per cent oil in whole seed  
 $g$  = per cent ammonia in whole seed  
 $l$  = per cent oil lost in the hulls, as made in the mill, due to imperfect separation  
 $p$  = lbs. of oil left in cake  
 $L$  = lbs. of lint removed in delinting  
 $V$  = lbs. of waste due to mott, dirt, loss in moisture, etc.  
 $A$  = per cent ammonia desired in the cake  
 0.2 per cent be assumed to be the average per cent of oil naturally found in the hulls as made in the mill  
 0.3 per cent be assumed to be the average per cent of ammonia naturally found in the hulls as made in the mill  
 $r$  = lbs. of hulls, which are necessary to mix with the kernels in order to dilute the cake to the desired per cent of ammonia  
 $z$  = per cent of  $r$  in the uncooked and unextracted meats.

$H$  = lbs. of hulls to be made to the ton of seed  
 $O$  = lbs. of oil to be pressed out per ton of seed  
 $C$  = lbs. of cake to be made to the ton of seed

Then:

$$H = \frac{A(2000 - 20f + p + 0.04b - 1.002L) - 2000g}{1.002A - 1(0.01A - 0.01) - g/a(3.334 - 0.67) - 0.3} \left(1 - \frac{V}{2000 - L}\right)$$

$$O = \left[ (20f - 0.04b - p + 0.002L) \left(1 - \frac{V}{2000 - L}\right) \right] H(0.011 - 0.002)$$

$$C = 2000 - (H + O + L + V)$$

$$r = b \left( 20 - \frac{V}{100} \right) - L = H(1.0067 - 0.0333L)$$

$$z = \frac{100r}{2000 - V - L - H}$$

$C$  may also be calculated by the formula

$$C = \left[ (2000 - 20f + p + 0.04b - 1.002L) \left(1 - \frac{V}{2000 - L}\right) \right] - H(1.002 - 0.011)$$

If it be agreed to consider the numerical values 0.7 per cent for  $l$ , 75 lbs. for  $L$ , and 57 lbs. for  $p$ , as standard values, then the above given formulae may be considerably simplified. They then appear as follows:

$$H = \frac{A(1981.85 - 20f + 0.04b) - 2000g}{0.995A - 1.66g/a - 0.3} \left(1 - \frac{V}{1925}\right)$$

$$O = \left[ (20f - 0.04b - 56.85) \left(1 - \frac{V}{1925}\right) \right] - 0.005H$$

$$C = 1925 - (H + O + V)$$

or  $C = \left[ (1981.85 - 20f + 0.04b) \left(1 - \frac{V}{1925}\right) \right] - 0.995H$

$$r = b \left( 20 - \frac{V}{100} \right) - 75 - 0.983H$$

$$z = \frac{100r}{1925 - H - V}$$

The formulae for  $r$  and  $z$  are especially valuable to the superintendent. Knowing the percentage of hulls which should be mixed with the kernels, and comparing it with the percentage obtained by an actual test on the meats, he is enabled to tell whether the proportions of kernels and hulls in the meats are correct or not, before the meats are carried to the crushing rolls.

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## ADDRESSES

### THE USE OF DIAGRAMS IN CHEMICAL CALCULATIONS

By HORACE G. DEMING

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The use of charts or diagrams for the solution of arithmetical problems is well known to the engineering profession, and several books have been written on the subject.<sup>1</sup> Thus we have the graphical representation of forces and moments, Kutter's formula for the flow of water, indicator diagrams for steam engines, and vector diagrams for the diagrammatic representation or graphical solution of problems in alternating current theory. In metallurgy we have diagrams for the representation of the composition of slags; in chemistry the familiar rectangular and triangular diagrams for the representation of the phase relations between the members of two-component and three-component systems; and, in chemical technology, diagrams for the calculation of mixtures for the manufacture of cement.

In spite of such scattering instances of the use of graphical

methods in industrial chemistry, it appears that chemists do not in general take advantage of the really remarkable opportunities that the use of diagrams presents for the quick solution of chemical problems met in every-day work; and but little systematic study of the possibilities of the graphical method in chemistry has ever been published.<sup>1</sup> The diagrams that are here presented are selected from among a large number devised by the writer with a view to illustrating some of the principal computations that may be solved by graphical means; they indicate at the same time what a great variety of problems are susceptible to such treatment, and what diverse types of diagrams may be used. It is hoped that those presented may suggest others better adapted to the individual needs of the readers of THIS JOURNAL; for this reason it will be necessary to mention the mathematical principles on which the construction of the different types of charts is based; but, since we are concerned rather with general principles than with details of execution, we can do no more than refer to many interesting charts that differ from those here given in but a few particulars.

<sup>1</sup> d'Ocagne, "Traité de Nomographie," Paris: Gauthier-Villars; Peddle, "The Construction of Graphical Charts," New York: The McGraw-Hill Book Co.; Turner, "Graphical Methods in Applied Mathematics," London: Macmillan and Co.

<sup>1</sup> But see a series of articles by Nickel, Z. physik. Chem., Vols. 10 to 14. Of somewhat different scope is Kremann, "Leitfaden der graphischen Chemie," Berlin: Geb. Borntraeger, 1910.

It is evident that any relation capable of exact mathematical expression may be given in graphical form. There are, in fact, many methods that might be used in any particular case. Considerations of ease of construction and accuracy of reading must determine which of the different possible charts is the one to be employed; or whether the desired result may not be most easily obtained by calculation with a slide-rule or by direct reading from a table.

The ordinary slide-rule is accurate to within about 1 part in 500, and the ordinary chart to within about 1 part in 250. The graphical method has the advantage that it can cover many complicated formulas involving operations impossible with a slide-rule; and a combination of slide-rule and chart will in many cases effect the greatest saving of time. For problems that demand a degree of precision not to be reached by the use of graphical methods, the latter often still afford a quick and convenient means of checking results, a fact which will lead us to consider one or two charts that we should otherwise regard as of little practical use.

#### RADIAL CHARTS

The familiar type of diagram, in which two variables are laid off along perpendicular axes on cross-section paper and the relation between them expressed by means of a curve, serves principally for the graphical representation of experimental results, presenting to the eye in an easily comprehensible form a collection of data that could not be so easily interpreted if given in a table. But, as a means of computation, charts of this form are of rather limited use, for the reason that the relation between two variables may generally be expressed most conveniently and accurately in the form of a table. It is only where the precise mathematical relation between two variables is unknown or very complicated, or where more than two variables enter that it may be worth while to construct a diagram to save a part of the labor involved in drawing up a table.

As an example of the simplest chart of this description let us consider the conversion of a temperature reading in Centigrade degrees into degrees of the Fahrenheit scale, according to the equation

$$F = 9/5C + 32.$$

This relation may be expressed as a straight line inclined to the horizontal axis at an angle whose tangent is  $9/5$ , and cutting the vertical axis 32 units above the origin. This chart is shown in Fig. 1, its use being self-explanatory. It is evident that any other relation between two variables that can be put into the form

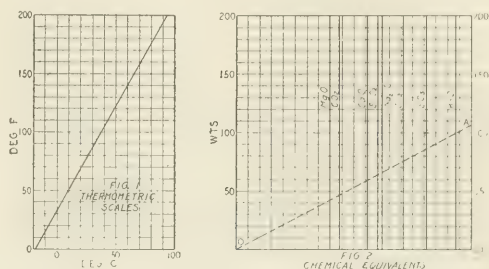
$$y = ax + b$$

can be expressed in a diagram of this type. In practice such a chart is best constructed by locating two points by calculation, then passing through them a straight line of indefinite length. The best sort of cross-section paper to use is that having heavily ruled square-centimeter divisions, with square-millimeter subdivisions (the so-called standard millimeter cross-section paper).

When the constant  $b$  in the above equation becomes zero we have a simple proportionality between the two variables. Problems of this sort are best solved with a slide-rule, where the quantity  $a$  is a real constant, invariable from problem to problem. But where  $a$  may have different values we make use of one of the types of charts illustrated in Figs. 2 and 3, which will be called *radial charts*, because they are characterized by a series of axes and construction lines that radiate from the lower left-hand corner.

In Fig. 2 we have a chart for the conversion of a given weight of one compound into the equivalent weight of another. In constructing this chart distances were first measured to the right along the horizontal axis, each equal (in centimeters) to one-fifth the molecular weight of some definite compound. From the points thus located vertical axes were erected and

labeled with the formulas of the compound or elements to which they correspond. Thus the axis for magnesium oxide is placed  $1/5 \times 40.32 = 8.06$  cm. to the right of the vertical axis; along

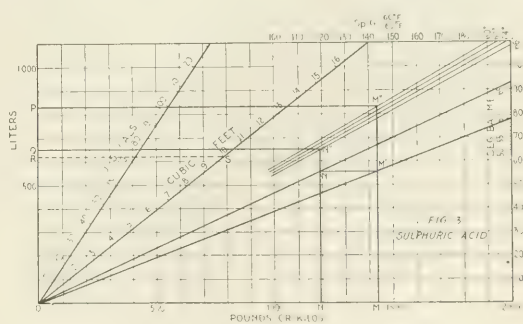


the left side of the chart is laid down a scale of weights, each cm. being equivalent to 10 mg.

If it be required to convert 100 mg. of potash into its equivalent weight of carbon dioxide, locate a point  $A$  on the  $K_2O$  axis, corresponding to 100 mg. wt. Connect this point with the origin  $O$ . Notice that the  $CO_2$  axis is crossed at an elevation corresponding to 47 mg., the equivalent of 100 mg. of potash.

An axis at the right-hand margin of the chart, 20 centimeters from the origin, gives the number of millimols of the substances concerned. Thus, in the problem we have just been considering, the dotted construction line cuts this axis at 1.06, the molecular equivalent of 100 mg. of potash or 47 mg. of carbon dioxide. It is apparent that the construction line  $OA$  need not actually be drawn, it being sufficient to lay a transparent straight-edge on the chart to connect the points  $A$  and  $O$ .

A chart of this kind might be used for calculating the weight of oxygen needed to burn a fuel of a given composition, the weight of silica necessary for combination with a mixture of basic oxides, or in general the weight of any one substance needed to react with definite weights of one or several others. Since the volume occupied by a given weight of a gas is inversely proportional to its molecular weight, we may use the same chart in calculating the volumes corresponding to definite weights of different gases, an additional axis in this case being erected 22.38 cm. to the right of the origin, since the gm.-mol.



volume of gases is 22.38 l., and the oz.-mol. volume (by a happy accident) is very closely 22.38 cu. ft. If the weight of the gases be expressed in grams, their volume, read from the volume-axis, will be given in liters; if their weight be given in ounces their volume will be in cubic feet. Each centimeter of distance along the volume-axis will represent 2 units of volume, this being dependent on the scale-units used in graduating the horizontal and vertical axes. A chart derived from that just discussed may be used for converting solutions of one strength of specific gravity into equivalent weights or volumes of another strength. In Fig. 3 weights in lbs. or kg. are plotted along a



horizontal axis, and percentages of sulfuric acid along a vertical axis at the right hand edge of the diagram. Specific gravities or degrees Baumé may conveniently be laid off along the vertical scale as well.

Let it be required to find what weight of acid of 66° B., corresponds to 1430 lbs. of acid of 60° B. Draw lines connecting the origin at *O* with the points corresponding to 60° and 66° B. From the point *M* corresponding to 1430 lbs. pass vertically to the 60° line at *M'*, thence horizontally to intersect the 66° line at *N'*, thence downward to *N*, where we read 1190 lbs. of 66° acid.

A slight modification of this chart will enable us to calculate volumes. At the left edge of the diagram lay down a scale of liters, and from the tenth main division of this scale lay off to the right a scale of specific gravities, in such a way that the slopes of straight lines drawn to connect points on the latter scale with the origin will in all cases be equal to the reciprocal of the specific gravity. In the figure, four such lines have been drawn, namely those passing through points on the specific gravity scale corresponding to 60°, 62°, 64° and 66° B.

Let it now be required to convert 1190 kg. of acid of 66° B. into liters. From 1190 on the horizontal scale (which in this case must be read in kg. instead of in lbs.) we pass upward to *N''* on the line drawn through the gravity corresponding to 66° B., thence horizontally to *Q*, where we read 650 liters, *Ans.*

Let us consider one more problem, in which 650 liters of acid of 66° B., are to be converted into liters of acid of 60° B. From the point corresponding to 650 liters, at *Q* on the vertical scale, pass horizontally to intersect the 66° gravity line at *N''*, thence vertically downward to intersect the 66° weight line at *N'*, thence horizontally to the 60° weight line at *M'*, thence upward to the corresponding gravity line at *M''*, thence horizontally to *P*, where we read 830 liters, *Ans.*

If weights of acid are not to be considered, but volumes alone, as in the last example, the chart as just described may be made to read in other units than those of the metric system, the vertical scale at the left being simply relabeled gallons or cubic feet. But if weights of acid are to be used in the calculation, it will be necessary to graduate new axes for the U. S. gallons or cubic feet. If the horizontal axis be read in lbs. the vertical axis will give the number of lbs. of water occupying the same volume at 60° F. Since 623 lbs. of water = 10 cu. ft., an axis for cu. ft. may be located by drawing through the point *R*, at 623, a horizontal line to intersect a 10 cm. radius from the origin at a point *S*, which is marked 10 cu. ft. The line *OS* is then drawn and graduated to that scale. An axis for U. S. gals. may be located in a similar way, having given that 833.7 lbs. of water at 60° F. = 100 U. S. gals.

In certain problems we have to deal with two constituents. For example, we may need to find the  $\text{SO}_3$  content of sulfuric acid of a given percentage of  $\text{H}_2\text{SO}_4$ . This is most conveniently done by graduating the scale at the right of the diagram, on one side with percentages of  $\text{H}_2\text{SO}_4$ , and on the other with percentages of  $\text{SO}_3$ . The vertical axis of Baumé degrees is in this case displaced to the right, and graduated by locating the points of intersections of radial lines passing through definite percentages. With such a chart we can calculate the amount of water to be added by fuming acid in order to convert it into commercial acid of any desired strength.

This type of chart might be used to calculate the amount of water to be added to a solution of definite strength to produce a solution of another strength, for the difference between equivalent weights of two solutions must represent the weight of water to be added to the stronger one. Charts of this type have also been devised for calculating the amount of filler to be added to a fertilizer to reduce it to a desired percentage of a single element; for determining the amount of water to be removed

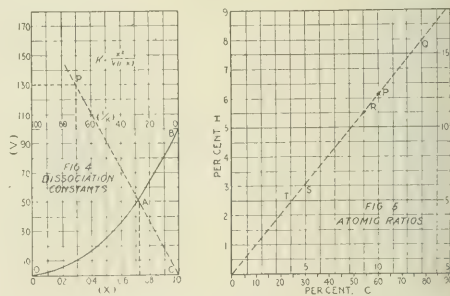
by evaporation during the concentration of a solution from a lower to a higher density; and for calculating the proportions in which two raw materials need to be mixed in order to produce a mixture containing a given percentage of some one constituent. But, since problems of this sort may be solved somewhat more conveniently by means of other charts to be described later, no description of these diagrams need be given.

It is worth while noting that radial charts, such as those described above and illustrated in Figs. 2 and 3, may be used for the solution of any problem, in which the relation

$$x/a = x'/a'$$

obtains,  $x$  and  $x'$  being distances along the horizontal axis, and  $1/a$  and  $1/a'$  being constants proportional to the slopes of the radiating lines. The constants  $a$  and  $a'$  should have unchanging values in all the problems that are to be solved by the use of a given chart, since in this case we may draw the radiating lines once for all when the chart is first constructed. If  $a$  and  $a'$  are variables, we are forced to draw new lines with slopes respectively proportional to  $1/a$  and  $1/a'$  for each problem to be solved, or to draw in the beginning a great number of radiating lines, and afterward resort to interpolation. For this reason a set of computations in which the constants  $a$  and  $a'$  vary from problem to problem is best carried out by a modification of the "figure-four" chart to be described later.

The principles involved in the preceding diagrams may frequently be applied in the solution of rather complex formulas.



As an example, let us consider that for the constant of dissociation of a gas yielding two gaseous products of dissociation:

$$k = \frac{x^2}{(1-x)^2}$$

In Fig. 4 the values of  $x$  are laid down along the horizontal axis and the curve *OAB* drawn through the calculated values of  $x^2$ . The values of  $V$  are then laid down along the vertical axis and the values of the reciprocal of  $k$  from right to left along a horizontal axis. Given 72 per cent dissociation, and a volume of 130 calculate the constant of dissociation. Enter the diagram at 72 on the base-line, pass upward to cross the curve at the point *A*. Connect *A* with *C* and produce the line thus obtained until it cuts the horizontal line passing through 130 units of volume, at *P*. Passing downward we read the value of  $1/k$ , viz., 70, from which  $k = 0.143$ . *Vice versa*, if we have a volume of 130 units and know that the value of  $1/k$  is 70, we locate the point *P* corresponding to these data and draw the line *PC*; from the point *A* where this line cuts the curve, we pass vertically to the base line, where we read 72 per cent dissociation.

Of course in practice it is unnecessary to draw the construction lines in this and similar diagrams. If the edge of a transparent triangle is passed through the desired points or, better yet, a straight line scratched on the under side of a sheet of celluloid, it will be possible to make readings directly. The horizontal scale through the middle of the diagram might also have

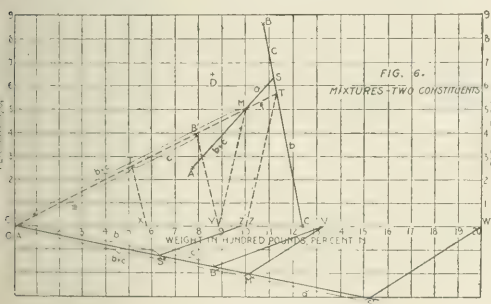
en graduated directly in values of  $k$ , instead of in reciprocal values, by laying down graduations proportional to the reciprocal of the numbers that appear in Fig. 4; but scales of reciprocals have the disadvantage that their divisions are not equal, hence there is a loss of accuracy in interpolation. For this reason it is better to read the values of  $1/k$  directly, and convert them to values of  $k$  by means of a slide-rule or table of reciprocals.

# RECTANGULAR COORDINATE CHARTS

Closely related to the preceding type of chart is one in which the composition of a compound or mixture is expressed by the rectangular coordinates of a point in a plane or in space. For example, let us take a chart for the determination of the ratio of the number of atoms of carbon and hydrogen in an organic compound, having given the percentage of each of these elements (Fig. 5).

Along the vertical axis of the diagram is laid down a scale of hydrogen, in such a way that the percentages of that element the compounds to be considered fall within the limits of the chart. Along the horizontal axis is laid down a scale of percentages of carbon, in such a way that 11.9 per cent of carbon the same linear distance as 1 per cent of hydrogen, since the atomic weight of carbon is 11.9 (on a basis of  $H = 1$ ). The horizontal and vertical divisions of the chart are also marked 10, 15, etc., to indicate the relative number of atoms of each element.

Let us suppose that a given compound contains 60.0 per cent



carbon and 6.1 per cent of hydrogen. Locate the point  $P$  corresponding to this composition and lay a straight edge through it. Where this line happens to pass through the corner of a square may be read the atomic ratio. It will be seen that there are four corners,  $Q, R, S$ , and  $T$ , which very nearly coincide with the given line.  $Q$  corresponds with the ratio  $C_{15}H_{16}$ , with  $C_3H_{11}$ ,  $S$  with  $C_6H_6$ , and  $T$  with  $C_4H_8$ . Which of these formulas is the correct one will of course need to be determined by other considerations; for the errors of organic combustion methods are of such a magnitude as to leave the matter a formula more or less in doubt, unless the percentages of the elements other than carbon and hydrogen be taken into consideration.

Another method of working this same problem is to convert the percentage of hydrogen found into its equivalent percentage of carbon by means of the radial diagram of Fig. 2. The ratio between this number and that giving the percentage of carbon actually found is then taken by means of a slide-rule. The chart just described may of course be modified for use with any other pair of elements.

In Fig. 6 we have a diagram for the adjustment of various raw materials to give a mixed fertilizer containing desired percentages of nitrogen and phosphorus. Percentages of nitrogen are laid off along the horizontal axis, and percentages of phosphoric acid ( $P_2O_5$ ) along a vertical axis. Suppose that we have to prepare a mixed fertilizer containing 10 per cent

nitrogen and 5 per cent  $P_2O_5$  (point  $M$ ) and that there are available for the purpose the four fertilizers whose compositions are expressed by the four points,  $A, B, C$  and  $D$ , together with filler, which, since it contains zero per cent of the elements of plant food, is of course represented by the point  $O$ . It will first be noticed that the point  $M$ , representing the required composition of the mixed fertilizer, lies within a triangle formed by connecting up the points  $A, B$  and  $C$ ; this means that it is possible to secure the desired mixture by a combination of these three raw materials. On the other hand, a triangle obtained by connecting the points  $A, C$  and  $D$  does not include the point  $M$ ; it is therefore impossible to produce the desired mixture by any combination of these three raw materials alone, in spite of the fact that some of the raw materials contain more and others less nitrogen or phosphoric acid than the mixture. The first use of the chart we have constructed is therefore to tell us which of the various raw materials placed at our disposal may be used in making up a mixture of the desired composition.

Now suppose that it is desired to make up 1000 lbs. of the mixture having the composition denoted by the point  $M$ , using for the purpose the raw materials  $B$  and  $C$  and filler. Connect  $B$  and  $C$ , and draw from the point  $O$ , representing filler, a line passing through  $M$ , which is produced until it cuts the line  $BC$  at  $T$ . From  $T$  draw the line  $TZ$  to the point representing 1000 lbs., the weight of mixture to be made. Draw the line  $MY$  parallel to  $TZ$  to intersect the base line at  $Y$ .

That portion of the line  $BC$  most distant from  $B$  is marked  $b$ , and that most distant from  $C$  is marked  $c$ ; in the same way that portion of  $OT$  most distant from  $O$  (filler) is marked  $f$ , while that most distant from  $B$  and  $C$  is marked  $b + c$ . The distances  $OB'$  and  $OT'$  are laid off equal to  $CB$  and  $CT$ , respectively and the segments thus found are marked  $b$  and  $c$  according to the portion of  $BC$  to which they correspond. Next connect  $B'$  with the point  $Y$ , previously located, and draw  $T'X$  parallel to  $B'Y$ . The distance  $OX$ , lying under the segment  $b$  of the line  $OT$ , is the amount of raw material  $B$  needed to make up the fertilizer; the distance  $XY$ , lying under the segment  $c$ , is the amount of  $C$  to be taken; while the distance  $YZ$ , lying under the segment  $f$ , is the amount of filler needed.

If for any reason it had been decided to make up the mixed fertilizer from  $A, B$  and  $C$ , without using any filler, the construction lines needed would have been those shown full length in the diagram to distinguish them from the broken construction lines of the preceding problem. Draw the line  $AM$  through  $M$ , the point representing the composition of the desired mixture, and produce it to intersect  $BC$  at  $S$ . Since the line  $AS$  does not pass through  $O$ , it will be necessary in this case to draw an auxiliary line  $A'S'$  making any convenient angle with the base line. Along this line take  $A'M'$  any convenient multiple of  $AM$  (say three times  $AM$ ), and  $A'S'$  that same multiple of  $AS$ . If 2000 lbs. are to be made, connect  $S'$  with the point  $W$  representing that weight, and draw  $M'V$  parallel to  $S'W$ . The segments  $MS$  and  $M'S'$  are labelled  $a$ , and the segments  $AM$  and  $A'M'$  are labelled  $b + c$ . The distances  $CS$  and  $CB$  are transferred to  $OS''$  and  $OB''$ , and the construction finished by drawing the parallel lines  $B''V$  and  $S''Z'$ . The distance  $OZ'$ , under the segment  $b$  of the line  $C'S'$ , represents the amount of raw material  $B$  to be taken; the distance  $Z'V$  represents the amount of  $C$ ; and the distance  $VW$  represents the amount of  $A$  that will be needed.

The preceding chart may be adopted very readily to the preparation of mixtures of any sort in which definite percentages of two different components are to be secured. If three different components are to be considered, the same chart may be used provided that the sum of the three adds up to 100 per cent; or a slight modification of the chart, which cannot be presented



here, will serve for more complex cases. If each of the raw materials contains but a single one of the constituents to be considered in the final mixture, the problem becomes simply one in inverse proportion, and may be most simply solved by means of a slide-rule. It is worth mentioning that another

modification of the chart last described will permit one to calculate the proportions in which feeding-stuffs need to be mixed in order to form a standard ration according to any one of the several systems in use.

#### LOGARITHMIC CROSS-SECTION CHARTS

Our next class of charts includes those plotted on logarithmic cross-section paper, namely, on that in which the graduations along the perpendicular axes are proportional to the logarithms of the variables, instead of to the variables themselves. This paper may be obtained from dealers in draftsman's supplies.

Since the equations

$$y = ax \text{ and } x/a = x'/a'$$

may be put in the logarithmic form

$$\log y = \log a + \log x, \text{ and, } \log x - \log a = \log x' - \log a',$$

it is possible to construct logarithmic cross-section charts to solve the same problems as the radial charts of Figs. 2 and 3. There is, however, nothing important to be gained by such a procedure, and there is even some loss of accuracy in so doing, since interpolations are less easily made on logarithmic cross-section paper.

The most important use of the logarithmic charts is in the solution of equations of the general form

$$y = a^m x^n;$$

but in equations in which several factors are to be multiplied together such charts are very convenient, providing that a reading to the nearest 2 or 3 per cent is accurate enough for the purposes in hand. In Fig. 7 is a chart for the capacity of cylindrical tanks in U. S. gallons, the diameter of the tanks and the depth of the liquid being given in inches. In this case the formula used is

$$C = \frac{\pi d^2 h}{4 \times 231},$$

where  $d$  is the diameter of the tank in inches, and  $h$  is the depth of the liquid it contains. Putting this into the logarithmic form we have

$$\log C = \log \frac{\pi d^2}{924} + \log h.$$

Note that all the constants in the equation are combined with a single variable  $d$ , the variable  $h$ , representing the depth of liquid in the tank, being kept free of constants.

To construct the chart work out the values of  $\frac{\pi d^2}{924}$  by means of a slide-rule for all the values of  $d$  that are likely to be used, and lay off the results along the vertical logarithmic scale. From the points thus located draw a series of lines sloping upward toward the right at an angle of  $45^\circ$  with the horizontal, and label each with that value of  $d$  to which it corresponds. Along the horizontal axis lay down a logarithmic scale of depths (values of  $h$ , in inches) and graduate the vertical axis in gallons.

Logarithmic cross-section paper is very useful in recording results that would extend over too great a range if plotted on

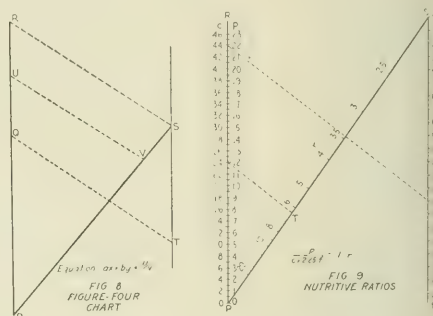
ordinary cross-section paper; for example, in the plotting of absorption spectra, the coordinates representing respectively logarithms of vibration frequencies and millimeters length of the absorbing layer of solution. In certain work experimental results plotted on logarithmic cross-section paper fall very nearly on a straight line, where ordinary cross-section paper would give a curve; this happens, for example, in a study of the volumes of filtrate delivered by a filter-press in varying periods of time. If an empirical equation exists connecting the variables in such a set of experimental data, a logarithmic chart will frequently reveal its form and the values of some of the constants that appear in it much more readily than they may be obtained in any other way.

#### FIGURE-FOUR CHART

An equation of the general form

$$ax + by = u/v$$

may be treated by means of a chart we are about to discuss, which has two parallel axes intersected by a third in such a way as to remind one of a "figure-four."



In Fig. 8 the axes of the chart are  $PR$ ,  $PS$  and  $ST$ . Let the distance  $PQ = ax$ ; let  $TS = by$ ; let  $PU = u$ ; and let  $PV = v$ ,  $UV$  and  $RS$  being drawn through  $U$  and  $S$  parallel to a line connecting  $Q$  and  $T$ . We have then  $QR = TS$ , whence  $PR = ax + by$ . From similar triangles we have then

$$PR : PS = PU : PV;$$

that is,

$$ax + by = u/v,$$

if the distance  $PS$  be taken as unity.

As a first example of the application of this chart let us consider the equation for finding the nutritive ratio of a foodstuff, *e. g.*,

$$p + 2.25f = \frac{1}{r}.$$

Putting this in the standard form for the type of chart we are discussing, we have

$$p + 2.25f = \frac{p}{1/r}.$$

To construct this chart (Fig. 9) lay down a scale of percentages of digestible carbohydrates along the axis  $PR$ , in such a way that the highest percentage met will fall within the limits of the chart. Draw an inclined axis making any convenient angle with the axis just drawn, and take  $PS$  a measured distance equal to, say, 30 centimeters. From  $S$  lay down a scale of percentages of digestible fat, and graduate it downward, using a scale unit 22.25 times that used in graduating the scale of digestible carbohydrates.

On the opposite side of the axis  $PR$  from the graduations representing percentages of digestible carbohydrates, lay down a scale of digestible protein. If the unit of this scale be taken as  $n$  times the unit of the carbohydrate scale, then unit distance

ing the inclined axis will be  $n$  times the distance  $PS$ . In particular case it will be convenient to have the divisions the protein scale twice as long as those of the carbohydrate scale; the unit distance along  $PS$  will then be  $2 \times 30 = 60$  cm. Now since the quantity  $1/r$  appears in the equation above in place of the variable  $v$  in the general equation of this type of chart, we must take the reciprocals of the various values of  $r$ , thus getting a series of fractions  $1/3, 1/4, 1/5$ , etc. Since the unit distance along  $PS$  is 60 cm. the point corresponding to the fraction  $1/3$  will be 20 cm. from the left end of the inclined axis. This point is marked with the value of  $r$ , which is of course 3, since  $1/r$  is  $1/3$ . In a similar way locate other points corresponding to other values of  $1/r$  and mark them with the values of  $r$ . A skillful combination of slide-rule and engineer's scale will enable any one to graduate this part of the chart in a few minutes.

To use the chart lay down the edge of a draftsman's triangle and connect the percentages of digestible carbohydrates and protein (say 44 and 14 per cents, respectively). Slide the triangle along the edge of another triangle until its ruling edge passes through the percentage of digestible protein (say 12 per cent). The place where this edge of the triangle cuts the inclined axis (at  $T$ ) gives the second term of the nutritive ratio, which in this case is read 1 : 6.3.

Another way to use this chart is to construct it on paper thin enough to be transparent to a series of heavily ruled parallel lines on a sheet placed beneath it. The chart is moved until one of these parallel lines, seen through the transparent paper of the chart, connects the percentages of carbohydrate and protein; then another parallel line, passing through the percentage of digestible protein, is followed up until it intersects the inclined axis, where the nutritive ratio is read.

A chart very similar to that just described might be constructed for calculating the rate of transfer of heat from circulating hot water to iron, according to the equation

$$\frac{H}{t} = \frac{1.67 + \sqrt{v}}{0.02}$$

where  $H$  is the number of calories of heat transferred in one second to a square meter of surface,  $t$  is the temperature difference between water and metal (degrees C.), and  $v$  is the velocity of the water in centimeters per second.

In Fig. 10 we have a chart for converting specific gravities greater than unity into degrees of the Baumé scale. In this case the inclined axis of the chart has been made horizontal, though this need not necessarily be done. A point  $P$  is located on the left axis 145 units above the horizontal axis; the right-hand axis is graduated in the same scale units as those used in locating  $P$ , while the horizontal axis is graduated in specific gravities, the distance between the two vertical axes being taken as unity. A line connecting the point  $P$  with the observed specific gravity will intersect the vertical axis in the corresponding number of the Baumé scale. The equation for this chart is

$$145 - b = 145, g.$$

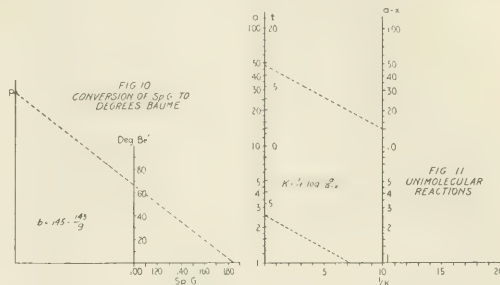
The values of  $b$  being laid off upward along the right-hand axis, because of the negative sign of  $b$  in the equation.

The equation for the constant of a unimolecular reaction may be put into the form

$$\log a - \log (a - x) = \frac{t}{1/k}$$

which is evidently one capable of being solved with the help of a chart of the kind we have been considering. In Fig. 11 the scales for  $a$  and  $a - x$  are logarithmic, while those for  $t$  and  $1/k$  are not. Of course the values of  $k$  corresponding to the different values of  $1/k$  might have been calculated and laid down on the chart, but in practice it will be found more convenient to convert values of  $1/k$  read from the chart into values

of  $k$  by the use of a slide-rule or table of reciprocals. The equation for the constant of a bimolecular reaction may be worked out with this same chart, the values of  $a(b - x)$  and  $b(a - x)$  being read from a slide-rule before the chart is entered.



A diagram of this sort is probably the quickest means of determining the order of a reaction being investigated for the first time.

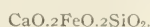
As a final example of a chart of this class, consider that in Fig. 12 for the representation of the composition of furnace slags. This chart is constructed on cross-section paper, each main (centimeter) division of the cross-sectioning representing 2 per cent silica in the slag, or some equally convenient figure. A scale of percentages of silica is plotted just within the left-hand border of the chart.

Just outside the scale of silica lay down a scale of lime, such that the point corresponding to 30.15 per cent silica ( $\text{SiO}_2 \div 2 = 30.15$ ) coincides with the point corresponding to 28.04 per cent lime ( $\text{CaO} \div 2 = 28.04$ ). At the right-hand side of the chart construct a scale of ferrous oxide, letting 35.92 per cent  $\text{FeO}$  occupy the same linear distance as 30.15 per cent  $\text{SiO}_2$ .

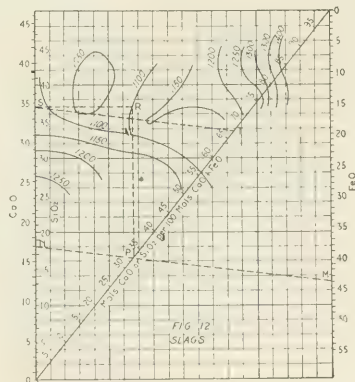
As an example of the use of the chart let us suppose that a slag is found to have the percentage composition  $\text{FeO}$ , 44;  $\text{CaO}$ , 17;  $\text{SiO}_2$ , 37; other substances, 2. Required its chemical formula and approximate melting point. Connect the point  $M$ ,

representing the ferrous oxide, with the point  $N$ , representing the lime; at  $P$ , where the inclined axis is crossed, we read "33 molecules of  $\text{CaO}$  in the slag for 100 molecules of  $(\text{FeO} + \text{CaO})$ ." From a point,  $S$ , representing the silica in the slag,

draw a line,  $ST$ , parallel to  $MN$ . The point  $T$ , where the inclined axis is crossed, will give the number of molecules of  $\text{SiO}_2$  for 100 molecules of  $(\text{CaO} + \text{FeO})$ . In the present case there are 33 molecules of lime, 67 molecules of ferrous oxide, and 67 molecules of silica for 100 molecules of basic oxides, hence the formula of the slag is very closely



This chart gives also the melting points of slags of various compositions. Thus, if we pass vertically upward from  $P$  to meet the horizontal from  $S$  at the point  $R$ , we find ourselves on the contour line marked  $1100^\circ$ , the melting point of the slag in question. The diagram shows, moreover, that a slight in-



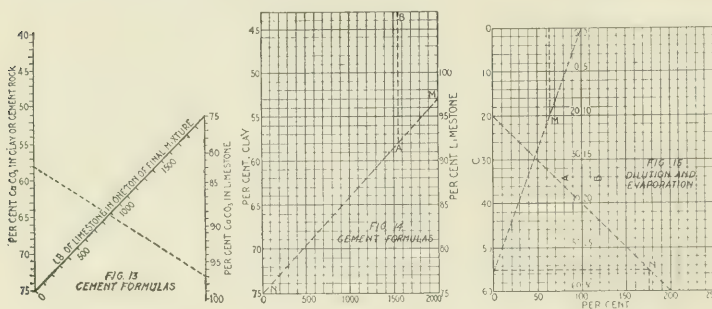


crease in the percentages of ferrous oxide and silica at the expense of the lime would result in a slag of lower melting point.

In the case of highly acid slags the point *T* will lie so far to the right as to fall entirely without the limits of the diagram. In this case it is best to enter the chart with half or one-fifth of the actual percentage of silica, the molecules of silica per 100 molecules of basic oxides read from the chart being multiplied by 2 or 5, respectively. Melting points are in this case best gotten by consulting a separate set of melting-point curves, which are always more accurately read than contour lines. The latter have, moreover, the disadvantage of being too much dependent on the judgment of the person who first plots them from experimental data; yet for rough approximations within a limited range, the melting point contour lines shown in the diagram will be found very useful.

#### MIXTURE CHARTS

Another class of charts closely related to the one just described is that for dealing with mixtures. Many special cases occur, according to whether the composition of the final mixture or either of its constituents is constant or variable in composition; according to whether results are to be calculated to a basis of a fixed weight of mixture or of one of its constituents; and according to whether or not different ingredients are to be reduced to a basis of chemically equivalent quantities, etc. Lack of space prevents us from giving more than three of the



many interesting charts that might be presented here, each with its own special advantages.

In Fig. 13 is a chart for preparing mixtures for the manufacture of cement from clay and limestone, assuming the content of alumina and silica in the raw materials to be so nearly constant as to permit the mixture being controlled by determinations of calcium carbonate alone. To construct this chart draw two vertical axes, any convenient distance apart, and graduate them, *both downward*, in percentages of calcium carbonate, choosing such a scale unit that the percentages of calcium carbonate likely to be met in the clay or cement rock (left axis) and in the limestone (right axis) fall within the limits of the chart. It is necessary to use the same scale unit in graduating both axes, but neither scale needs to be carried upward to zero, nor is the relative position of the lower limits of the two scales a matter of any importance. If the final mixture is to be adjusted to 75 per cent  $\text{CaCO}_3$ , connect the points marked 75 per cent on the two scales, and divide the inclined axis thus gotten into twenty equal parts, each representing 100 lbs. of limestone in one ton of final mixture.

As an example of the use of this chart, suppose that we have a cement rock containing 58 per cent  $\text{CaCO}_3$ , and a limestone containing 97 per cent  $\text{CaCO}_3$ . Connect these two points, best by means of a straight line scratched on the lower surface of a sheet of transparent celluloid. Where the inclined scale is crossed is read 87.5 lbs., the weight of limestone to be contained in one ton of the mixture.

Not only may diagrams similar to that just described be

used to calculate the proportions in which two raw materials of variable composition need to be mixed in order to give a mixture of constant composition, but the converse problem may be solved: if the ingredients of a mixture are of constant composition the proportions in which they are present in a given mixture may be readily determined. Thus, if a sample of red lead is assumed to consist of a mixture of litharge and lead dioxide (disregarding the possible presence of other oxides of lead) the percentage of each may be gotten from a determination of the percentage of lead in the mixture, points representing the percentages of lead in litharge and in lead dioxide, respectively, being located on separate axes and connected by a line, which is graduated from left to right in percentages of that oxide whose composition has been located on the right-hand axis. By connecting points on the two vertical axes representing the percentage of lead found in a given sample of red lead, the percentage of litharge and of lead dioxide may be read directly from the chart. The reader will have little difficulty in adapting this chart to other cases of indirect analysis.

Returning now to a consideration of the preparation of mixtures of limestone and clay for the manufacture of cement, if we wish to calculate the weight of limestone to be taken, not for a ton of mixture as before, but for a ton of clay, we have the diagram shown in Fig. 14. Notice that here the percentages of calcium carbonate are laid down along vertical axes, starting from a horizontal base-line, the graduations of one scale running downward, and those of the other upward. To use this chart pass a straight line through the point denoting the percentage of calcium carbonate in the limestone (*M*) and that denoting the percentage of calcium carbonate in the final mixture (*N*). This line intersects a horizontal line (of the cross-sectioning) passing through the percentage of calcium carbonate in the clay at some point *A*. From this point pass upward to the point *B*, where we read the number of pounds of limestone that will be needed for one

ton of clay. Thus, if the clay contains 58 per cent  $\text{CaCO}_3$ , and the limestone 97 per cent  $\text{CaCO}_3$ , there will be needed 153.5 lbs. of limestone for every ton of clay. If the percentage of calcium carbonate in the clay is so low that there will be needed more limestone than clay, the cross-sectioning of the chart may be carried further to the right; or the problem may be so changed as to calculate the number of pounds of clay to be used for one ton of limestone.

In Fig. 15 we have a chart for determining the number of pounds of water that must be added to a given weight of solution of definite specific gravity or percentage strength in order to produce a definite diluted solution; or the number of pounds of water that must be evaporated from a given solution in order to produce a more concentrated one.

The chart is constructed with three vertical axes, *A*, *B*, and *C*, the unit of scale *B* being twice that of scales *A* and *C*. The horizontal distance between the axes *A* and *C* is divided into 100 equal parts representing percentages of evaporation or dilution. Since dilution may amount to more than 100 per cent, the graduations are carried out to the right of scales *A* and *B*, say to 250 per cent.

As an example of the use of this chart, let us suppose that a sugar solution of 20° Brix is to be evaporated to a syrup of 55° Brix. Connect this point on scale *C* representing 55° Brix with the zero of scale *A* (representing water). At the point *M*, where the horizontal through 20° Brix is crossed, we read 64 per cent evaporation.

Conversely, if 64 per cent of water were to be evaporated

in a solution of 20° Brix, locate the point *M* where the vertical through 64 per cent intersects the horizontal through 20° Brix (scales *A* and *C*). Connect the point *M* with the zero of scale *B* and produce the line thus gotten until it cuts the *C*-scale at 55°, the required Brix of the syrup.

In a similar way we might calculate the amount of water that would need to be added to a syrup of 55° Brix to dilute to 20° Brix. Note that in this case the result is the number of pounds of water to be added for every 100 pounds of diluted solution.

If it is desired to calculate the dilution for 100 parts of syrup in any generally the case, instead of for 100 parts of diluted solution, a somewhat different method is used. Thus, if we wish to determine the water that would have to be added to a solution of 55° Brix in order to produce one of 20° Brix, connect points representing 20° Brix on scales *B* and *C*. Where this line cuts the horizontal through 55° Brix (scale *A*) we read the number of parts of water to be added to one hundred parts of syrup (by weight).

Since scale *A* is used only in problems dealing with dilution, it may be omitted from the chart if only evaporation is to be considered. In any case it is better to letter scale *A* in red ink, since there is otherwise some danger of interchanging scales *A* and *B* in reading the chart. The reader will perceive that a chart of this sort may be used for diluting concentrated solutions of any kind from one percentage strength to another. If specific gravities or degrees Baumé are to be used the scales are graduated, first in percentages, the percentage graduations being erased for a scale of specific gravities or degrees Baumé have been laid down. It is only with sugar solutions and the Brix scale that the percentage length of the solution will be directly given by areometer reading. If volumes of solutions are to be brought into consideration in dilution problems, a modification of the diagram given in Fig. 3 will be found to offer the most convenient solution.

#### ALINEMENT CHART

The next type of chart to be considered is that in which three variables are connected by the equation

$$ax + by = cz.$$

This chart consists of three parallel axes (Fig.

17), the left-hand one being for the values of *x*, the right-hand one for *y*, and the middle one for *z*. To construct this chart draw the left and right axes exactly parallel, at any convenient distance apart. Graduate the left axis in values of *x* at the rate of *A* units per centimeter, beginning the graduations at any convenient point on the axis, *A* being so chosen that the scale for *x* and the scale for *z* (to be graduated afterward) will not be inconveniently long or short. In a similar way graduate the right axis at the rate of *B* units per centimeter. Now it may be shown by geometry that if each value of *z* is to lie on the same straight line with corresponding values of *x* and *y* (on the other two axes), then the distance *m* from the left axis to the middle axis must be such that

$$m = \frac{bBn}{aA + bB'}$$

where *n* is the distance between the two outside axes; and that the middle axis must be graduated with values of *z* at the rate of *C* units per centimeter, where

$$C = \frac{aA + bB}{c}$$

The chart is used by lining up corresponding values of *x*, *y* and *z* by means of a straight edge, whence the name *alignement* chart.

In Fig. 17 we have a chart for determining the milligrams of sodium oxide and of potassium oxide, respectively, shown by an analysis in which the two metals are first weighed as chlorides, the potassium being afterward collected and weighed as potassium chloroplatinate. Since the factor for converting potassium chloroplatinate into potassium chloride is 0.3068, and that for converting sodium oxide into sodium chloride is 1.583, we have

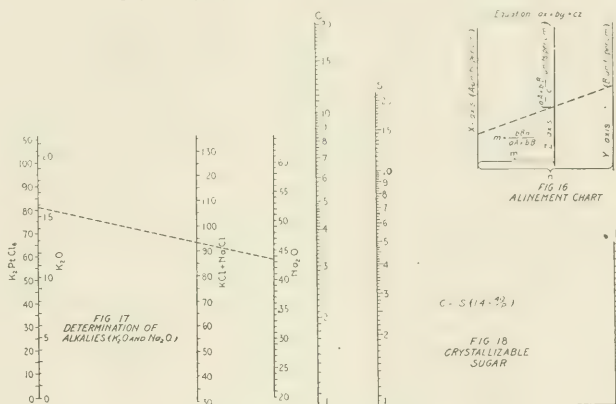
$$0.3068x + 1.583y = z,$$

where *x* is the number of milligrams of potassium chloroplatinate obtained, *y* is the number of milligrams of sodium oxide in the sample, and *z* is the combined weight of sodium and potassium chloride.

Let the outside axes be taken 20 cm. apart. Graduate the left axis at the rate of 5 mg. of potassium chloroplatinate per centimeter. The right axis is to be graduated in milligrams of sodium oxide at the rate of 2 mg. per centimeter, beginning with 20 mg. (if that is the least weight of sodium oxide that is likely to be met in any of the analyses). The distance from the left axis to the middle axis is then

$$m = \frac{2 \times 1.583 \times 20}{5 \times 0.3068 + 2 \times 1.583} = 13.47 \text{ cm.}$$

Locate the middle axis at this distance to the right of the left axis. Now 40 mg. of sodium chloride are equivalent to  $40 \div 1.583 = 25.25$  mg. of sodium oxide. Therefore lay a straight



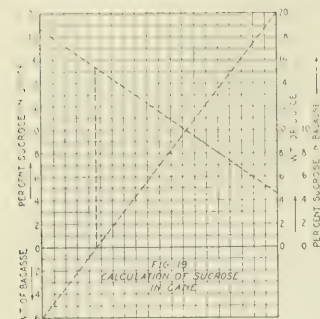
edge to connect the zero of the potassium chloroplatinate scale with 25.25 of the sodium oxide scale. The point where the middle axis is crossed is marked 40. In the same way 100 mg. of sodium chloride correspond to 63.16 parts of sodium oxide; therefore connect the zero of the potassium chloroplatinate scale with 63.16 on the sodium oxide scale, and mark the point where the middle axis is crossed 100. The distance between the points 40 and 100 on the middle axis is then divided into sixty equal parts and the graduations continued upward and downward to the limits of the chart.

As an example of the use of the chart, let us suppose that a mixture of the chlorides of sodium and potassium weighs 94 mg. and that 81.8 mg. of potassium chloroplatinate are obtained. Connect these points on the middle and left axes, respectively, by a straight edge; where the latter intersects the right axis is read 43.5 mg. of sodium oxide, while just within the left margin of the chart we read 15.9 mg. of potassium oxide. The scale of potassium oxide here referred to is constructed by dividing the space between 0 and 100 of the potassium chloroplatinate scale into 19.38 equal parts, since the factor for converting potassium chloroplatinate into potassium oxide is 0.1938.

Of course the preceding chart might have been constructed with any other rate of graduation for the outside axes, the



middle axis being placed accordingly, and either of the outside axes might have been begun at any convenient point. When one point of the middle axis has been located by calculation, the other graduations may be laid down by the method just described; or, if the calculated value of  $C$  in the equation above happens to be a round number all the divisions of the middle



each of several gases in a mixture is determined from the decrease in volume observed and carbon dioxide formed when the mixture is burned. A modification of the chart in Fig. 13 will frequently serve the same ends. Other uses for the alinement chart are in calculating the formulas of isomorphous mixed minerals from analytical data, in calculating heat exchange and loss by radiation in evaporation problems, and in finding the amount of a given substance necessary to react with a mixture of two others.

Fig. 18 is an alinement chart for determining the crystallizable sugar in sugar-cane juice, according to the formula

$$C = S(1.4 - 40/P),$$

where  $C$  = per cent crystallizable sugar;  $S$  = per cent sucrose; and  $P$  = per cent purity of the juice. Putting this in logarithmic form we have

$$\log S = \log C - \log(1.4 - 40/P).$$

Plot values of  $\log C$  along the left axis, letting unit logarithmic distance equal 25 centimeters ( $A = 1/25$ ). Plot values of  $-\log(1.4 - 40/P)$  along the right axis, letting unit logarithmic distance equal 100 centimeters ( $B = 1/100$ ). Since the quantity  $(1.4 - 40/P)$  is less than unity, its negative logarithm will be positive, and is hence measured upward along the right axis. If the total distance between the outside axes is 20 cm., the middle axis will need to be 4 cm. from the left axis. The middle axis is graduated at a rate which may be calculated to be 1/20 unit per centimeter (from the general equation for the value of  $C$  in the discussion above of the principle of the alinement chart).

This chart is given, not so much because of its practical importance, as because it illustrates as well the way in which a very complicated equation may often be solved by the alinement chart method. In practice it would be easier to calculate crystallizable sugar from another formula, in which the Brix of the solution is used instead of its purity, *e. g.*,

$$C + 0.4 B = 1.4 S.$$

This may be charted at once by the alinement method, without recourse to logarithms, or even as a figure-4 chart.

#### COMBINATION CHARTS

Other types of charts might be described, but it will be found that in practice the ones here given will serve for the solution of almost any problem that does not demand greater accuracy than that of which the graphical method is capable. The different types of charts are all interrelated, and there are so many intermediate types that the classification here adopted is but

<sup>1</sup> Tabulated by Geerligs, "Methods of Chemical Control in Cane Sugar Factories," Altrincham: Norman Rodger, 1905.

a very arbitrary one. A single chart may illustrate at once the principles of several different types, so that we have what might be termed combination charts, illustrated in Figs. 19 to 21.

Fig. 19 is a chart that is a combination of an alinement chart with a mixture chart, for calculating the percentage of sucrose in sugar cane, having given the weight and composition of the bagasse and expressed juice (dry grinding). It is worth noting that this chart may be used to solve the most general case of mixtures, namely, that in which two constituents of varying composition are mixed in any proportion to give a final mixture of varying weight whose composition is to be calculated.

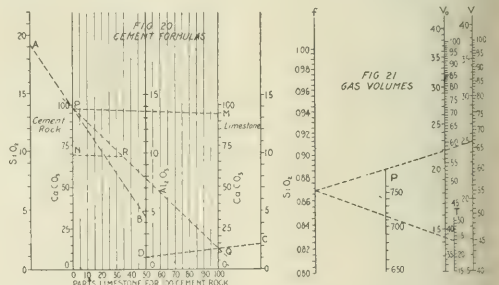
In Fig. 20 is a combination of two alinement charts with a mixture chart for calculating the number of pounds of limestone to be added to one ton of cement rock to prepare a mixture for the manufacture of cement, according to the formula of Meade,<sup>1</sup> which demands 90 per cent of the calcium oxide that would be needed to form tricalcium silicate and tricalcium aluminate with the silica and alumina in the raw materials.

In Fig. 21 is a double logarithmic alinement chart for reducing the volumes of gases from one temperature and pressure to another. It might easily be constructed for problems in which the temperature is expressed in degrees Fahrenheit, and the pressure in inches of mercury. Since the reader who has been sufficiently interested to follow us thus far will be able to discover for himself the exact manner of construction of these last three charts, they are here presented without further comment.

#### CONCLUSION

In constructing graphical charts one should take care to use only drafting tools of tested accuracy, since triangles and T-squares not perfectly straight are often discovered. There are certain knacks in drafting that enable one to rule parallel lines with precision and subdivide the main graduations of the axes very rapidly. The drawings that illustrate this article have been so much reduced in photographing that none of them has been subdivided to the degree which would be advisable in practice, and only the larger divisions of the cross-sectioning appear.

In conclusion, it need hardly be remarked that one should consider carefully which one of the various charts that may be used in any given case is the simplest to construct, and which the easiest to read. It will often be found that a slight change in the conditions of a problem, or a simple transformation of



the manner of its expression, will suggest methods of charting far more suitable than the one first brought to mind.

Since the writer expects to publish in book-form a more detailed description of these charts and others than is possible in a periodical like this, he will be obliged to those who direct his attention to published or unpublished work on the subject.

In conclusion, he wishes to express his obligation to his assistant, Mr. Francisco Quisumbing, who drew many of the charts used to illustrate this article.

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<sup>1</sup> Meade, "Portland Cement," Easton, Pa.: Chem. Pub. Co., 1907

NECESSITY FOR AN AMERICAN DYESTUFFS INDUSTRY  
TO AID EXPORT TRADE IN TEXTILES<sup>1</sup>By HENRY HOWARD<sup>2</sup>

A year ago, at St. Louis, I discussed the chemical industry under the general subject of "Problems Arising in War and Commerce." At that time importation had fallen off only 1/4 per cent from July to November inclusive, as compared with the same period in 1913. Importations of dyestuffs were coming in regularly from Germany and there was no actual shortage. As I pointed out, the greatest effect of the war upon the chemical industry was a national awakening to the absolute dependence of American upon foreign countries for products which are essential to our national welfare.

Germany was strictly limiting us to 75 per cent of the tonnage of dyestuffs that we bought from them during the twelve months preceding the war; that is, she allowed us to buy only one-fifth of this quantity each month, so that, if we attempted to increase the volume of our textile business and of other businesses using dyes beyond what it was the preceding year, we would be confronted with a shortage of dyes, and I further pointed out that this was likely to prove a serious obstacle in the development of any large foreign business in the goods affected. How true this statement was is now apparent to every one.

## GERMAN FIRMS RESPONSIBLE

Mr. I. F. Stone, President, National Aniline & Chemical Company, recently said:

"I say, therefore, that the German firms are responsible for the difficulty and the acute position of the American consumers. Their primary reason for this holding back of shipments was obviously due to the fact that they did not want American consumers to get an oversupply of colors so that they could make extra quantities of goods which they might use for export customers in other countries who had formerly bought the same goods from Germany, but who could no longer obtain them.

Within three months after our St. Louis convention, the importation of all chemical products from Germany was stopped, and we have since been getting along with what had been accumulated outside of Germany plus the amount that our small dyestuffs industry could produce in this country.

There is no doubt that at present Germany has some dyes available for distribution, and the British Order in Council limits its shipment to this country. We must, therefore, draw our own inferences whether Germany does not want us to have these dyes unless we give cotton in exchange or whether she wishes to restrict our activity in foreign trade.

## DYE SHORTAGE DISASTROUS

The result has been disastrous to what we all desire—namely: an increase in our foreign trade in textiles. Many textile mills have been obliged to curtail their output at a time when, if we had been independent of other countries, with a dye industry well established, these same mills could have been running night and day manufacturing goods for export and establishing foreign connections by aid of which a considerable percentage of this business might have been retained after the close of the war. Let us go back for a moment now and see why there is no adequate coal-tar industry in this country. Investigation shows that the fault cannot be charged to the Democratic party but to the strenuous efforts of the foreign manufacturers and American importers, ably assisted by the short-sighted selfishness of these same textile manufacturers who are now the principal sufferers. I believe that, in many cases, these textile manufacturers did not act of their own initiative but were influenced by the clever arguments of American representatives of foreign coal-tar manufacturers.

<sup>1</sup> Address before the Third National Foreign Trade Convention at New Orleans, January 27 to 29, 1916.

<sup>2</sup> Vice-President Merrimac Chemical Company; Chairman of Executive Committee of the Manufacturing Chemists' Association of the United States.

In the winter of 1908-9 I took active part in Washington on behalf of the chemical manufacturers to try and maintain the small protection we had left, and to get suitable protection on basic coal-tar products so that the industry could be established here on a firm foundation from the ground up, because in no other way can it be independent of other nations. Yet our efforts failed, largely as the result of the opposition of the well-protected textile manufacturers.

## COAL-TAR DUTY INCREASE PROTESTED

If you will look on Page 146 of the Tariff Hearings before the Committee on Ways and Means of 1908-9, you will find a memorial and protest in opposition to any advance in duties on coal-tar colors and dyes signed by the following companies:

AMOSKEAG MANUFACTURING COMPANY, Manchester, N. H.  
HAMILTON MANUFACTURING COMPANY, Lowell, Mass.  
PACIFIC MILLS, Lawrence, Mass.  
MASSACHUSETTS COTTON MILLS, Lowell, Mass.  
MERRIMAC MANUFACTURING COMPANY, Lowell, Mass.  
COCHECO MANUFACTURING COMPANY, Dover, N. H.  
AMERICAN PRINTING COMPANY, Fall River, Mass.  
THE U. S. FINISHING COMPANY, New York.  
THE APPONAUG COMPANY, Apponaug, R. I.  
GARDNER & COMPANY, Pleasant Valley, N. Y.  
PASSAIC PRINT WORKS, Passaic, N. J.  
ARNOLD PRINT WORKS, North Adams, Mass.  
WINDSOR PRINT WORKS, North Adams, Mass.  
RENFREW MANUFACTURING COMPANY, Adams, Mass.  
QUEEN DYEING COMPANY, Providence, R. I.  
S. H. GREENE & SONS CORPORATION, Riverpoint, R. I.  
ASPINOOK COMPANY, Jewett City, Conn.

The folly and unreasonableness of the textile manufacturers in lending their powerful influence to the foreign manufacturers of dyestuffs in their successful effort to crush out our coal-tar industry may be appreciated by a consideration of the following figures given by Mr. I. F. Stone in an address before the National Exposition of Chemical Industries, held in New York City last September:

The lines of manufactures which are dependent on their supply of dyestuffs, to continue their regular production, the most important, perhaps, are the textile manufactures, comprising cotton, wool, carpets, knit goods, silk, cordage, shoddy dyeing and finishing. The following figures are taken from the Census of 1909:

	Establish- ments	Em- ployees	Capital	Salaries and Wages	Value of Product
Cotton.....	1,324	387,771	\$822,237,529	\$147,270,903	\$628,391,813
Wool.....	985	175,176	430,578,574	82,523,776	435,978,558
Carpets.....	139	34,706	75,627,010	17,745,092	71,188,152
Knit Goods.....	1,374	136,130	163,641,171	52,431,680	200,143,527
Silk.....	852	105,238	152,158,002	46,097,364	196,913,667
Cordage.....	164	27,214	76,020,366	10,935,545	61,019,986
Shoddy.....	88	2,320	6,886,825	1,196,376	7,446,364
Dyeing and Fin- ishing.....	426	47,303	114,092,654	26,261,634	83,556,432
	5,352	915,858	\$1,841,242,131	\$384,522,370	\$1,684,636,499

When you consider that the value of the coal-tar products annually imported is normally only \$10,000,000, of which not more than 75 per cent or \$7,500,000 is used for textiles, an increase of 10 per cent in the duty if the whole amount had been paid by the textile manufacturer would have been \$750,000, or less than 4 1/2 cents

$$(\$750,000 \div \$1,684,636,000 = 0.00044)$$

for each \$100 worth of textiles produced, a sum so insignificant that it could have had no appreciable influence on the ability of the textile interests to meet foreign competition, and would have been money well expended, not only as an insurance against the condition which now exists, but would in many cases have resulted in the ultimate lowering of the price of goods in which there is no competition at present.

## FATAL TARIFF REDUCTION IN 1883

Few people remember that in 1882 we had quite a flourishing young coal-tar industry which, with consistent protection, would have long since been a large—if not a dominating—factor in our color supply. The fatal tariff reduction was made in 1883



through the initiative of the importers, backed up by the co-operation of users of colors. Let me quote from a statement made by E. P. Wheeler, Vol. 1, page 230, of Report of the Tariff Commission, 1882:

Would it be a wise policy for us to build up a manufactory of aniline dyes in this country when they can be made more cheaply abroad because the raw material is found in a cheaper condition in England? The English coal, as everybody knows, is richer in the hydrocarbons or inflammable matter than our American coal, and it is well known that we do import to some extent English coal to make gas, although the duty on it is a high one. The only objection that has been or could be made in regard to that would be that if we got into a war with some of the European countries we should be at a disadvantage in regard to these colors. I suggest that that is a very contingent and remote disadvantage; that the possibilities of such a war are insignificant.

#### AMERICAN DYESTUFFS INDUSTRY GAVE PROMISE IN 1882

In Vol. 1, page 207, there is a letter from H. K. Lansing, Treasurer of the Albany Aniline Works, dated Feb. 8, 1882, from which I will quote, and which shows the promising state of the industry at that time:

We are now engaged in the manufacture of all the fine aniline blues, and expecting ere long to make all the finer colors made in Europe. As an illustration of the benefit the country has derived from our efforts, we can state that large crystals of red were sold in 1868 at \$6.50 gold. We now supply the trade with an acknowledged better color at \$2.50 per pound. Blues were sold one year ago at \$4. Since we commenced making, the price has dropped to \$2.50. We think we deserve the sympathy and encouragement of the powers that be.

In refreshing contrast to the textile manufacturers' action in 1908, allow me to quote from a statement of James Hendrick, President of the Albany Aniline & Chemical Works, page 256, Tariff Commission's Report, 1882:

The Pacific Mills and other like manufactories in this country express the strongest hope that we shall receive from you the encouragement we are entitled to. In a letter addressed to me within a week by Mr. Saltonstall, the treasurer, he said there were some importers, or the agents of foreign color companies going through the mills in New England, expecting to get a petition signed in favor of the reduction of the duty on aniline colors, and he said they would have no sympathy from them and cautioned me against them.

#### EUROPEAN DYE MAKERS URGED TARIFF REDUCTION

Again, in a communication from V. G. Bloede, representing the American Aniline Works of Parkersburg, W. Va., dated Aug. 21, 1882, Vol. 1, pages 565-568, Tariff Commission Report, 1882, Mr. Bloede says:

The actual disposition of the largest consumers of the anilines is fairly represented by the following sentence in a letter recently received by me from one of these consumers: "The representatives of a large European aniline works are making a great push to have the duties on anilines reduced. I enclose you their circular, which they are sending to all the manufacturers to obtain signatures. What do you as a manufacturer think of it, and what would you propose? We can stand it as it is, and, having all the protection we need on our manufactures, are willing to give all that is required to others."

The subsequent history of the aniline industry is lamentable. The Tariff Act of July 1, 1883, made a heavy reduction in the duty. No new factories were started, and within one year after the new tariff took effect, five of those already established were forced to succumb and go out of business, leaving only four to continue the work. These have since stayed in the business, but have not been able to develop to any extent.<sup>1</sup>

#### AMERICAN MANUFACTURERS READY TO COÖPERATE

In bringing to light past history I do not wish to be understood as bearing grievance against the textile manufacturers for any mistaken policy which they may have heretofore adopted. No one recognizes the error of this policy more keenly than these manufacturers themselves, and I am credibly informed that they now stand ready to coöperate in any way possible in order

to establish a permanent coal-tar industry within the United States.

It is instructive to compare the present condition of textiles in this country with that of iron and steel. The latter industry, thanks to the consistent protection which for years was extended to every branch of the business, is now absolutely independent of the rest of the world in its ability to manufacture all standard grades of iron and steel products in this country, with the result that not only are all American users of iron and steel products getting their supplies as regularly as before the war began, but a large export business is being developed as the result of the paralysis of this industry abroad. In textiles the saving of a possible 4½ cents on \$100 worth of product has resulted in so throttling the textile industry that it is having hard work to supply our local markets, much less to gain a strong foothold in the foreign markets formerly supplied by the belligerent countries.

Now what lesson can we learn from these disquieting facts?

#### PERMANENT NON-PARTISAN TARIFF COMMISSION

It seems to me that first and foremost it points to the absolute necessity of a permanent non-partisan tariff commission of experts that will sift the facts, analyze the situation and recommend rates consistent with the tariff policy of the party in power, and thus enable Congress to accomplish what it wants to do.

Such a commission should be created at the earliest possible moment by Congress, and if our textile industry is to take any active part in foreign trade during the war the first business the Tariff Commission should tackle is the study of the Chemical Schedule with the object of enabling Congress to amend the tariff so as to develop a permanent coal-tar dye industry on a large scale in this country. At present, in spite of high prices, chemical manufacturers have been afraid to invest any large sums in permanent equipment, realizing as they do that as soon as the war is over the industry would quickly disappear under the present inadequate tariff.

#### DESTRUCTIVE SELLING POLICY OF FOREIGN DYE MAKERS

Unfair competition is another means by which the foreign syndicates have kept the coal-tar industry from getting a foothold here. For instance, aniline oil, one of the primary products, was selling at a high price a number of years ago, and an American company built a plant and started to market its product. Then the price was immediately cut on the imported article to a point about 10 per cent below the cost of production in this country, and kept there until the American firm gave up the business. When this result was accomplished, the price was advanced to about the original level.

Again, in 1913, a duty of 10 per cent was placed on aniline oil, and the manufacture was again started, with the result that the foreign producers not only absorbed the whole of the duty but actually lowered the price again to a point where the business showed a loss to the American manufacturer—and this condition was maintained until the war intervened.

Now such competition is manifestly unfair. It is not what might be called legitimate dumping to dispose of surplus product in some foreign country, but is a well-considered policy designed to destroy a new American industry. Such a practice ought not to be permitted, and I think I am right in saying that the present administration has under consideration legislation to prevent it.

#### GERMAN DYESTUFFS PLANTS AS MUNITION FACTORIES

There is one other reason—one of public policy—why a coal-tar dye industry is important to the future of this country. At present every one is thinking and talking of preparedness, and one of its most essential items is our ability to produce enormous quantities of high explosives when they are needed. Germany was able to do this over night in the plants used for coal-tar dyes in times of peace. England, France and Russia, substantially without this industry, were almost helpless in this respect, and it may be said justly that the existence of the highly developed

<sup>1</sup> See "Who Killed Cock Robin?" Hesse, *THIS JOURNAL*, 7 (1916), 694.

industry in Germany, coupled with its non-existence in Russia, France and England, has been a determining factor in their relative ability to obtain high explosives, and in the remarkable successes Germany has maintained in the war up to date.

Returning again to textiles. We already produce the cotton for the fabric and all the raw materials necessary for the dyes—how much better it would be for the cotton growers of the South and for manufacturers and laborers of the whole country if more finished goods and less raw cotton were exported, and the domestic consumption of raw cotton enormously increased.

In closing, I cannot do better than quote from the conclusions of my discussion of this subject a year ago as follows:

Our dependence upon foreign countries for chemicals, whether they be in the nature of raw materials, intermediate products, or finished articles, is a matter of national concern, and I sincerely hope that the Government, the consumer and the chemical manufacturer may unite in friendly cooperation in working toward a common end, *viz.*, the establishment of a coal-tar dye and chemical industry in this country free and independent of the world.

NORTH WOBURN, MASSACHUSETTS

## MAGNESIUM<sup>1</sup>

By W. M. GROSVENOR

The alkali earth division of the second group in the Periodic Table consists of more or less soft, white metals and all show great activity for oxygen, decomposing water more or less readily. One except aluminum has found large commercial use but of the others magnesium leads the list by a long distance. Its chief uses are:

1—Scavenging alloys, *i. e.*, clearing up oxides of other metals and making far denser, cleaner, stronger and more homogeneous alloys. It is valuable in aluminum, nickel, copper, brass, bronze, etc., and special steels, because of its intense avidity for both oxygen and nitrogen.

2—Alloying itself, with aluminum or aluminum containing traces of one or more of the other metals Cu, Ni, Zn, Pb, Bi, Sb, Fe, etc. Magnesium greatly modifies crystallography and physical properties and alloys readily with most metals and melts at a convenient heat.

3—Illumination, as in military uses, for shrapnel trailers, star bombs, flare lights, etc. and in photography for flashlights. Its easy inflammability (about 800° C.), the high heat of combustion (134,000 cal.), the relatively low heat of vaporization (100° C.), the intensely white oxide produced and the high temperature of volatilization of this oxide, are the essential factors.

## MARKET AND PRICES

How much is used? Records of imports for the year prior to the war indicated 38,000 lbs. About 100 lbs. a day, therefore, seemed to be a safe production to undertake. Prices before the war had been very steady around \$1.45 per lb. but it seemed reasonably certain the cost need not exceed \$1.00 per pound, and after the war began the prices being paid for remnants of imported lots quickly rose to \$2.50. Some of the first demands were from wholly unexpected quarters, in surprising amounts and at amazing prices. The most urgent, almost pitiful demands, came from quarters that were not even suspected to be interested in the least. One consumer has contracted for 24,000 lbs. and another 15,000, these two alone taking for strictly domestic use more than was supposed to be the total importation. There are at least three other buyers of similar quantities but exact amounts are not yet established. Sales are largely made yearly contract and even at present prices the consumption for strictly domestic use is about 50 tons. We found that a great deal of the material was being imported under other names and most carefully disguised—secrecy being preferred to economy.

<sup>1</sup> Address before the New York Section of the American Electrochemical Society, in joint session with the New York Section of the American Chemical Society, 'Chemists' Club, February 11, 1916.

Prices as high as \$10.00 per pound were gladly paid at first for domestic product. For some months then the prices jumped around from \$5.00 to \$7.50 but every effort was made to reduce conditions to some sort of order by dealing direct with the consumer. This was partly the result of a deliberate policy for better and more intelligent service of the consumer's precise demands as to quality and delivery, but partly also the result of meeting quite unexpectedly the competition of our own product at prices from 25 per cent below to 50 per cent above the prices we had made. Some of New York's clever War Goods brokers added 10 per cent each through a chain of four or five middle men. Others assumed direct quotations to have already been through this process and knocked off 20 per cent, trusting that "real cash business" would squeeze down the middle men they supposed to exist and still leave 5 per cent for the real seller. Now, however, for a number of months the price has been practically fixed at \$5.50 per lb. of "Guaranteed 99%," actually about 99.5 per cent. Occasionally a lot that has been picked up in the antebellum market for speculation is let go at lower figures, or a lot of lower grade material comes on the market from abroad, but there is practically no volume of these sales.

In spite of the beautiful appearance of the German bars they rarely exceeded 98 and often fell as low as 96 per cent. The process of extrusion conceals impurities by drawing them out into minute threads. It is safe to say that the regular commercial grade of metal made here now is superior to anything ever imported.

## REASONS FOR THESE PRICES

It may seem ridiculous to ask or pay such prices. Let us consider. The alloy market constitutes the bulk of the business, and governs prices. In aluminum castings, for instance, less than 2 per cent of magnesium cleans up the aluminum and leaves  $\frac{3}{4}$  to  $1\frac{1}{2}$  per cent in the casting, about doubling its tensile strength, and quadrupling its resistance to shock or jar. It reduces the cost of machining more than 50 per cent, halving the number of resets on the cutting tool, giving clean-cut machine surfaces, and permitting a polish to be secured with the last cut instead of a separate operation. With care,  $1\frac{1}{2}$  per cent of magnesium at \$5.50 per lb. is all that is needed, *i. e.*,  $8\frac{1}{4}$  c. per lb. of casting actually required to do the same work. The increase in strength means, in some cases, a reduction in weight of casting of 50 per cent and generally not less than 25 per cent. The saving in machine work alone when the casting is to require much machine work more than pays for the use of magnesium.

So much for the consumer or user. Now the manufacturer of magnesium has at present certain considerations (of necessity rather than mere excuse) for the high prices. Cost of production abroad prior to the war approximated \$1.00 per lb. Sales in England were about \$1.30 and here about \$1.45 per lb. At that time  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  was selling for about \$18 per ton. Present prices here are now about \$60. Other chemicals used in the manufacture have increased to ten times their normal price. One other factor, *i. e.*, insurance, must be considered in two forms: *First*, the insurance against cut prices and dumping that may come immediately upon the close of the war, making the plant and market-development work absolutely worthless. *Second*, the insurance against partisan interference. As a matter of fact in the case of two plants not a pound of material from either of which has gone for foreign military purposes so far as we know, there have been repeated efforts at molestation and some serious interruptions.

In considering prices it is well to mention separately export prices. Before the war nearly all the magnesium for England, as well as the U. S. and France came from Germany. Since the war both France and England are producing in considerable quantities of excellent purity. This fact and the failure abroad to realize the strenuous conditions here, account for the un-



willingness of buyers abroad to pay more than \$3.50 for powdered metal (all the above-named prices were ingot or bar).

#### PRESENT PRODUCTION

At present there is being produced here at two points about all the present alloy market will absorb, and an increase of plant is being made of about 25 per cent the present capacity. One other producer makes only about his own requirements. Two others are soliciting business but have failed to fill orders—in one case the order is not over a year old and still stands unfilled. All told, we believe the present production is at the rate of something over \$1,000,000 a year and will be slightly in excess of the present domestic needs.

#### POSSIBILITIES

The use of the metal for scavenging purposes depends on price of metal compared with price of material to be scavenged. For use with copper, brass, bronze, etc., the magnesium can be used at far higher prices than for steel. But the big consumption of the material can come only when it directly replaces aluminum as the predominant metal in the alloy, and arrives at a correspondingly low price. It makes beautiful castings, machines easily and well, is about a third lighter than aluminum and can be made about two to four times as strong. The coefficient of expansion reported is practically the same as for aluminum. When properly pure (over 99.5 per cent) it is apparently quite as resistant to corrosion as aluminum, equal if not superior in electrical conductivity (about half that of copper) and superior in heat conductivity to aluminum (also about half that of copper).

#### PROCESSES

I—REDUCTION OF FUSED  $MgCl_2$  WITH SODIUM involves the production of metallic sodium; we have been using the Castner process for this purpose to satisfy ourselves just what the sodium would cost and what the possibilities in this direction were. Existing conditions, the demand for sodium and sodium peroxide, forbid its consideration with a minimum of about 2 lbs. of sodium consumed for every lb. of magnesium produced, and the necessity of producing dehydrated fused  $MgCl_2$  to start with.

II—ELECTROLYSIS OF THE FUSED DOUBLE CHLORIDE (usually  $MgCl_2 \cdot 2KCl$ ) has been perfected and is very largely used abroad. We have commercially used and studied the process here and, with the cheapest water power and chloride, prices even under normal conditions by this process *must* rule above \$1.00.

III—REDUCTION WITH CARBON (PATENTED) is absolutely fascinating in its possibilities. The product is a black or gray powder. Believing such a product would be valuable, the manufacture was carried out on a scale of about 25 lbs. per hr. As the difficulty of selling the product became apparent, much time and effort were devoted to attempts to recover the metal in fairly pure form. Owing to serious objection both on the side of cost and regularity of product this process was superseded.

The other processes—electrolysis of dissolved  $MgO$ ,<sup>1</sup> reduction of fused  $MgCl_2$  with aluminum,<sup>1</sup> reduction of oxide or carbonate to slag-forming residues,<sup>1</sup> etc.—will be discussed on some other occasion when the engineering problems they involve are believed to be finally solved in the best way and the patent office has finished considering them. The chemical side of each has been thoroughly worked out, however, so that some conclusions may be drawn from the large laboratory or small commercial operations. These may be of considerable interest.

At least one of the processes appears to be adapted to produce directly metal averaging 99.6 per cent purity in tons per day instead of pounds. Laboratory tests give a raw material cost of 4 c. per lb. of magnesium and indicate a fuel cost which approaches 3 c. as a theoretical limit, though the practical figure will probably be several times as high. The final selection of various possible engineering means and methods remains to be worked out, but it scarcely seems possible that either labor

or repairs should exceed 2 c. per lb. Thus if commercial yields maintain the experimental level and three times the theoretical power is commercially required, we have prospects of a net factory operation cost (without interest, amortization, insurance, patent, administration or selling) of 17 c. per lb. If only 75 per cent yield is obtained this net factory cost would be about 22 c. or a total cost with all overhead expenses of 35 c. and a selling price of 40 c. to 50 c. according to tonnage.

It may be asked with perfect propriety, "Why talk about it now? Some fool will certainly want you to make a contract with him at lower prices, possibly at 50 c. He will not realize that it is only the present price of \$5.50 that justifies or even makes possible the \$1000 and \$10,000 experiments that have been tried and must be tried again and perhaps again during the next three to five years before the tide turns. You will be pestered for years with this 17 c. talk." We have carefully considered this probability. The men who are doing this work do not cultivate talkativeness as a preference. Just at this time, however, certain consideration of public welfare should take precedence of preference. National self-preservation demands the subordination of personal interest. If we expect representatives at Washington to jettison the pork barrel, the army post, the high-tide navy yard, and political trading generally, and give us a fighting chance for our lives in the scrap that is certainly coming, we must set the example of considering national interest first. If we are to have the army and navy preparedness for which we have already wasted more money than Germany has paid for her wonderfully efficient fighting machine, if we are to have any preparedness instead of repairs or regrets, we must coöperate with all we have in service, information and suggestion.

Therefore, at the risk of criticism and possible financial sacrifice it seems to be a duty at this time to point out what may possibly be expected of magnesium. Few realize the extent to which it is valuable in military work. One of the great foreign explosive experts stated that he would be glad to pay \$1.50 per lb. for 500 tons. A single contract for shrapnel being executed in this country would require about 50 tons. The illuminating bombs to make daylight over the enemies' works and trenches consume large quantities. The trailers attached to shells serve at night to show the effectiveness of the fire. For all these purposes magnesium produces a result that cannot be approached by antimony or aluminum. But consider what it means to aeroplane, dirigible, and motor construction, to high-speed engines of every type, to reduce weight one-third and double strength. This material has a density of 1.75 and may be hot-rolled to a tensile strength of 35,000 lbs. per sq. in. or cold-rolled very much higher. Although five or six men are being kept practically all their time on the development of these possibilities, the broad, quick development is a task for the energy of hundreds, even thousands. Feeling the responsibility which knowledge of the possibilities entails, it became the duty of those in charge of this work to let others know and be active in their side of preparation—the application of the material.

50 EAST 41ST STREET, NEW YORK

#### THE RÔLE OF THE CHEMIST IN THE CEMENT

##### INDUSTRY<sup>1</sup>

By C. N. WILEY

Received January 3, 1916

Much mystery attended the processes employed in the early manufacture of Portland cement. When the brick layer of Leeds discovered that he could make an artificial water cement from a mixture of Thames chalk and Medway mud, he took every precaution to insure that none should discover the secret of his process. When engaged in making his raw mixture, it is said that he attired himself in flowing black gown and the pointed hat of the mystic and performed curious incantations over his

<sup>1</sup> Address presented before the Alabama Section of the American Chemical Society, December, 1915.

<sup>1</sup> Patent applied for.

erations. I. C. Johnson in 1845 wrote: "Thus he had a kind tray with several compartments and in these he had powdered phosphate of copper, powdered limestone and several other matters. When a layer of washed and dried slurry and the coke had been t into the kiln, he would go in and scatter some handfuls of these powders from time to time as the loading proceeded, so the whole thing was surrounded by mystery."

One can imagine with what intense interest Mr. Johnson served this remarkable procedure and it is small wonder that he was fired with a stronger determination to know of what the composition of this cement consisted. Procuring a sample, he did one of the most prominent chemists of England make an analysis and the chemist's report that the substance contained 10 per cent phosphate of lime mystified Johnson still further. In thinking that at last he had won the secret of this hydraulic compound, he made a large collection of bones from the butchers of the city and proceeded to calcine them. Needless to say, he is induced to discontinue his operations by the outraged citizens of the vicinity.

So up to this time, the chemist proved rather an obstruction to a help to the solution of the cement problem. But by the old method of trial and error, Johnson at last succeeded in making a cement which was equal in every respect to that of Portland and from this on the industry began to expand and thrive.

In the early days of the Portland cement industry, the correct judgment of the proportion of carbonate of lime to clay was purely an empirical process. In the first place, mixtures were made in varying proportions from which samples of cement were prepared and the proportion giving the best cement was adopted. Any irregularity due to variations in the chemical composition of the materials, or carelessness on the part of the workmen, was ascertained by sampling the mixture frequently, the samples being burned in a trial kiln. From a close observation of the resulting cement, when tested for soundness, color etc., the "sampler" was, by long experience, enabled to judge whether the correct proportions were being maintained. This was a tedious and an unsatisfactory process, for while a sample was being prepared and tested, the bulk it represented had passed beyond the reach of alteration. If the slurry was run into backs, any error was corrected by altering the mixture and luting or stirring the contents of the back, from which a sample was occasionally prepared. With the Goreham process, no alteration of the previously prepared mixture was possible; it would probably be dry and ready for the kiln before the results of the sample were known. If the contents of any particular drying-flat or chamber proved to be over- or under-clayed, the burner could be instructed to burn it lightly or heavily as the case might be and this was really all that could be done.

When it is remembered that if the materials are in the first place suitable, success depended on the proper proportion of the carbonate of lime to clay and that for the same material this proportion was a constant one, it is evident that, if the carbonate of lime in a normal sample was known, the correctness of the mixture could be checked by the determination of this substance in the trial sample. And it was upon this determination that the chemists depended largely for the proper composition of their mixtures.

An instrument known as Scheibler's calcimeter, originally devised by Dr. Scheibler for determining the amount of carbonate of lime present in animal charcoal used in sugar refining, was frequently employed for determining carbonate of lime in Portland cement mixtures. The principle of its action is well known to chemists and it was the principal instrument for mixture control in the cement industry up to ten years ago. The results obtained through it, although "near enough" for any technical purposes, were far from accurate. The carbonic oxide evolved is collected over water in which it is to

some extent soluble and a correction has to be made dependent, of course, upon the volume of gas evolved. The Lunge nitrometer, in which the gas is collected over mercury, was also commonly used. Very little knowledge of chemistry or chemical manipulation was necessary for the use of the calcimeter or nitrometer.

Thus in the early days, the chemist was hardly known in the cement industry and it was unthought of for a cement manufacturer to employ the exclusive services of a professional chemist. The employee responsible for the maintenance of a correct and uniform mixture of raw materials was but a workman of more than the ordinary intelligence whose success depended on the rapidity with which he could make his test burnings and the degree of memory he possessed in profiting by past experiences.

Redgrave remarks in his book on calcareous cements that "the sample kiln should not be ignored when working with new and untried materials and much may be learned from the methods of the old-time sampler, his methods of work and the unconscious instinctive way in which he reasoned from the appearance of his samples. It should not be forgotten that Portland cement was discovered by a bricklayer and that its reputation was established long before the process of manufacture became a scientific question."

In this country, the early manufacture of Portland cement was chiefly confined to the Lehigh Valley region through which ran a belt of argillaceous limestone, the composition of which was almost in the exact proportions for making a high-grade cement equal in every respect to the more complicated mixtures of European manufacturers. The process of trial and error was largely responsible for the early success of men like D. O. Saylor and it was not until somewhat later that the chemist was first called into consultation and his advice was asked more for the purpose of locating new deposits of suitable rock and in the working out of problems which arose in the operation of the manufacturing process.

John W. Eckert may be called the father of cement chemists in this country. At the time Saylor and his associates were perfecting their processes above Allentown, Eckert was working as an assistant to Professor W. H. Chandler at Lehigh College, now University, South Bethlehem, Pa. He was asked to make analyses of rock from the different beds in the quarries of the Coplay Cement Works, of which D. O. Saylor was president. Cement was then made from each of these distinctive rocks and these cements were analyzed. In this way it was determined which beds were suitable for Portland cement and the other beds could be used in the manufacture of their Anchor brand natural cement. In his report of 1875-6, the State Geologist commenting on this says that "much technical and scientific supervision is necessary to determine which stone to use and which to reject in order to make a cement capable of undergoing the tests now applied by engineers and architects." So it might be said that the activity of the chemist in the cement industry depended greatly on the increasing severity of the specifications laid down by engineers and architects.

Eckert was finally engaged by the Coplay Cement Works to devote his entire time and knowledge to the process of manufacture and he thus became the first cement chemist in this country. His efforts resulted in more certainty and less chance in the preparation of proper mixtures and a more uniform product naturally resulted.

Somewhat later, Robert W. Lesley, of the pioneer manufacturers, was experimenting with the bricks into which the slurry was pressed preparatory to burning and he solicited the cooperation of George W. deSmedt, then a Government chemist engaged in the study of asphalts and kindred materials. Together these two men worked out various problems and were the first to mix the slurry with hydrocarbons before casting into



bricks. The incorporation of this hydrocarbon not only made an excellent binder but in the kiln the burning out of this binder rendered the brick more or less porous so that the mass could be more evenly burned.

Lesley and deSmedt also discovered the difference between crystalline and gelatinous silica and Lesley took out a patent for the manufacture of gelatinous silica which they thought was of great importance.

All cements in those days were quick-setting and many efforts were made to retard this setting for obvious reasons. When P. I. Giron, affectionately called "Pig Iron" by his men, a French chemist in the employ of the Atlas Cement Co., was in France he had noticed the workmen adding a white substance to cement before they applied same in building sidewalks. As gypsum was in common use in France in building operations, he suspected that this was the white material and he found that by adding a small amount of this substance to the cement, the setting time would be materially lengthened. Dyckerhoff in Germany was also making use of plaster to season his cement and he obtained a slower setting cement. Lesley took out a patent for seasoning cement, the principle of which was to sprinkle the clinker with sulfuric acid.

The question as to what Portland cement really is early received much attention from investigators. Chemical investigations, so far, have failed more or less completely to throw light on the complex structure of this substance, although mineralogical examinations have been more successful. Although chemical methods have failed to reveal the actual structure of Portland cement, much has been learned by the study of synthetic compounds. Probably Vicat was the pioneer in this line of research, followed by Rivot, Chatoney and Fremy.

In Germany, Heldt, Fuchs, Schott, Michaelis, Erdmenger, Dyckerhoff, Meyer and others were attacking the problem along this line. Up to 1885 the various theories advanced defined more or less definitely the chemical composition of the cement, but all believed that upon addition of water the cement broke down into simpler compounds and free calcium hydrate. Believing that if this free lime could be removed from the anhydrous cement much more could be learned of the actual composition, investigators sought reagents by which this extraction could be accomplished. Rebuffat was the first to make use of an aqueous sugar solution, but Michaelis and Feret objected that results obtained in this way must be incorrect.

Probably the most satisfactory test which we have for free lime is that devised by Professor A. D. White. The method is based on the formation on the slide of a microscope of a characteristic crystalline calcium phenolate readily recognizable in polarized light. The reagent is prepared by dissolving crystallized phenol in an immiscible and rather non-volatile solvent, such as nitrobenzol, and adding a trace of water. Thus it is

possible, by this test, to determine whether the chemical balance between the calcium and the other constituents in a good cement has been attained.

As mentioned above, much has been learned of the constitution of cement through mineralogical investigations. As these investigations were conducted in many cases by chemists, it is only proper to grant the chemist credit for his part in solving the problem. LeChatelier was one of the first to attack the problem along these lines and he was followed by many investigators. In this country, the work was being carried on by such chemists as Richardson, the Newberrys, Campbell and others and much was learned from their experiments. Several years ago, Day and Sheperd and scientists of the Geophysical Laboratory have, from extensive investigations, come to a conclusion as to the true constitution of Portland cement and they are now engaged on studies of hydration.

The technical chemist has not had the time to devote nor the opportunity to pursue investigations like the above but he has contributed to the knowledge of the subject in no small degree by working out technical processes whereby a high-grade product may be made and maintained. He has found that the cement rocks of the Lehigh Valley are not necessary for the production of a high-grade product but has gone into almost every State of our Union and has found there materials which when properly combined would produce a Portland cement of high quality. On account of the variation in composition of these raw materials, he has developed methods for their proper control. The increasing severity of cement specifications has caused a greater watchfulness throughout the process of manufacture until at the present day the chemist has in control every step of the process from the time the rock is won from the deposit until the finished cement is placed in the hands of the ultimate user. And he has gone yet further, for he has shown the user how this cement may be used to best advantage and has pointed out the necessity for closer inspection of the materials with which it is combined.

The chemist has shown that a true Portland cement can be made from blast furnace slag, heretofore a waste product. The utilization of this waste product has resulted in a great industry producing over 10 per cent of the total production in this country.

So in these years of progress and expansion, the cement industry has seen the humble "sampler" develop into the present highly trained scientist whose word is law concerning the process of manufacture. The chemist alone is responsible for the quality of the product, and the fact that American-made Portland cement is recognized as superior to that made in other countries is a tribute to the untiring efforts and ability of our chemists.

BIRMINGHAM, ALABAMA

## CURRENT INDUSTRIAL NEWS

### SELENIFEROUS PYRITES IN THE MANUFACTURE OF SULFITE CELLULOSE

Some selenium, says the *Paper Maker*, is contained in all pyrites. The percentage of selenium is ascertained by the hydrosulfide method and the ratio between sulfur and selenium fluctuates between 1 : 10,000 and 1 : 100,000. The quantitative determination is best carried out as follows: a mud rich in selenium is deposited in the colder parts of the gas pipes of chemical pulp mills; the mud is lixiviated until the reaction is neutral and treated in the water bath with concentrated potassium cyanide solution until its reddish color disappears; the solution is then filtered and the selenium is precipitated as cherry-red flakes by hydrochloric acid. When pyrites is roasted, the selenium escapes as selenium dioxide and enters into the

roasting gases and the cooking liquor. As a rule, however, small quantities of selenium do not matter. Sulfurous acid is oxidized in the air but selenious acid is reduced, red selenium being deposited. This reduction forms an excellent contact surface. Both the flying dust and also the selenium formed can be only partially removed from the roasting gases even with very good scrubbing apparatus. Some selenium will always be contained in the liquor.

The flying dust acts catalytically on the sulfur dioxide and the lime, which are converted respectively into sulfuric acid and plaster of Paris and are thus lost to the cooking process. In the cooking stage, when the percentage of sulfur dioxide and lime suddenly falls, the sulfuric acid, which is formed, colors the pulp dark, makes it brittle, difficult to bleach and thus ren-

ers it of inferior quality. This defect is met with especially when making readily bleachable chemical pulp because a longer time and a higher temperature must be employed. Systematic investigations have shown that the percentage of selenium in pyrites is primarily not an injurious constituent but the percentage of dust, in the same pyrites, containing dust, yielded bad liquor while one free from dust but with the same percentage of selenium yielded a perfect liquor.—McMILLAN

### SPANISH PLATINUM DEPOSITS

Careful inquiries, says the *Mining Journal*, have been made regarding the recent platinum discoveries in Spain. The locality may be indicated by following the direction of the Sierra Nevada it enters the province of Malaga. The end of the chain is called the Sierra de Ronda and contains several ranges of igneous rocks of the peridotite family, the most extensive covering an area of 45 mi. by 12½. The rock-system shows a striking analogy to that of the Urals. The peridotites of the Spanish rocks vary considerably according to the proportion of basic and acid elements they contain. The central mass is formed of the most basic rock, dunite, which consists of a combination of olivine and chromite, the platinum being always associated with the latter; further the metal is not concentrated but scattered through the mass. The rocks have been submitted to a careful examination, both chemical and spectroscopic, and their composition minutely studied. The platinum zone was determined to be 40 ft. deep with an average thickness of 5 feet and, from this, an estimation of the profitable tonnage has been made. Of the samples taken, one-third were rejected as too high, owing to pure grains of metal having been picked up; of the remainder, one-third gave from 2 to 3 grams per ton of wash, another third gave from 0.25 to 2 grams, and the remaining third was considered too poor for treatment. Little alumina is found to be present in the treatment of these alluvials would be cheap and easy, and it is generally taken that the working of platinum sands may be economically undertaken from the level of 0.25 gram per ton.

Further investigations are being made to embrace the whole of the district and the Spanish Government, recognizing the importance of the discovery, is supplying the necessary funds for carrying out the work.—M.

### SULFURIC ACID FROM NITRE CAKE

Investigations have been made by a committee of sulfuric acid users in Yorkshire, England, with a view to combating the scarcity of this acid; nitre cake, a by-product of the manufacture of sulfuric and nitric acids, has been found a suitable substitute. The cake contains the equivalent of 30 per cent pure sulfuric acid and has hitherto been looked upon as a waste product. Experiments made with the cake indicate that its use presents certain difficulties, but it is hoped that these will be overcome. Since it has only 30 per cent available sulfuric acid, it must be used in larger quantities and on account of the acid which drains from it, its storage and transport give rise to difficulties. It is also pointed out that the general use of the cake for the above purposes will probably entail a sudden disorganization in the textile and other trades.—M.

### CULTIVATION OF MEDICINAL HERBS

In consequence of the shortage of drugs due to the war, steps are being taken, according to the *Pharmaceutical Journal*, to experiment on the home cultivation of these in Queensland, under the control of the Board of Agriculture. Ample funds are to be provided.

It is proposed to work in conjunction with a hospital and, thus, to make the experiments of practical value. As a first step, seeds and plants will be imported and distributed to the various

high schools to be tested in the school gardens, and the plants will be sent to districts where the soil appears to be most suitable to give successful results. The products will be tested in the laboratories of the hospital and the Board of Agriculture. The results will be published and will give an idea of the districts best suited for the cultivation of certain plants. When this stage is reached, persons desiring to take up drug growing will be invited to communicate with the Board and will get the necessary instructions. Growers will be guaranteed a certain market and a definite price for their produce.—M.

### MINING IN THE GREEK ISLANDS

Recent official reports show that previous to the war, the mining industry in the Greek Islands was suffering from depression.

In 1914 the iron mines at Syra were not worked at all, and the production from Syphnos, Seriphos, and Kythnos amounted to only 133,825 tons compared with 206,416 tons of the previous year. The Naxos emery industry, which suffered severely from strikes in 1913, showed a production of 6,876 tons, the greatest part of which was exported to the United States.—M.

### BRITISH RUBBER TRADE FOR 1915

According to figures published in the *India Rubber Journal*, the import of raw rubber during the past year reached the record figure of 182,565,900 lbs. The value was \$97,080,288, which works out at a little over \$0.50 per lb. The greatest bulk of the import is now of British growth. Forest production seemed to have been somewhat ousted by plantation production and the import of forest-grown rubber now ranks at but little over one-quarter of the total.

Thus, in a very few years, a trade has been built up which renders every manufacturing country dependent on Britain for its raw material. From the figures it would seem that more material has been re-exported than one should have expected under present conditions. It cannot, however, be said that neutrals have been much inconvenienced by the hoarding up of supplies at home.—M.

### SHELLS

Dr. J. E. Stead in a paper to the Cleveland Institute of Engineers reports on analyses made by him of a large number of fragments of German shells. According to his opinion, which is that of an expert, a shell should not be rejected on the result of its chemical analyses provided the mechanical tests are satisfactory. The shell used by the Germans, he found to be, generally, of relatively high tenacity and is much more liable to break up by shock than the material found in British shells. It seemed probable that some of the German shells were made by the basic Bessemer process judging from the relatively high percentage of nitrogen found present in one of the toughest and best fragments examined. This specimen also contained 0.07 per cent sulfur and phosphorus. Shells with between 0.07 and 0.1 per cent phosphorus did not burst in the gun, hence it does not seem to be absolutely necessary that great freedom from that element is required.—M.

### SULFUR CEMENT

It is often necessary, according to the *Engineer*, to seal up holes in transformer or oil-switch cases where wires pass through. For this purpose, the most commonly used material seems to be a mixture of sulfur and plaster of Paris. Either material used by itself may answer the purpose in some cases but, if the two are mixed half and half, it gives a very hard substance when it has set and one which is impervious to transformer oil. The sulfur may be melted in a ladle or pot and then an equal quantity of plaster of Paris mixed thoroughly into it. The mixture should



be poured into place while hot. Trouble is often experienced from oil being siphoned out of transformer cases on account of the braided insulation on the lead wires. When this occurs it is usually found that the insulation on the wires dips down into the oil. If the oil level is lowered below the terminal board inside the case and the insulation on the leads scraped off so that where the wire enters the surface of the oil its metallic surface only is exposed to possible contact with the oil and the leads are properly sealed, there will be little trouble due to siphon action.—M.

#### MINING IN KOREA

Korea is reported to be rich in minerals. The districts of Pingyang and Kangtong, Province of Pyong-an produce large quantities of anthracite coal, the mines in the former place being under Government control. The naval briquette factory at Tokuyama (Japan) uses up annually over 84,000 metric tons of Pingyang anthracite valued at about \$165,000. A new coal mine, opened at Anzu in the Province of South Pyong-an, in 1911, is being developed.

Japanese capitalists are beginning to pay more attention to the gold mines in Korea, and several new claims, *viz.*, Chik-san, Kungsong, Syonchon and Syn-an in the district of Pingyang show promise. The principal placer gold deposits are found in Syn-an district.—M.

#### BRITISH FOREIGN TRADE IN 1915

Official figures for British Foreign Trade in the year 1915 have now been published. In the chemical industry, imports of nitrate of soda were 132,158 tons as compared with 171,910 tons for 1914 and 140,926 tons for 1913. Nitrate of potash was imported to the extent of 276,580 cwts. as against 209,439 cwts. and 237,880 cwts. for the two preceding years. The imports of calcium carbide were 521,523 cwts. against 575,443 cwts. in 1914 and 513,797 cwts. in 1913 and of sulfur 711,102 cwts. against 435,979 cwts. in 1914 and 364,283 cwts. in 1913, while the exports of pyrites amounted to 903,401 tons against 803,249 tons and 781,711 tons for the preceding two years. The value of acids imported for last year was £4,231,216 against £1,575,836 for 1914 and £1,718,922 for 1913, the increase, of course, being due to the war. The coal-tar products were much the same as for the previous year; benzol and toluol amounted to 7,334,436 gallons; tar oil and creosote to 35,687,286 gallons. The exports of China clay show a decrease: the amount exported last year was 333,206 tons as against 628,620 in 1914 and 629,703 tons in 1913. Petroleum imports also show a slight decrease, the total being for last year 595,158,694 gallons against 646,712,631 gallons for 1914 and 488,106,963 in 1913. Exports of mining machinery were valued at £571,000 against £819,486 for 1914 and £1,018,150 for 1913.—M.

#### EFFECT OF BOMBARDMENT ON CONCRETE AND BRICKWORK

A feature of the pictures of the Belgian forts bombarded by 42 cm. guns, is, says a contemporary, that the walls and roofs struck by projectiles are not pierced by shots but completely shattered even where the explosive force of shells plays no part. These fortifications were built chiefly of concrete and armored concrete.

Professor P. Rohland states that the same phenomenon has been observed in experimental practice with targets of reinforced concrete. Shots did not break holes as in steel targets but caused the whole target to crumble to small fragments. The reason for this, he further holds, lies in the fact that there is a condition of high tension in sheets or walls, roofs, etc., of concrete due to the colloidal chemical nature of cement where separate particles are pressed extraordinarily close together.

When this tension is relieved at any point by a bursting shell, the complete crumbling of the entire sheet of concrete is the inevitable result. Hence, he advises a return to the use of brick for fortifications. When a brick wall is struck by shot, the result is merely the tearing of a big hole, since, owing to the looseness of structure, only the parts in immediate contact with the spot hit are affected.—M.

#### MANUFACTURE OF DRUGS AND CHEMICALS IN JAPAN

Further particulars have been published regarding the scheme, devised by the Japanese Government, for subsidizing the manufacture of dyestuffs, drugs and chemicals. The products provided for under the new law, according to the official organ of the Board of Trade, are the following: acetanilide, benzoic acid, carbolic acid, salicylic acid, antipyrin, chloral hydrate, chloroform, cresol, formalins, glycerine, guaiacol, caustic soda, potassium carbonate, creosote, alkaloids; also, the by-products from coal tar by dry distillation, *viz.*, light oil, neutral oil, crude and refined benzol, toluol, xylol, naphthalene and anthracene. Three companies have been formed, one to specialize in glycerine, the second in formaline and the third in drugs.—M.

#### THIOPHENE IN BENZENE

The following method for estimating the amount of thiophene in benzene is said to give good results. A little more than the calculated quantity of mercuric oxide is dissolved in glacial acetic acid and the liquid cooled, mercuric acetate being deposited. The benzene to be tested is added and the mixture heated on a boiling water bath for about 15 minutes. The precipitate formed, which consists of thiophene tetra-mercuriacetate, is separated from the cold liquid, washed several times with ether, dried at 100° and weighed.—M.

#### POTASH FROM THE ASH OF THE PRICKLY PEAR

The *Chemical News* states that spraying with arsenic trichloride solution is being used to exterminate the prickly pear pest in the Cactus Estates of Dulacca in Queensland.

The ash of the pear contains 15 per cent potash and a yield of 7 tons of ash per acre has been obtained. Half a ton of 80 per cent potassium carbonate was collected from the ash of 5 acres of the burnt cactus. The ash is gathered up by means of a suction plant.—M.

#### AUSTRALIAN METALS

According to a recent statement made by the Commonwealth Premier, the outlook for the Australian metal market at the beginning of 1915 was very gloomy, due mainly to German domination. The whole metal industry seemed to be on the point of collapse. Now, however, things have changed somewhat; the industry is in a flourishing condition and prospects are bright. Copper ores can now be treated locally without the need for exportation and arrangements are being made for the establishment of zinc and lead refineries.—M.

#### BRITISH SULFATE OF AMMONIA

In view of the uncertainty in Great Britain as to the sufficiency of supplies of sulfate of ammonia to meet home demands during the next few months, it has been decided on the recommendation of the Fertilizers' committee, with the government's approval, to suspend for the present the issue of licenses for the export of sulfate of ammonia. Under normal conditions, the production of this substance considerably exceeds home requirements, but it is hoped that farmers will this year greatly increase their demands for fertilizers so as to stimulate as far as practical the production of the land and so reduce the importation of foodstuffs into British Isles.—M.

# METHOD FOR DETERMINATION OF HARDNESS

Mr. M. F. Turpin, in the *Revue de Metallurgie* for February, 1915, describes a simple device adapted to determine hardness in any manufacturing processes. It entails the use of a steel ball protruding from the end of a hollow mandrel backed by a cylindrical slug of known hardness according to the Brinell scale. The slug is surmounted by a plunger which protrudes from the opposite end. When a test is to be made the ball is brought to contact with the sample and the free end of the plunger struck with the hammer. The indentation made is then compared with the standard slug. The device is 30 mm. in diameter and 90 mm. long.—M.

## BRITISH BOARD OF TRADE

During the month of January the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles. Firms which may be able to supply information regarding these things are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall Street, London, E. C.

Aluminum powder  
Asbestos, crude  
Automatic gas lighters  
Angles, imitation ivory  
Antidotes for poison  
Ares, small tin, printed in colors  
Burners, paraffin oil lamp  
Calcined bone ash  
Cassia, liquid or powder  
Cells, suitable for accumulator  
Clay, flint boulders  
Coins, small unsilvered  
CHEMICALS  
Acetone  
Potassium carbonate  
Magnesium chloride  
Calcium sulfide (luminous)  
Saltpetre (at least 99% sodium nitrate)  
Sodium peroxide  
Uranium oxide  
Cream of tartar substitute  
Cotton wool, absorbent for surgical purposes  
Electric pocket lamps

Frames, photograph  
Glass tubes  
Gold leaf  
Hoop iron  
Incandescent lamps  
Incandescent mantles, upright and inverted  
Jars, stone  
Lampwick  
Margarine  
Machinery for making lead pencils  
Metallic vessels for resisting corrosion by acids  
Orpiment, red  
Oil, crude for use in Semi-Diesel engines  
Pearls, imitation  
Porcelain articles for wreaths  
Presses, copying  
Paper for artificial flowers  
Rings, steel for leather purses  
Sewing machines  
Stockings, knitted ramie, for incandescent mantles  
Talc sheets  
Vacuum flasks

—M.

## MINERAL PRODUCT OF UNITED KINGDOM FOR 1913 AND 1914

The following table showing quantity and value of minerals produced in the United Kingdom is taken from the general report on Mines and Quarries.

MINERAL	1913 Tons	1913 Value (£)	1914 Tons	1914 Value (£)
Coal Shale.....	8,741	874	6,078	607
Semical Pyrites.....	35	29		
Asbestos.....	1,695	16,616	1,988	19,052
Aluminum compounds.....	50,045	42,136	48,930	43,506
Sulphate.....	6,055	1,363	8,286	2,159
Copper Ore.....	3,335	959	2,342	585
Lead.....	4,858,126	213,479	4,291,170	197,154
Mercury.....	74,858	12,781	76,213	13,304
Pyrites.....			100	50
Calcium and Shale.....	13,892,807	1,790,805	13,124,361	1,731,779
Alumina.....	287,430,473	145,535,669	265,664,393	132,596,853
Copper ore.....	2,569	21,138	2,373	16,985
Mercury precipitate.....	163	5,891	185	5,529
Aluminate.....	154	308		
Uranium.....	53,663	14,955	33,816	11,005
Uranium Ore.....	4	434	47	318
Travel and Sand.....	2,409,152	184,818	2,498,872	215,351
Pyrites.....	285,338	90,450	265,365	83,868
Aluminum Rocks.....	7,098,473	1,386,022	7,135,243	1,369,242
Alumina Ore.....	15,997,328	4,543,558	14,867,582	3,921,683
Pyrites.....	11,427	5,988	11,654	4,759
Aluminate.....	24,282	293,525	26,013	309,813
Aluminate.....	81	40	300	150
Aluminate (other than chalk).....	12,740,664	1,369,168	12,158,441	1,295,512
Aluminate.....	15,135	14,460	11,069	10,635
Aluminate Shale.....	3,280,143	822,394	3,268,666	837,249
Aluminate.....	2,247,758	608,869	2,069,989	560,893
Aluminate.....	3,977,303	1,143,431	3,464,528	1,057,096
Aluminate.....	370,756	926,739	318,912	806,196
Aluminate.....	40	30	180	90
Aluminate of Strontium.....	18,425	14,287	13,157	10,439
Aluminate (dressed).....	8,355	960,134	8,085	661,865
Aluminate.....			344	Not stated
Aluminate.....	182	17,483	205	19,722
Aluminate Ore.....	17,294	69,502	15,419	56,652
Total £.....		160,112,607		145,863,032

—M.

# BLEACHING OF FATS AND OILS

According to *Nature*, palm-oil, which is used in very large quantities in the soap industry, may be bleached (1) by exposure in thin layers to air and sunlight, (2) by blowing air through the hot oil, (3) by action of bleaching powder or chromic acid.

The great development in scientific methods of catalytic reduction as a means of hardening fats and oils appears to have suggested the idea that similar methods might be applied to the oxidation and bleaching of oils. Experiments reported in the *Transactions of the Chemical Society, London* (107, 1828) shows that a large number of metallic compounds can be used to stimulate the oxidation, the most effective being those containing manganese and cobalt, although nickel, iron and lead were also active. Of the compounds employed, the borates were found to be more effective than the oxalates, palmitates, sulfates or oxides, and the most effective of a dozen catalysts was cobalt borate. Using only 0.01 per cent of this salt a reddish sample of oil was bleached white in the course of 3½ hours by passing air through it at 80 to 90° C. The bleaching was found to be permanent during 15 months and did not destroy the faint odor of violets which is characteristic of the oil; the bleached oil also gives a colorless soap and its soap-making qualities were in no way interfered with.—M.

## THE CRUCIBLE SITUATION IN THE UNITED STATES

The crucible manufacturers have been put to sore straits for the past eighteen months in the securing of their raw materials. The embargo on Ceylon plumbago (lifted after a few months) left the market in a depleted condition: the natural result was a tremendous advance in price.

Next came the exhaustion of the foreign clay, which is used in crucible making as a binder. The clay used, as far back as crucible history in this country goes, has come from the little principality of Klingenburg in the Black Forest in Bavaria, where, it is said, the entire government expenses are paid out of the export duties collected from the clays shipped out. This Klingenburg clay has, for years past, been the only clay the crucible makers seemed to think they could satisfactorily use. No shipments of this clay have been made since the beginning of 1915. Some makers have husbanded the enormous supplies of the foreign clay which they had on hand when hostilities started. This husbanding the stock of the now almost priceless raw material, has been done by partially substituting clays from various parts of the United States, and mixing with the Klingenburg clay.

The tests and trials made by the crucible makers during the past 12 months have been almost endless. The fact that it takes from 6 to 10 weeks to prepare a graphite crucible for service in the foundry gives some slight idea of what the crucible maker has to contend with. Added to this delay, and before he can even start in on these goods that will not be marketable for two months to come, the chemists' laboratory tests and trials must be made: these run into the thousands. Then must come the practical tests in a small way in the foundry, for the crucible maker would stare bankruptcy in the face, if he were to continue making up hundreds of thousands of dollars worth of goods out of Ceylon plumbago, costing from 17½ to 25 cents per lb., only to find at the end of two or three months that the product was useless.

However, in many cases the crucibles made with American clays have gone a surprisingly long time in the fires. In one instance there is a report on a No. 300, which ran 40 heats on manganese bronze, and dozens of others as high as 38 and 40 heats on No. 100's melting car box-metal. The annoyances now seem to be the non-uniformity of the products secured, crucibles made by the same potter, out of similar materials, at the same time, and burnt in the same kiln, when run by one melter on same grade of metals, rise and fall to a variation that



is a shock to both user and maker. But all this will in time be rectified. As soon as the manufacturers have become more familiar with the mixing and blending of our native clays, they will no doubt be able to produce in time a crucible as satisfactory, or superior to those manufactured heretofore.

The user, however, must exercise more care in handling the American clay crucibles. It is imperative that these crucibles be thoroughly dry and warm before going into the fire and that they be heated up *very slowly* on the initial heat. Some users make a little fire with charcoal inside the crucible, and others put hot ashes in before placing the pot in the fire, so that the crucible is hot when it goes into the fire for the first heat. There are certain advantages in heating the crucible from the inside first rather than the outside.

The matter of wedging must also be guarded against, as American clays have not the same tensile strength when hot, as foreign clay.

The advance in prices of crucibles is due to the unusually high price of Ceylon plumbago just at present, just as with zinc, copper, aluminum, lead, etc., but as soon as the war insurances are a thing of the past, plumbago will be at a normal figure once more, and crucibles will again be marketed at as low or lower prices than they have been for many years past.

#### CENSUS BUREAU'S SUMMARY FOR THE PETROLEUM REFINING INDUSTRY FOR 1914

A preliminary statement of the general results of the 1914 census of manufacturers for the petroleum-refining industry issued by the Bureau of the Census, Department of Commerce, reports the quantity of crude petroleum used by the refineries

and the value of the various products manufactured. It also gives the production of casing-head gasoline in 1914 and includes the following summary of the production of crude petroleum by fields in that year as reported by the United States Geological Survey.

#### CRUDE PETROLEUM PRODUCTION

	1909	1914	% Increase
California.....	55,471,601	99,775,327	79.9
Mid Continent (Kansas, Oklahoma, etc.).....	50,833,740	97,995,400	92.8
Pennsylvania grade (Appalachian).....	26,535,844	24,101,048	-9.2
Illinois.....	30,898,339	21,919,749	-29.1
Gulf.....	10,883,240	13,117,528	20.5
Lima Indiana.....	8,211,443	5,062,543	-38.3
Colorado, Wyoming, and other fields..	336,667	3,790,940	1125.5
Total production (barrels—42 gallons)	183,170,874	265,762,535	45.1

The value of the annual production has increased by \$159,363,746, or 67.2 per cent over those of 1909.

The gasoline product of the petroleum refineries does not include casing-head gasoline condensed from natural gas at the gas wells. The total gasoline production, including casing-head gasoline, was 24,711,565 barrels of 50 gallons, or 1,235,578,250 gallons.

The production of lubricating oils here reported does not include that of establishments engaged in the compounding or blending of petroleum oils, but only the output of petroleum refineries.

Of the 176 refineries in 1914, 48 were in Pennsylvania, 38 in California, 23 in Oklahoma, 13 in Kansas, 9 in Texas, 9 in Illinois, 8 in New Jersey, 7 in Ohio, 6 in New York, 4 in Colorado, 3 in Maryland, 3 in West Virginia, 2 in Wyoming, and one each in Indiana, Louisiana and Missouri.

The comparative statistics for 1914 and 1909 are summarized in the accompanying table.

	1909		1914		Per cent Increase	
	Barrels	Value	Barrels	Value	Bbls.	Value
PETROLEUM REFINING IN THE U. S.						
No. of Establishments	147		176		19.7	
Total Production Crude Petroleum.....	183,170,874		265,762,535		45.1	
Crude Petroleum Used.....	120,775,439	\$152,307,040	191,262,724	\$249,727,856	58.4	64.0
PRODUCTS						
Naphthas and Lighter Products:						
Gasoline (from Crude Petroleum).....	10,806,550	39,771,959	23,908,242	106,140,170	170.2	206.5
All others.....			5,292,522	15,779,137		
Illuminating Oils.....	33,495,798	94,547,010	38,705,496	96,806,452	15.6	2.4
Fuel Oils.....	34,034,577	36,462,883	74,669,821	84,017,916	119.4	130.4
Lubricating Oils.....	10,745,885	38,884,236	10,348,521	55,812,120	-3.7	43.5
Residuum or Tar, including Liquid Asphaltic Road Oils.....	1,787,008	2,215,623	2,696,887	4,017,858	50.9	81.3
Greases.....	138,302	1,567,647	280,128	3,536,491	102.5	125.6
Paraffin Wax.....	946,830	9,388,812	1,150,776	8,897,106	21.5	-5.2
Asphalt, other than Liquid Asphalt—Tons (2000 lbs.).....	233,328	2,724,752	465,157	4,867,213	99.4	78.6
All other products.....		11,434,737		16,486,942		44.2
Total Value of Products.....		\$236,997,659		\$396,361,405		67.2
Gasoline from Natural Gas (casing-head gasoline, not included in refinery products) barrels (50 gallons) (United States Geological Survey) ..						853.053
Total Gasoline Production, excluding duplication as far as possible, barrels (50 gallons).....						24,711,565

## NOTES AND CORRESPONDENCE

### FOREIGN APPRECIATION OF THE AMERICAN CHEMICAL SOCIETY

*Editor of the Journal of Industrial and Engineering Chemistry:*

All members of the American Chemical Society, which for some time has had the largest membership of any chemical society in the world, should be interested in the following, translated from p. 3 of the *Chemiker Zeitung* for 1916:

"The technical chemical literature of America is very important but it has hitherto been altogether too little appreciated in Germany. The most distinguished of the American publications is the *Journal of Industrial & Engineering Chemistry*, published by the American Chemical Society; this journal furthermore publishes comprehensive articles on the economic phases of chemistry."

Further, they should be interested in the following, translated from p. 35 of England's "*Handelskrieg und die Chemische Industrie*," by A. Hesse and H. Grossmann:

"It should here be pointed out that the Americans have most skillfully avoided that division into scientific and technical societies which has so unfortunately occurred with us, and that they have succeeded in very rapidly building up a large and, therefore, very efficient organization which provides for and embraces all interests."

This first and very much belated foreign recognition of our having one of the most efficient chemical organizations in the world, of publishing the best technical chemical journal in this country, and that heretofore American chemical work has been insufficiently appreciated abroad, ought to be a great satisfaction to every American; it ought to make each American chemist not now a member of the A. C. S. most anxious to become one of us. Above all it should make all of us ready and willing to leave nothing undone to maintain the proud position we have now reached after forty years of continued effort and during which long time recognition both at home and abroad has been largely withheld from us and from those of our members who have labored unostentatiously but effectively.

All of us who are now reaping the benefits of this self-sacrificing and arduous labor cannot escape and must not shirk the great duty of doing everything that may be needful to prevent any retrogression in the good work of those who have preceded us, and further, to enhance and to advance this proud achievement which is now placed in our keeping.

BERNHARD C. HESSE

25 BROAD STREET, NEW YORK  
February 14, 1916

## SOME OVERLOOKED INVESTIGATIONS ON WHEAT

*Editor of the Journal of Industrial and Engineering Chemistry:*

The Chemical Section of the Colorado Experiment Station has been engaged for several years in a study of Colorado wheat, to find out, if possible: (1) whether Colorado wheat has any distinctive quality which may be considered characteristic of it; (2) to determine the factor or factors in our conditions which are accountable for the same.

The result of our first two years' work was the publication of *Bulletin 205* of this Station, entitled "Yellow-berry in Wheat; Its Cause and Prevention." Further reports on this work are contained in *Bulletin 208* already issued, and *217* which will appear soon.

I endeavored to give credit in these publications to everyone to whom I am in any way indebted. I hold this to be the imperative duty of every author, even if his production should be of insignificant importance. Since the manuscript of *Bulletin 217* was turned over to the Director of the Station, I have found that H. Ritthausen and Dr. R. Potts carried out a series of experiments in 1872, an account of which may be found in *Die landwirtschaftlichen Versuchs-Station*, Band XVI, 1873, pp. 384-399, which, in the main, is parallel to mine to such an extent, and the conclusions are so similar, that it might be thought that I had copied their plan of experimentation and adopted their conclusions. This applies to the bulletin on Yellow-berry to such an extent that some of my conclusions look like paraphrases of theirs. It does not apply to *Bulletins 208* and *217* to the same extent. Still, it applies in some measure, and a portion of the work still to be reported will again be parallel.

Ritthausen and Dr. Potts used spring or summer wheat. They used nitrates and phosphorus on some of their plots alone and in excessive quantities. I, also, did these things, and for the same reasons, but I used potash on some other plots and they did not.

They hold that climatic conditions as a cause for the quality of wheat is so general, indefinite and unsatisfactory that one must seek some more evident one—a view that I have repeatedly expressed, and which I, in a general way, maintain in *Bulletin 205*, in which I show that it is insufficient as an explanation.

They state that their check plots produced light-colored, half-mealy or transitional kernels. The plots to which phosphoric acid or superphosphates were applied, produced the same kind of seed.

I record that my check plots produced grain affected with yellow-berry, mealy or half-mealy kernels, and that this condition was not affected by the application of phosphorus as superphosphate.

They record the effects of nitrate to be the production of small, well-formed kernels which were hard, flinty and dark-colored.

My statement is that the application of nitrate depresses or entirely prevents yellow-berry and produces small, flinty, and often shrunken berries.

They observed that nitrates used in conjunction with other fertilizers produced effects similar to those produced by nitrates alone. I have made the same observation.

I used potash on three series of plots and they did not. I observed that potash greatly increased the amount of yellow-berry. They did not.

The examination of the kernels and flour also will run in their larger features parallel, which, of course, is to be expected. The two studies are not identical, but the general features are so similar that one might readily be considered a copy of the other, which is not the case.

My work was planned and three seasons' work done on my general project before I learned of the existence of this article, giving the record of this work done by these authors at Poppelsdorf. I shall in no wise change the plan of my work, as I hoped from the beginning to carry my investigation far beyond its

present stage. The work so far done seemed necessary, before it would be justifiable for me, or anyone else, to assign any cause or causes for the characteristics of our wheat. Indeed, it is not even yet certain that one can properly speak of Colorado wheats as having any predominant and fixed characteristic.

It is a matter of surprise to me that this work of Ritthausen's has received apparently no attention. I found an abstract of the article in the *Journal of the Chemical Society*, London. This abstract did not give a very adequate idea of the facts presented in the article. I have also found it mentioned in the literature given by Schindler, in his "Der Getreidebau" at the end of the section "Der Weizen."

COLORADO EXPERIMENT STATION  
FORT COLLINS, COLORADO, January 21, 1916

W. P. HEADDEN

## TEMPERATURE CONTROL IN WOOD DISTILLATION

*Editor of the Journal of Industrial and Engineering Chemistry:*

The note by Mr. R. B. Goetschius in *THIS JOURNAL 8* (1916), 196, on "Temperature Control in Wood Distillation Plants" has been read with much interest. Since much of the agitation on this subject referred to by him has been largely the result of experiments made by the United States Forest Products Laboratory the discussion is timely and of especial interest, as it affords an opportunity to clear up several points which are apparently misunderstood.

It is probably correct that the present design of wood distillation plants is not adapted to the greatest possible increases in products resulting from scientific temperature control but experiments in the laboratory, and also in commercial plants, subject to all the variables of factory operation have shown much greater possibilities along this line than is generally supposed by plant operators. The results of preliminary experiments which form the basis for this statement were given in *THIS JOURNAL 7* (1915), 663.

Fortunately, it is not possible to control the distillation irrespective of any variation in size of pieces in a commercial size retort, so that all the water is distilled out of the charge before destructive decomposition takes place. Any control embodying such a conception would certainly result in a very great absence of control during the latter stages of the distillation as the decomposition of a large volume of very dry wood is likely to be extremely violent.

Experiments by the Forest Products Laboratory have shown that apparently certain well defined relations exist between the rate of rise of the temperature in the retort, the flow of distillate, and the yield of products. The interaction between the various products in the retort in the presence of the hot charcoal undoubtedly plays an important part in the yields. Temperature control in the distillation of wood, as interpreted by these experiments, is then to make the greatest possible proportion of the distillations follow the proper combination of these factors which will give the best yields. A technical operation involving the rate of rise of the temperature as an important factor is obviously best conducted by employing pyrometers.

In a continuation of these studies in longer tests in commercial plants, results of which have not yet been published, it was found, strangely enough, that about equal mixtures of large pieces of split wood and smaller pieces of sawed wood more readily gave the desired rate of rise of temperature than either of the two kinds alone. Therefore, instead of requiring evenly sized wood in order to secure good results with pyrometers, possibly by proper control the variability of the size of wood may even prove an advantage.

Aside from this more scientific basis for the application of control there are other reasons which it would seem were alone sufficient for employing pyrometers in wood distillation plants. The great variability of raw material in size, moisture content,



etc., has been well pointed out. Would not any method which would tend to overcome some of these difficulties be an advantage? Also, operators who have, unfortunately, had to rely on untrained firemen have found pyrometers to be of great assistance in preventing excessive firing and other injurious practices.

It is undoubtedly true that the proper combination of the various factors, such as flow of distillate and temperature rise, will vary somewhat with different plants because of differences of size and condition of wood and the best adaptation of these principles will have to be worked out for the individual plant. The great value of knowing as accurately as possible these conditions in applying scientific control has been well demonstrated, and it is believed that a general adoption of pyrometer temperature control in the primary distillation will help to bring the wood distillation industry out of the somewhat empirical condition which has marked it up to within the last few years.

FOREST PRODUCTS LABORATORY  
MADISON, WISCONSIN, February 11, 1916

R. C. PALMER

### REMARKS ON THE PRODUCTION OF RADIUM BY THE BUREAU OF MINES

*Editor of the Journal of Industrial and Engineering Chemistry:*

The work of the Bureau of Mines in coöperation with the National Radium Institute Company in the production of radium has been given an unusual amount of newspaper publicity. The statements supplied by Dr. Parsons and others interested in the work have often been considerably altered or abbreviated in publication and a great deal of misconception in regard to the work prevails in the public mind. However, we read in the memorandum for the press, issued several months ago by the Secretary of the Interior, that the Bureau of Mines has "devised methods for the production of radium from carnotite ore of Colorado and Utah at an average cost of \$36,500 a gram, two-thirds cheaper than the market price of \$120,000 asked by foreign producers, the new cheaper methods making it more certain that medical institutions will be able to procure a sufficient quantity of radium for the treatment of cancer and malignant growths," etc.

The writer has been interested in the commercial production of radium from carnotite since 1912 and naturally has followed with interest the work of Dr. Parsons and his associates along this line. The problem to be solved was clearly appreciated<sup>1</sup> before any work was carried out by the Bureau of Mines and it was somewhat of a shock to the writer to see how little has been accomplished in the attack on the real problem as testified by the data given in a recent bulletin.<sup>2</sup> Briefly, the problem consists in devising means for economically working up the low-grade carnotite ore, which forms by far the greater proportion of the radium ore occurring in Colorado and Utah. This would involve an economical process for concentrating the ore, as well as an efficient chemical method for extracting the radium, uranium and vanadium from the concentrates, and the refining of these products.

The carnotite ore from the Colorado field will average about 1 per cent, or less, of uranium oxide and by hand-picking from 5 tons of mine ore, it is usually possible to sort out a ton of material averaging between 1.5 and 2.0 per cent of uranium oxide. The remaining ore has in the past been considered too poor to ship and so has accumulated on the ore dump, where through weathering, etc., losses of the values result. Up to date the company with which the writer is associated has shipped about 5,000 tons of carnotite ore from its mines to the reduction plant at Canonsburg, Pa. Naturally, the endeavor has

been to ship as high a grade of ore as possible, consistent with the quantity requirements, since the ore must be packed to the foot of the trails by burro, then hauled 40 to 60 miles by wagon to the nearest railroad, making transportation charges very high. Rich claims have been stripped bare in this effort, and still the average on all of the shipped ore was 1.6 per cent of uranium oxide. Approximately 20,000 tons of low-grade ore were either not mined or not shipped owing to the poor quality of the ore.<sup>3</sup>

The results so far attained by the Bureau of Mines may be summarized briefly. About 1000 tons of high-grade carnotite ore (2.5 to 2.6 per cent  $U_3O_8$ ) have been treated (without concentration) by a method (extraction with concentrated nitric acid) which is not directly applicable to concentrates, and a fairly high extraction of radium has been attained (85 to 90 per cent). The uranium in the ore has been extracted as crude sodium uranate with an efficiency of about 85 per cent, and the vanadium as iron vanadate with an efficiency of 21.4 per cent. Nearly 5 grams of radium (element) have been extracted from the ore in the form of raw radium barium sulfates containing about 1 mg. of radium per kg. of salt, and of this material about half has been worked up to yield radium salts of sufficient purity for the designed therapeutic uses. Nothing essentially practical has been contributed to the art of radium production, and the cost data, as given, are of no great significance for actual large scale production of radium, since the conditions under which the Bureau of Mines produced the radium were abnormal and cannot be duplicated in present practice on account of the lack of high-grade ore.<sup>2</sup> In *Bulletin 104*, there is no summary which would show the total amounts of each chemical required per ton of ore, and there is no cost price stated for the acids and alkalis. The result is that there is no simple way for an outsider to figure costs on the Bureau of Mines process. Furthermore, in figuring the cost of any article it is necessary to add

<sup>1</sup> Since the beginning of 1911, the carnotite ore shipped in Colorado and Utah had a uranium oxide content of approximately 200 metric tons. Of this ore, about 55 per cent has been treated in the United States and the balance has been shipped abroad. In the earlier years a large proportion of the carnotite ore was shipped abroad by the General Vanadium Company for the recovery of vanadium. The radium is the residue after the extraction of the vanadium was not refined; however, these residues have since been offered for sale—so that the radium will probably be extracted. The total amount of radium in the carnotite ore so far mined and shipped amounts to about 66 grams and assuming an efficiency of extraction of 70 per cent the recovered radium would be about 46 grams, of which 25 grams should have been extracted in the United States and about 21 grams (including General Vanadium Co. residues) abroad. This represents the bulk of the world's present supply of radium, since none of the other deposits of radium compare with the Colorado and Utah deposits.

<sup>2</sup> Considering that these investigations were made in part (*Bull. 104*, p. 13) "to enable the miner and prospector to obtain a just return for the ores" it is hard to reconcile this statement with the pitifully inadequate prices paid to the miners by the National Radium Institute for high-grade ore—after the war had cut off the European ore market. Before the war carnotite containing 2 per cent  $U_3O_8$  was sold to French buyers at \$3.30 per lb. of  $U_3O_8$ , and offers went as high as \$4.00 for this ore. These prices figure \$132 and \$160 per ton of 2 per cent ore, and at the same rate, would give \$178.20 and \$216 per ton of ore containing 2.6 per cent  $U_3O_8$ , such as was worked by the Bureau of Mines, and shown in *Bull. 104* in the costs at \$96.36 per ton. In addition to the ore mined from the Crucible Steel Mining and Milling Co.'s claims, ore was purchased directly from miners and for this ore the National Radium Institute paid in one known instance \$1.70 per lb. of  $U_3O_8$  in about 25 tons of ore, f. o. b. Placerville, Colo., that averaged 3.19 per cent  $U_3O_8$  or at the rate of \$108.46 per ton of ore. For ore containing from 2 per cent to 5 per cent  $U_3O_8$  they offered, f. o. b. Denver, \$2 per lb. of  $U_3O_8$ , or \$80 per ton of 2 per cent ore. (Freight rate Placerville to Denver \$6 per ton, Placerville to New York \$11.57 per ton, Placerville to Hamburg or Liverpool, via Galveston, \$14.50 per ton.) When it was evident that the National Radium Institute was in the field to buy ore, the State Commissioner of Mines in Colorado made public announcement advising miners to hold their ore for at least \$2.50 per lb. of  $U_3O_8$  in 2 per cent ore and proportionally higher prices for higher grade ore. Yet it is on the basis of the rich ore obtained "for a song" that the Bureau bases its production figures for cheap radium. Consistency seems lacking in the argument that the miner will profit by cheaper radium. It is possible that the various arguments are to apply independently, one to the miners others to the physicians and hospitals, etc.

<sup>1</sup> Bureau of Mines, *Bull. 70* (1913), 8.

<sup>2</sup> Bureau of Mines, *Bull. 104*. "Extraction and Recovery of Radium, Uranium and Vanadium from Carnotite," by C. L. Parsons, R. B. Moore, S. C. Lind and O. C. Schaefer.

the cost of marketing (which has not been done in the \$37,599 per gram of radium—*Bull.* 104, p. 117) and a sum for the safe and certain profits on the investment. These charges are indispensable and very considerable items for an article like radium. Indeed, with an uncertain market such as radium has, the allowances for these items must be far higher in proportion to the cost of production than on such staples as gasoline, copper, etc., and for these articles the selling price is by no means the best of production of the most favored producer.

Average mining costs cannot be estimated by stripping out a few tons of high-grade ore from one rich claim, nor will the mining of several hundred tons of ore on adjacent claims give an average for the whole Colorado field. In actual practice a great deal of preliminary work must be done before the ore is uncovered and only in rare cases are considerable bodies of high-grade ore found which would compare with the *Maggie C* claim, from which the Bureau of Mines secured most of the ore. With claims advantageously located, so that little if any packing or burro was necessary and with the good roads already constructed, it is not surprising if ore costs were low.

Dissolving carnotite in strong nitric acid was the analytical method used more than ten years ago in the quantitative determination of radium in this material. This is the basis of the Bureau of Mines method and when applied to rich ore ground through 20 mesh gives an efficient extraction. The same method, however, will not apply to the 200 mesh concentrates, since the finely powdered silica in the concentrates makes it almost impossible to filter the mixture (see also *Bull.* 104, p. 111). Low-grade ore containing 0.8 to 1 per cent  $U_3O_8$  must be concentrated. A 2.5 per cent  $U_3O_8$  concentrate from such ore is much higher in Mg, Al, Fe and Ca salts than a straight 2.5 per cent ore and would require more nitric acid than the unconcentrated ore. It is not yet shown that the presence of considerable amounts of gypsum (which frequently occurs with the carnotite and would be found in the concentrates) would not introduce difficulties in the way of a poor extraction, should mechanical or other means be found to overcome the filtration difficulty. These are the problems of the practical radium process which the Bureau of Mines has barely touched, problems of the highest importance for the real conservation of our radium deposits.

Under the agreement made, the Crucible Steel Company, which owns the claims that were worked (*Bull.* 104, p. 8) "agreed that if the National Radium Institute should be formed these claims would be leased to the Institute on a 15 per cent royalty basis under an agreement providing for the return of the uranium and vanadium content of the ore to the company." Vanadium in the form of ferro-vanadium has a high value in the steel industry, and yet the Bureau was satisfied with an extraction process for radium where the vanadium recovery is shamefully low. This is admitted for we read (p. 107): "The process described in this bulletin could not be recommended were the recovery of the vanadium in the ore the main object." However, in the text of the contract to deliver to the Crucible Steel Co. the uranium and vanadium, we find that little effort was made to extract this vanadium for (p. 109) "lately, on an average 15.5 per cent of the vanadium in the ore remains in the residue, and 13.6 per cent remains in the iron-calcium precipitate, while 1.5 per cent appears in the sodium uranate and 21.4 per cent in the iron vanadate. The total average recovery in vanadium, including that from the sodium uranate, is, therefore, a little less than 30 per cent." No statement is made as to the amount of this material delivered nor as to the opinion of the Crucible Steel Co., with regard to the results of the process for uranium and vanadium. Doubtless such a method of extraction could hardly appeal to that company as satisfactory.

As regards the mining and concentration of lower grade ore, *ibidem* 104, p. 11, says: "A separate report on the mining

and concentration of radium ores is being prepared and will shortly be published by the Bureau." Dr. Parsons in a lecture at the Chemists' Club in New York, before the New York Section of the Society of Chemical Industry, on December 17, 1915, stated that the concentration experiments were being made using the air separator, the Raymond mill being used. He was not prepared to state results. However, the writer can say, as a result of the experiments of one company, that this mill will not give an economical treatment of low-grade ores, and it can hardly be said that this result is due to lack of experience, since the Raymond separator has been in use by the Standard Chemical Company since the beginning of 1912. In trying this particular apparatus the Bureau of Mines was only borrowing a method already in use.

The National Radium Institute has profited largely by the cooperative agreement with the Bureau of Mines, since the conditions under which the agreement was made were such as to insure either the delivery of the radium or the termination of the work if the radium could not be produced. However, it does not require the production of 5 grams of radium from high-grade ore by a "skimming the cream" method to determine whether or not radium could be produced by the Bureau of Mines, and it is significant that costs were figured on this method rather than on a method involving the use of the average ore. Costs, using the Bureau process and based on normal conditions, would show nearly double the stated cost of production and would, of course, not verify the earlier assertions of the officials of the Bureau with regard to their process. Having demonstrated the ability to prepare radium, it is rather odd that the purposes of the Bureau and the National Radium Institute, namely, the study of the mining and concentration of ores and the working up of the concentrates, has been delayed while radium was being extracted for a private corporation for use—in one instance at least—in a private hospital for private gain. According to *Bull.* 104 (pp. 8 and 9), such a cooperative agreement is legal and justified in view of similar cooperative work between the Department of Agriculture and farmers, and the Assistant Secretary of the Interior approved of the arrangement. This explanation, however, really does not seem to justify the actual arrangements made, for in the case of the Department of Agriculture the results obtained benefit many others since the results are general in nature, whereas here a corporation has, through some considerable expense to the Government, profited in securing much valuable material under special arrangements, and under conditions which do not offer equal opportunity to all. Ostensibly the purpose of this work by the National Radium Institute is to further the cause of radium therapy—and the production of radium. The results so far have been the exact reverse. The market for radium for therapeutic purposes in America has been killed, since the physician who reads in the newspaper that the Government has produced radium for one-third the present selling price hesitates to buy radium, and as a result of the statements widely spread both by the Bureau of Mines and by the president of the National Radium Institute to the effect that it is useless to try to cure cancer without the application of comparatively enormous amounts of radium,<sup>1</sup> we find the surgeons and physicians hesi-

<sup>1</sup> In connection with the matter of high dosage it is of interest to note that the London Radium Institute, a charitable foundation not for gain, which has over 2 grams of radium for application, in the last report of work shows the following amounts of radium element as the highest used in the treatment of those malignant conditions which require heavy dosage: Cancer esophagus, 61 mg.; cancer uterus, 107; cancer bladder, 64.2; cancer breast, 187; cancer thyroid, 225; cancer rectum, 134; cancer prostate, 97; periosteal sarcoma, 86; lymphosarcoma, 225; lymphadenoma, 268; splenic leukemia, 145; fibroid disease of the uterus, 107; mediastinal tumor (patient died suddenly less than 2 months after treatment), 480. The quantities given are maximum and more frequently smaller amounts suffice.

To the certain knowledge of the writer, there are in the United States, besides the hospitals benefited by the radium produced by the Bureau of Mines, 3 institutions and medical men possessing 200 or more mg. of radium



tating to venture into the field of radium therapy. The result, practically, is to confirm the National Radium Institute in a monopoly of radium for therapeutic purposes. Legislation in regard to the Government radium lands is again pending and it seems more than a coincidence that *Bulletin 104* should appear with its glitter of cheap radium—at this moment.

STANDARD CHEMICAL COMPANY  
PITTSBURGH, FEBRUARY 16, 1916

CHARLES H. VIOL

## COMMENTS ON "GAUGING OF STORAGE TANKS"

*Editor of the Journal of Industrial and Engineering Chemistry:*

We have studied the above-mentioned article by Mr. Ogden with a great deal of interest. There is certainly a very real need of a simple and accurate method of gauging the volume of material contained in these storage tanks. Such a method should take account of the material contained in the bumped heads, should be reasonably accurate and should be simple and easy to apply. The writer is inclined to be of the opinion, however, that Mr. Ogden's method scarcely meets this need satisfactorily, basing this opinion upon the following features of Mr. Ogden's method: (1) *lack of accuracy*, (2) *lack of simplicity or general applicability*.

### DESCRIPTION OF METHOD

Mr. Ogden treats the contents of the tank as consisting of two component parts, (1) the content of material in the cylindrical portion of the tank, *i. e.*, the tank exclusive of the bumped heads, and (2) the content of material held by the bumped heads. By determining the values of these component volumes for each vertical inch of height and adding them together, Mr. Ogden obtains the total content of material for each vertical inch of height. This amounts to a virtual calibration of the tank for each inch of height.

In discussing this article, we shall endeavor to follow this method of Mr. Ogden in treating the two-component volumes separately and we shall designate them as Vol. *A* (*volume of cylindrical tank*) and Vol. *B* (*volume of a single bumped head*). Then *Total Vol.* = Vol. *A* + 2 Vol. *B*.

Volume *A* is equal to the product of the length of the tank and the cross-sectional area of the liquid formed in a plane perpendicular to the axes of the tank. This cross-sectional area is the segment of a circle. Mr. Ogden correctly states that its value can be obtained by integral calculus but that a simpler method consists in the use of trigonometry and geometry. Mr. Ogden seems to feel, however, that the latter method is still too complex for his purposes and he, therefore, adopts an approximation consisting substantially as follows: Vol. *A* is considered as consisting of a number of flat slabs 1 in. thick, of trapezoidal cross-section, and piled one upon the other. Mr. Ogden obtains by geometry the value of the medial line of each trapezoid. Multiplying this value in inches by the length of the tank in inches, he obtains the volume of each slab. Adding the volumes of these slabs, he obtains the varying values for Vol. *A*. Clearly this is quite cumbersome and only an approximation with its degree of accuracy dependent upon the ratio of the "unit of calibration" (in this case 1 in.) to the total diameter of the tank. If the value of this ratio is small, the inaccuracy introduced is not very considerable. On the other hand, if this ratio is large, the method becomes very inaccurate. Regardless, however, of the degree of accuracy attained, there scarcely seems to be a very real need of a method of approximation since we have very accurate Engineering Tables which give accurately the area of element, and, besides these there are 10 institutions and physicians that possess 100 or more mg., and 16 that have 50 or more mg. available. The results in radium therapy reported by these institutions and physicians show that the quality of their work compares favorably with the work in institutions where over a gram of radium is available, the number of patients treated, of course, being smaller.

the circular segment from a knowledge of the ratio of its height to the diameter of the circle.<sup>1</sup>

In determining Volume *B* there is more warrant for an approximation since no method has apparently up to the present time been published which gives this volume content accurately. Vol. *B* consists of a portion of the segment of a sphere. Mr. Ogden treats the radius of this sphere as equal to the diameter of the tank which assumption, in view of the practice of tank design, is essentially correct. Mr. Ogden's method of determining Vol. *B* is substantially as follows: Volume *B* is considered as consisting of a number of 1 in. slabs piled one upon the other. Through the center of each of these slabs, Mr. Ogden passes a horizontal plane. The area of the plane section is, strictly speaking, a circular segment, but is regarded by Mr. Ogden as parabolic. The base and altitude of this parabolic section are determined geometrically by Mr. Ogden and the area of the section taken as  $\frac{2}{3}$  of their product. The volume of each slab is then determined as the product of this area and the thickness 1 in. and Vol. *B* is determined for varying heights as the sum of the volumes of these slabs. This method of calculation is not only inaccurate by reason of the assumption of the section being parabolic, but it is also inaccurate in assuming the volume of each slab to consist of the product of the area of the medial section and the thickness of the slab. As in the case of Vol. *A*, the magnitude of the latter error is dependent upon the ratio of the "unit of calibration" to the diameter of the tank.

ACCURACY—As stated previously, Mr. Ogden's method introduces a number of inaccuracies, the magnitude of which is chiefly dependent upon the ratio of the "unit of calibration" to the diameter of the tank. For a given tank of 7 ft. diameter, the error introduced is not very large if the tank is calibrated for each 1 in. of height. The calculation, however, involved in making this calculation for each 1 in. of height is very large and consumes a great deal of labor. On the other hand, if the calibration is made for 3 or 4 in. intervals, the labor of calculating is decreased, but errors of considerable magnitude are introduced. It, therefore, becomes a method which requires the sacrifice of accuracy or of simplicity of calculation.

At the conclusion of Mr. Ogden's article, he gives an example attempting to compare the true volume of a cylindrical tank and the volume obtained by using his method. This comparison is somewhat misleading. In the first place, it is made between the total volumes of the tank and not between volumes of material partially filling the tank. The errors introduced by Mr. Ogden's method are by no means at their maximum percentage value in the case of the calculation of the total volume of the tank. A true index of the accuracy of Mr. Ogden's method can be obtained only by making the comparison at the point at which the errors of Mr. Ogden's method are at their maximum percentage value.

SIMPLICITY OF CALCULATION AND GENERAL APPLICABILITY—The main criticism of Mr. Ogden's method does not rest, however, with its inaccuracy, but rather with its lack of simplicity and difficulty of application. As seen from the foregoing description of Mr. Ogden's method, the determination of the volume content of material in any tank requires a long and laborious calculation of the volume content of each inch of material in the tank, which amounts to a virtual calibration of the tank. Clearly the labor involved in such a calculation which must be made in the case of each tank containing material to be measured, is a feature which argues strongly against this method. In the past, it has been the custom of engineers to treat these storage tanks as though they were true cylinders. The vertical "innage" of material in the tank is measured and is expressed as a decimal fraction of the diameter. Reference is then made to the engineering tables for "Area of Circular Segments" and a factor is found which corresponds to the above

<sup>1</sup> R. I. Ogden, *THIS JOURNAL*, 8 (1916), 58.

<sup>1</sup> See Kent, "Mech. Eng. Handbook," 8th Ed., pp. 121-122.

mentioned decimal fraction. This factor multiplied by the product of the square of the diameter of the tank and the length represents the volume content of material in the tank regarding the same as a true cylinder. Thus, from a knowledge of the height of material in the tank and the tank dimensions, the volume content of the material can be obtained with fair accuracy and by means of a very simple calculation. While this method is convenient in so far as it fails to take account of the bumped heads of the tank, yet it does not require a long or laborious calculation of the volume contents of each inch of the tank. In conclusion, the writer feels that there remains a very real and present need for a method of gauging these storage tanks which will be more accurate and less laborious than Mr. Hayden's method and which will, at the same time, take account of the material contained in the bumped heads.

THE BARRETT CO., 17 BATTERY PLACE  
NEW YORK, January 19, 1916

K. B. HOWELL

## U. S. DYESTUFF SITUATION AT CLOSE OF 1915—CORRECTION

In my article under the above title, THIS JOURNAL 8 (1915), 16, the following corrections should be made:

Page 167, Col. 2: monthly output of naphthalene should read "1,000;" phenol, "830 tons."

Page 168, the following additions should be made:

### MANUFACTURERS OF COAL-TAR CRUDES

"The United Gas Improvement Co., Philadelphia.  
"The Smet-Solvay Co., Pittsburgh.  
"A number of firms engaged in the manufacture of high explosives, organized for the special purpose, are engaged in the production of synthetic phenol."

### MANUFACTURERS OF COAL-TAR INTERMEDIATES

"In addition to the above, mention may well be made of the following companies, which have put up large plants for the manufacture of aniline, which consume the bulk of the output in their own works:

Millville Manufacturing Co., Millville, N.  
B. F. Goodrich Co., Akron, Ohio.  
Goodyear Chemical Co., Akron, Ohio.  
Lyman G. Bourne, Inc., Auburn, Ind.  
Naugatuck Rubber Goods Manufacturing Co., Naugatuck, Ct.  
Merck & Co., Rahway, N. J.  
The du Pont de Nemours Co., Wilmington, Del.  
The Aetna Explosives Co., Pittsburgh, Pa."

### MANUFACTURERS OF ARTIFICIAL DYESTUFFS

"The United States Coal-Tar Products Co., New York City.  
"The Sherwin-Williams Co., New York City."

WASHINGTON, February 9, 1916

THOMAS H. NORTON

## ALUMINA IN ALUMINUM SALTS—CORRECTION

The factor weight to be taken in the analysis of aluminum salts by my rapid method should be "3.4067" and not 3.4038 as given in my paper printed in THIS JOURNAL 7 (1915), 1059.

This factor is based on titration with  $N/2$  acid. When acids are prepared without reference to normality strengths, this factor weight is derived as follows: the value of 100 cc. of the acid, in terms of  $H_2SO_4$ , is multiplied by four times the factor that gives the equivalent  $Al_2O_3$ ; i. e., if the standard acid used has a strength of 0.02 g.  $H_2SO_4$  per cc. the factor would be:  $2 \times 0.3473 \times 4 = 2.7784$ .

LAUREL HILL, LONG ISLAND  
NEW YORK, January 3, 1916

WILFRED W. SCOTT

## RADIUM, ETC., FROM CARNOTITE—CORRECTION

In my article in THIS JOURNAL, 8 (1916), 51 will be found the statement: "Three or four crystallizations only are necessary to bring the major part of the radium to a concentration of 60 to 80 per cent radium bromide." This should read: "Twelve to twenty crystallizations only are necessary."

January 22, 1916

C. L. PARSONS

# SCIENTIFIC SOCIETIES

## FIFTY-SECOND MEETING OF THE AMERICAN CHEMICAL SOCIETY—UNIVERSITY OF ILLINOIS URBANA-CHAMPAIGN—APRIL 18 TO 21, 1916

The Fifty-Second meeting of the American Chemical Society will be held at the University of Illinois, Urbana-Champaign, on Tuesday, April 18th, to Friday, April 21st, inclusive. The Beardsley Hotel, Champaign, has been chosen as headquarters. Additional accommodations can be obtained at Hotel Inman, located on University Avenue, one block from Illinois Central station and on the car line to the University. Meetings will be held at the University of Illinois which can be reached by car from the corner of Main and Neil Streets, one block south of the Beardsley Hotel.

### CHAIRMEN LOCAL SECTION COMMITTEES

EDWARD BARTOW, General Committee.  
W. A. NOYES, Finance.  
C. W. BALKE, Reception and Registration.  
C. G. DERRICK, Entertainment and Program.  
D. M. McFARLAND, Transportation and Excursions.  
E. W. WASHBURN, Smoker.  
S. W. PARRE, Banquet.  
G. D. BEAL, Press and Publicity.  
H. I. OLIN, Exhibits.  
MISS ISABEL BEVIER, Entertainment of Ladies.

### PROVISIONAL PROGRAM

MONDAY, April 17th, Evening, Council Dinner followed by Business Meeting.  
TUESDAY, April 18th, Morning, General session.  
Afternoon, Excursions to University buildings and grounds, including exhibition of live stock, floral display, and a visit to the plant-breeding laboratories. Review of University bridge.  
Evening, Concert by the University Military Band. Smoker.  
WEDNESDAY, April 19th, Morning, Sectional meetings.  
Afternoon, Dedication of the new Chemistry Building. Governor Edward J. Dunne of Illinois will preside. Addresses will be given by President Edmund J. James, W. R. Whitney, of the General Electric Company, and member of the U. S. Naval Board, and Professor Alexander Smith, of Columbia University. Reception and inspection of Chemistry Building.  
Evening, Subscription dinner.  
THURSDAY, April 20th, Morning, Sectional meetings.  
Afternoon, Excursions on University campus, including laboratories of mechanical, mining, hydraulic, electrical and railway engineering. Sectional meetings.  
Evening, PUBLIC LECTURES: "Production of Radium," by C. L. Parsons, Bureau of Mines, Washington.

"Use of Radium in the Cure of Cancer," by C. F. Burnham, M.D., Baltimore.

FRIDAY, April 21st, Excursion to Danville, Illinois, for the purpose of visiting:  
Hegeler Brothers' Zinc Smelter and Sulfuric Acid Plant;  
Western Brick Company's Kilns;  
Three Rivers Coal Company's Strip Coal Mine.

Special attention is called to the excursion by special train to Danville on Friday, April 21st. The smelter of the Hegeler Zinc Company was built in 1908, and is one of the most modern and best arranged in the country; the capacity has recently been trebled; the smelter utilizes the fumes from roasting the zinc ore. The brick and tile plant of the Western Brick Company is one of the largest in the country. Of unusual interest are the open-pit shale and coal mines furnishing material and fuel; the strip-pit coal mine gives a splendid illustration of the location of coal; usually a bed of coal a quarter to a half-mile long and fifty to one hundred feet wide is exposed. Arrangements are being made for optional visits to other plants.

All titles of papers should be in the Secretary's hands on or before April 7th or in the hands of the secretaries of divisions by April 5th in order to be placed on the final program. By vote of the Council no papers can be presented at the meeting the titles of which are not printed on the final program.

### ADDRESSES OF DIVISIONAL SECRETARIES

Agricultural and Food Chemistry, G. F. Mason, H. J. Heinz Company, Pittsburgh, Pa.  
Biological Chemistry, I. J. Phelps, Bureau of Chemistry, Washington.  
Fertilizer Chemistry, F. B. Carpenter, Virginia-Carolina Chemical Company, Richmond, Va.  
Industrial Chemists and Chemical Engineers, S. H. Salisbury, Jr., Lehigh University, So. Bethlehem, Pa.  
Organic Chemistry, H. L. Fisher, Columbia University, New York City.  
Pharmaceutical Chemistry, Dr. George D. Beal, University of Illinois, Urbana, Ill.  
Physical and Inorganic Chemistry, James Kendall, Columbia University, New York City.  
Water, Sewage and Sanitation, Dr. H. P. Corson, U. S. Public Health Service, Grove City, Pa.

C. L. PARSONS, Secretary



## NEW YORK SECTION OF AMERICAN ELECTRO-CHEMICAL SOCIETY

## ELECTROCHEMICAL WAR SUPPLIES SYMPOSIUM

The New York Section of the American Electrochemical Society met jointly with the New York Sections of the American Chemical Society and the Society of Chemical Industry at Rumford Hall, Chemists' Club, February 11, 1916.

The introductory address, by W. L. SAUNDERS, of the Naval Board, emphasized the lack of relation existing between our industries among themselves, as well as the lack of information possessed by the United States Government concerning the capacities of the industries of the country. Mr. Saunders feels that the training of the men of the United States in the industries is far more important than training them as soldiers. He called special attention to the fact that industrial efficiency of a nation may be measured by its coal consumption, and gave the per capita consumption of coal by countries as follows: United States, 5 tons per annum; England, 4 tons per annum; Germany, 4 tons; Russia,  $\frac{1}{4}$  ton; and France, 1.6 tons. Special emphasis was put on the fundamental importance of the chemical industries of the United States, since chemistry is the basis of all industrial projects. It is Mr. Saunders' opinion that our industries could scarcely be organized along lines of preparedness for war in a period of ten years.

**Electrochemical War Supplies.** By LAWRENCE ADDICKS. On account of illness, Mr. Addicks was unable to be present, but the chairman, Mr. Colin G. Fink, read a brief letter from Mr. Addicks, in which he emphasized the basic importance of the electrochemical industry in its relation to war supplies and preparedness for war.

**Air Saltpeter.** By W. S. LANDIS. Mr. Landis called attention to the fact that, at the outbreak of the war, Germany had no plants for the making of nitric acid from air, but it possessed in its various well organized and highly developed chemical industries plants and trained employees that were easily made available for the manufacture of ammunition and various war products. For instance, at the beginning of the war, Germany possessed only three Cyanamid factories with combined capacities of a little over 50,000 tons per year; at that time it was importing nitrogenous products that approximated 850,000 tons of nitrate of soda, 40,000 tons of nitrate of lime and at least 20,000 tons Norwegian cyanamid per annum. Eighteen months after the beginning of the war, Germany was producing nitrates for war purposes and for agricultural purposes on an annual basis of 600,000 tons Cyanamid, and 10,000 tons are process nitric acid. The present German investment in the air-fixation processes is over \$100,000,000.

It was pointed out that in order to accomplish this result the strain on the staffs of the chemical works must have been enormous and the importance of the United States having within its boundaries plants that could be thus diverted from their original purpose was especially emphasized. The manufacture of Cyanamid on this side of the Atlantic is now conducted on Canadian soil under American direction.

Mr. Landis reports that the manufacture of Cyanamid at Niagara Falls is carried on at a considerably higher efficiency than that existing in Germany at the time of his visit to the works there, which was just at the beginning of the present war. Furthermore, the product being made is of higher grade and the transformation into ammonia is at an efficiency equal to that of the German process, while the operation is actually conducted with fewer men and a simpler form of apparatus. Furthermore, the American manufacturers possess intimate knowledge of the design of such plants and very shortly a fair-sized plant will be producing nitric acid from Cyanamid by oxidation of the ammonia which can be obtained directly from Cyanamid. [For further reference to the making of ammonia from Cyanamid

and reference to the apparatus now in use at Niagara Falls see *THIS JOURNAL*, 8 (1916), 156.] Mr. Landis concluded with the statement that this country is now in as good, if not a better position to supply nitric acid in case of war than Germany was in the fall of 1914.

[Dr. Baekeland asked concerning the cost of obtaining nitrogen from air for use in making Cyanamid and other air-nitrate products. Dr. Landis replied that this process was very simple and the cost so slight as to make it an exceedingly minor feature in the process.]

**Hydrogen for Military Purposes.** By E. D. ARDREY (U. S. Army). The speaker discussed the preparation of hydrogen and various methods by which it can be produced. He also went into considerable detail concerning the methods used by the different nations in recent war times for the production of hydrogen for use in military balloons.

**New War Products.** By ALBERT H. HOOKER. Mr. Hooker called attention to the wonderful development of electrochemical industries at Niagara Falls since the Niagara Falls power plant started, about 1891. The list of products without which it may be safely said the industries of the United States would be practically paralyzed includes the following: chloroform; crystallized graphite and carborundum used in preparation of parts for autos, shells, machines of all kinds; ferrotungsten and ferromolybdenum—75 per cent of the steel products of the United States to-day depend on the supply from Niagara; caustic soda—for refining of oils and general use in all chemical industries; metallic sodium; hypochlorites, for which the Niagara plants are the main source; liquid chlorine; cyanamide—used as fertilizer and as an intermediate product in the manufacture of ammonia from air nitrogen. Mr. Hooker deprecated any attempt to injure the spectacular beauty of Niagara Falls, but stated that many times the power now taken from the Niagara River could be developed without changing the appearance of the falls any more than ordinary changes caused by the winds and regular variations in the level of Lake Erie. He also emphasized the wisdom of having available the maximum possible power that might be developed from the Niagara Falls in case of war, since under war conditions it would be absolutely necessary to make air nitrates by electrical methods as our supply of ammunition would be entirely dependent upon our supply of saltpeter in case the natural resources of Chile were made unavailable.

**Magnesium.** By W. M. GROSVENOR. This paper is printed in full in this issue of *THIS JOURNAL*, page 275.

**Liquid Chlorine.** By G. ORNSTEIN. The author discussed the various chemical processes for producing chlorine and showed slides of the various types of cells now in use for this purpose. He took up the history of liquid chlorine and showed the machinery used in handling it. He discussed its use for making bleaching solutions and its various advantages over ordinary hydrochloric. He also described in considerable detail the use of liquid chlorine in water sterilization. The last part of the paper was given up to a brief discussion of the market price of liquid chlorine and the possible injuries caused by the inhalation of chlorine. It is the author's opinion that the newspaper accounts of these effects have been exaggerated. The use of liquid chlorine in the manufacture of picric acid was mentioned but it was the speaker's opinion that liquid chlorine is more valuable for peaceful purposes than those of war.

**Electric Steel.** By G. W. SARGENT. Mr. Sargent reported that he had understood that the meeting was to discuss informally the subject of electrochemical supplies and that he had not prepared a formal paper, but would do so and present the same at the regular meeting of the Society at Atlantic City.

**Electrolytic Zinc.** By W. R. INGALLS. In the absence of Mr. Ingalls his paper was briefly abstracted by Dr. J. W. Richards.

## PERSONAL NOTES

The nineteenth annual meeting of the American Society for Testing Materials will be held at Atlantic City, N. J., June 27 to July 1, 1916.

The United States Civil Service Commission announces the following open competitive examinations: *Analyst*, for men only, at a salary of \$800 to \$1,020, on March 8, 1916. *Junior chemist*, qualified in fuels, for men only, at a salary of \$1,020 to \$1,200 per annum, on March 22 and 23, 1916. Further information may be had from the United States Civil Service Commission, Washington, D. C.

John A. Hill, president of the Hill Publishing Co., died suddenly from heart failure on January 24th, at the age of fifty-seven years. Mr. Hill was the organizer and largest stockholder of the Hill Publishing Co., which prints the following technical journals: *The American Machinist*, foreign editions of which are issued in London and Berlin, *Power*, the *Engineering and Mining Journal*, *Engineering News*, and *Coal Age*. He was also president of the McGraw-Hill Co., Inc. Mr. Hill was vice-president of the Machinery Club and a member of the Engineers' Club of New York, the Railroad Club, the Campfire Club and the American Society of Mechanical Engineers.

Prof. H. V. Tartar, head of the Oregon Experiment Station Department of Chemistry, has been granted a two-year leave of absence to pursue research work at some of the leading eastern universities.

News has been received from Sweden that the actual delivery of the Nobel prize in Chemistry for 1914, awarded to Prof. Theodore W. Richards, of Harvard University, together with the other Nobel prizes for 1914 and 1915, will be postponed until June 1st of this year. The prize winners are invited to go then to Sweden in person to receive their prizes, and to give their Nobel lectures.

Charles V. Mapes, an industrial agricultural chemist of New York City, died January 23rd, in his eightieth year.

The Oklahoma Chemical Co., Sand Springs, Okla., contemplate the erection of a sulfuric acid plant at Lake Station. Other chemicals, including silica and caustic soda, will be manufactured.

It is reported that work has been actively commenced and new machinery is being erected to produce potash from Searles Lake, Cal. A reduction plant will be established at San Pedro, Cal., by the company, which is an English corporation.

Mr. James H. Payne, a consulting chemical and metallurgical engineer of Baltimore, died January 26th, at the age of thirty-four. He was educated at the Massachusetts Institute of Technology and had been successively employed by the Eastman Kodak Co., Texas Portland Cement Co., Security Cement and Lime Co., Virginia Portland Cement Co., Jamestown Portland Cement Co., with Richard K. Meade and with the Braden Copper Co., in Chile. For the past year he had been occupied with independent consulting work. He was a specialist in the use of rotary furnaces and had designed plants for re-burning lime waste, nodulizing pyrites cinder, etc. At the time of his death he was interested in the manufacture of barytes compounds.

At a meeting of the Council of the Royal Society of Arts, London, January 24th, the Society Albert Medal was awarded to Sir J. J. Thomson for his researches in chemistry and physics and their application to the advancement of arts, manufacture and commerce.

Prof. W. H. Perkin, F. R. S. of Oxford University, has been

appointed head of the research department of the British Dyes Limited, and chairman of the Advisory Committee to succeed the late Prof. Raphael Meldola.

The Institute of Arts and Sciences of Columbia University, New York City, gave the following series of lectures during the month of February on Highway Engineering:

"The Regulation of Different Classes of Traffic on Public Highways," by Edwin Duffey, Commissioner of Highways of the State of New York.

"Limitations of Tests which Define the Essential Properties of Stone Block, Paving Brick, Wood Block and Cement-Concrete when Used in Pavements," by W. W. Crosby, Chief Engineer, Maryland Geological and Economic Survey.

"The Manufacture of Paving Brick," by W. P. Blair, Secretary, National Paving Brick Manufacturers' Association, Cleveland.

"Essential Details of the Construction and Maintenance of Brick Pavements," by W. A. Howell, Engineer of Streets and Highways, Newark, N. J.

"Aggregates, Mixing Plants and Expansion Joints for Cement-Concrete Pavements," by L. R. Ferguson, Assistant Secretary Association of American Portland Cement Manufacturers, Philadelphia.

"Bond Issues as a Source of Revenue for Highway Improvements," by E. P. Goodrich, Consulting Engineer to the President of the Borough of Manhattan, New York City.

"The Legal Status of Highway Boundaries and Disposal of Surface Waters," by J. C. Wait, Attorney-at-Law, New York City.

The Chattanooga Chemical Co., of Chattanooga, Tenn., has started work on its new plant to cost \$150,000, to manufacture phenol, toluol, etc. The machinery and other equipment have been purchased and the plant will shortly be ready to start operations. Lewis T. Wolle, president of the Chattanooga Gas and Coal Products Co., is president and general manager of the new concern.

Mr. William H. Bowker, of Boston, died on January 4th, at the age of sixty-five years. Mr. Bowker was for forty-three years actively at work in the fertilizer trade and was one of the best informed men connected in any way with the fertilizer industry.

The regular monthly meeting of the Detroit Section of the A. C. S. was held on February 17th. Mr. Matthew H. Bishop, president of the "Lawyers' Club," addressed the meeting on "The Law for the Business Man." The March meeting will be held on March 16th, at which Mr. Joseph M. Bourg, of the Park Chemical Co., will lecture on "The Chemical Composition of Steel in Its Relation to Its Industrial Uses."

The thirty-eighth regular meeting of the Connecticut Valley Section of the A. C. S. was held on February 12th. The program consisted of the following papers: "The Chemistry of Synthetic Caoutchouc," by Prof. Joseph S. Chamberlain, and "The Color Problem in the Paper Industry," by Mr. R. F. Hatch.

Morse Hall, home of the chemistry department at Cornell University, was destroyed by fire on February 13th with a loss of \$300,000; the insurance amounts to \$200,000. The blaze started in the photography rooms of J. P. Troy on the third floor. Records of research, and valuable apparatus and chemicals, which owing to the war cannot be duplicated at present, were lost in the flames. Five thousand books from the chemical library on the first floor were saved by students. The university department of chemistry announces that it purposes to continue its work.

Waldemar R. Kremer was appointed general sales manager of the Vilter Manufacturing Co., at the recent meeting of the board of directors succeeding the late Mr. Fred Ulrich. Mr. Kremer has been connected with the company for nearly ten years as consulting electrical and mechanical engineer in the sales department. He is a graduate of the electrical and mechanical engineering courses of the Royal Polytechnical Institute, Munich, Germany, and the Massachusetts Institute of Technology, Boston. In his new capacity he will have general charge of sales and supervision of branch offices and agencies in this and foreign countries.



# GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

## BUREAU OF THE MINT

**Annual Report and Report on the Production of the Precious Metals in the Calendar Year 1914.** DIRECTOR OF THE MINT. 304 pp. Cloth, 60 cents. "The gold production of the United States, including its insular dependencies, for the calendar year 1914 is estimated to have been \$94,531,800, and the production of silver is estimated at 72,455,100 fine ounces.

"The output of gold in the United States, including its outlying territories in 1914, exceeded that of 1913 by \$5,647,400. Of this excess \$1,300,000 was from Alaska, nearly \$1,800,000 from Colorado, and \$1,000,000 from California. Gains and losses in other sections were unimportant.

"The construction of a Government railway into Alaska is looked forward to as a step likely to have great influence upon future developments in that territory. Otherwise there is nothing in sight upon which to base a prediction as to an expansion or falling off of mining operations except that the effect of the European war in controlling copper and lead production will have the incidental effect of reducing the yield of gold and silver from copper and lead ores.

"The amount of gold consumed in the industrial arts during the calendar year 1914 was \$42,728,893, of which \$34,621,619 was new material. Silver consumed amounted to 29,233,117 fine ounces, of which 22,474,787 fine ounces were new material. The net exports of United States gold coin for the fiscal year 1915 were \$23,445,028."

Full data are given for the production of gold and silver in each state and in other countries of the world and the movement of gold and silver together with a number of other interesting statistics are discussed.

The charge for ore assays made by the mint and assay offices of this Bureau has been reduced from \$3.00 to \$1.00 for gold and silver and \$1.00 for each of the following metals: Copper, tin, zinc, iron, lead, and tungsten. In this connection it is interesting to note that the average cost per assay at the Philadelphia mint was \$0.686 for approximately 53,000 assays made, including apparently all overhead expenses. At some of the other mints the cost of assay is reported as low as \$0.30 for gold or silver, apparently not including overhead expenses, however.

The purchases of silver for coinage amounted to 3,400,000 fine ounces at an average price of \$0.51 per ounce. These purchases "so stimulated the market, whose unsteadiness had threatened a partial paralysis of the silver-mining industry all over the world, that production of silver has continued practically without abatement. It also had the effect of aiding the production of gold, inasmuch as all silver bullion carries a certain amount of gold."

The sale of electrolytic slimes containing platinum has been partially discontinued in order to permit the melting and spinning of the platinum for the use of Government laboratories. During the past months, platinum melting equipment has been installed in the New York office and the Philadelphia mint has perfected machinery for spinning the metal and manufacturing

it into utensils for use in Government laboratories. In this connection it is interesting to note the quantity of these by-products obtained, which are reported as follows:

	Ounces	Value
Platinum.....	2,507.08	\$92,677.82
Palladium.....	320.24	12,540.88
Iridium.....	102.00	5,100.00
Osmiridium.....	4.79	167.65
Copper.....	14,880.97	2,738.55

## BUREAU OF MINES

### Gasoline Mine Locomotives in Relation to Safety and Health.

O. P. HOOD and R. H. KUDLICH; with a chapter on *Methods of Analyzing Exhaust Gases*, by G. A. BURRELL. Bulletin 74. 83 pp. Paper, 15 cents. This article discusses the volume and character of exhaust gases under different conditions of operation and describes results of tests on locomotives to determine the extent to which they vitiate mine air, and results in the production of carbon monoxide. The methods of gas analysis described are the same as those in Bureau of Mines Bulletin 42.

**Sampling and Analyzing Flue Gases.** HENRY KREISINGER AND F. K. OVITZ. Bulletin 97. 64 pp. Paper, 15 cents. "This bulletin is intended to be a companion to Technical Paper 80,<sup>1</sup> and is written in non-technical language, as far as possible, so that it may be readily understood by persons who have not had the advantage of a technical education. Whenever possible, illustrations of apparatus and methods of handling have been used rather than elaborate descriptions."

Practically none of the material describes new work and the descriptions are extremely elementary, including illustrations and descriptions of equipment with which every person who has ever done any chemical work would be thoroughly familiar.

**Manufacture and Uses of Alloy Steel.** HENRY D. HIBBARD. Bulletin 100. 77 pp. Paper, 10 cents. "The object of this report is to give briefly information of present value relating to the manufacture and uses of the various commercial alloy steels, with the hope of stimulating the demand for such steels and extending their practical use. The report is issued by the Bureau of Mines as a contribution to the increase of efficiency in the preparation and utilization of the mineral resources of the United States."

For each of the steels discussed, methods of manufacture and working, properties and uses, composition and general information of interest are given, including in several instances a brief bibliography and a discussion of the theory involved. Alloy-treated steels and structural alloy steels are discussed, including the following: (1) Simple tungsten steels; (2) simple chromium steels; (3) manganese steel; (4) simple nickel steels; (5) nickel-chromium steels; (6) silicon steels; (7) high-speed tool steels; (8) chromium-vanadium steels.

**The Limits of Inflammability of Mixtures of Methane and Air.** G. A. BURRELL AND G. G. OBERFELL. Technical Paper 119. 30 pp. Paper, 5 cents. The conditions influencing the explosibility of methane and air mixtures are discussed and experiments to determine the limits are described in detail. The smallest proportion of methane that was found to permit self-propagation of flame was 4.9 per cent; this result was obtained by ignition at the bottom of a box containing this mixture with an electric flash produced by pulling apart two copper wires through which a current of 7 amperes and 220 volts was flowing. The maximum percentage which permitted self-propagation of flame was between 15 and 15.4 per cent methane.

<sup>1</sup> Henry Kreisinger, "Hand Firing Soft Coal under Power-Plant Boilers," *Tech. Paper 80*, Bureau of Mines, 1915, 83 pp.

## PUBLIC HEALTH SERVICE

**Standards for Milk; Their Necessity to the Welfare of the Dairy Industry.** JOHN F. ANDERSON. *Public Health Reports*, 31 (Jan. 7, 1916), pp. 2-8. This is an address before the International Association of Dairy and Milk Inspectors, delivered in Washington, October 27, 1915. The contrast between the standards of different communities is pointed out and the importance of greater uniformity emphasized.

## SANITARY LEGISLATION

**Production, Care and Sale of Milk and Milk Products.** The following ordinances establishing standards for milk and milk products and prescribing regulations as to the production, care and sale of these articles are printed in *Public Health Reports*, 31 (1916). In each case certain requirements as to fat, water, total solids, or bacterial count are included. Great diversity of standards is to be noted. The page reference and date in parenthesis is in each case the page and date of the report in *Public Health Reports*. The last regulation gives a modified standard for grade "B" milk and specifies new regulations to be pasteurized.

Kansas City, Missouri, Ord. 23314, July 17, 1915. (P. 34, Jan. 7th.)  
Phoenix, Arizona, Ord. 64, August 14, 1915. (P. 96, Jan. 14th.)  
California State Act, June 11, 1915, Chap. 742. (P. 147, Jan. 21st.)  
Wichita, Kansas, Ord. 5261, November 18, 1915. (P. 292, Feb. 4th.)  
Bay City, Michigan, Ord. December 6, 1915. (P. 280, Feb. 4th.)  
Richmond, Virginia, Reg. Board of Health, December 13, 1915. (P. 346, Feb. 11th.)  
N. Y. State, Reg. Public Health Council, October 5, 1915, Chap. 3. (P. 344, Feb. 11th.)

**Use of Boric Acid as a Preservative.** United States Supreme Court Decision in the Case of *Price v. State of Illinois*, 35 Sup. Ct. Rep. 892. Decided June 21, 1915. This decision upholds the Illinois Pure Food Law which prohibits the use of boric acid in a preservative for foodstuffs. It is concluded that "the law to prohibit the use of boric acid in a preservative, although such preservative was not a food in itself and was not shown to be injurious or unwholesome," was proper and valid.

**Analysis of Ice.** Kansas Board of Health Regulation, October 4, 1915. (Pp. 275-6, Feb. 4th.) These regulations require the analyses of ice in the State Board of Health laboratory at intervals, and set a limit of 100 bacteria per cubic centimeter and a requirement that no organisms of *B. coli* group be found by test of 1 cubic centimeter. Ice which does not meet these requirements must be sold for refrigeration purposes only and not for domestic consumption.

## BUREAU OF STANDARDS

**United States Standard Tables for Petroleum Oils.** ANONYMOUS. Circular 57, issued January 29, 1916. 64 pp. and 2 insert cards. This circular contains the following 5 tables:

- 1—Specific gravity at 60°/60° F. of oils having, at the designated temperatures, the apparent specific gravities indicated.
- 2—Degrees Baumé at 60° F. of oils having, at the designated temperatures, the apparent degrees Baumé indicated.
- 3—Volume that would be occupied at 60° F. by a quantity of oil, of various specific gravities, occupying unit volume at the designated temperatures.
- 4—Degrees Baumé, pounds per gallon, and gallons per pound corresponding to the designated specific gravities.
- 5—Specific gravities, pounds per gallon, and gallons per pound corresponding to the designated degrees Baumé.

"The expansion tables contained in this circular are based upon the results of experiments carried out at this Bureau between July, 1912, and December, 1914. During that time about 100 samples of crude and refined petroleum oils from various parts of the United States were examined and their densities determined at various temperatures.

"This investigation has shown that within the limits of ordinary measurements the rate of change of specific gravity with change of temperature is the same for all oils of the same specific gravity. In the calculation of the expansion tables (Tables 1, 2 and 3) the average rate of expansion found for all oils of each designated specific gravity has been used."

The tables contained in this circular apply to all petroleum oils, both crude and refined, produced in the United States. Each grade of oil, gasoline, illuminating oil, lubricating and fuel oil, etc., falls into its proper place in the tables by reason of its specific gravity. In the case of oils containing paraffin or other materials that become solid at low temperatures the expansion shown by the tables is somewhat too small at temperatures below the point of solidification.

**Microstructural Changes Accompanying the Annealing of Cast Bronze.** HENRY S. RAWDON. Technologic Paper 60, issued January 25, 1916. 17 pp. [For extended abstract see THIS JOURNAL, 8 (1916), 109.]

**The Determination of Barium Carbonate and Barium Sulfate in Vulcanized Rubber Goods.** JOHN B. TUTTLE. Technologic Paper 64, issued January 21, 1916. 5 pp. [To appear in full in the next issue of THIS JOURNAL.]

**Detection of Resin in Drier.** E. W. BOUGHTON. Technologic Paper 66, issued January 15, 1916. 9 pp. "A method has been developed for the detection of resin in driers which is reliable except when the resin content is very small, *e. g.*, less than 6 per cent of the ash-free non-volatile portion."

Three separate procedures are described. The first is comparatively simple but less sensitive. If this does not detect the resin, the second, more complicated but more sensitive procedure, may be followed; and if this in turn gives negative results, the third practically conclusive test, but one which requires greater time for its performance, can be applied.

**Some Qualitative Tests for Gum Arabic and Its Quantitative Determination.** C. E. WATERS AND J. B. TUTTLE. Technologic Paper 67, issued January 31, 1916. 15 pp. "An incorrect report to the effect that a certain sample of mucilage contained no gum arabic led to a study of many of the published tests for this gum, as well as to a search for others than the few that proved to be reliable.

"The object of this paper is to bring together all the more important qualitative and quantitative methods that have been published and to present a new procedure for the determination of gum arabic.

"It was found that basic lead acetate gives the most characteristic reaction, while mixtures of copper sulfate and sodium hydroxide, and of neutral ferric chloride and alcohol are of value as confirmatory tests.

"A summary of the more important methods that have been proposed for the quantitative estimation of gum arabic is next given, followed by a description of the steps that led the authors to the use of alcoholic copper acetate-ammonia solution for this determination."

**Turpentine Tables.** ANONYMOUS. Supplement to Technologic Paper 9. 2 Cards. These tables include the following four sheets of conversion data:

- 1—For reducing observed specific gravities of turpentine at various temperatures to true specific gravity at 60°/60° F.
- 2—For reducing observed degrees Baumé of turpentine at various temperatures to true degrees Baumé at 60° F.
- 3—Showing the degrees Baumé, pounds per gallon, and gallons per pound corresponding to various specific gravities.
- 4—Showing the specific gravity, pounds per gallon, and gallons per pound corresponding to various degrees Baumé.

## BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**Tests Used in Cotton Industry.** W. A. GRAHAM CLARK. Special Agents' Series 105. 22 pp. Paper, 5 cents. This bulletin explains briefly the correct use of common terms including the various systems of cotton-yarn numbering, designation of various kinds of cloth, and the translation of foreign terms; 25 conversion tables applicable to the industry are included.

**Cotton Goods in China.** RALPH M. ODELL. Special Agents' Series 107. 242 pp. Paper, 25 cents. In addition to a de-



tailed study of the cotton goods trade of China and a description of cotton growing and manufacturing in that country, there are included descriptions of about 200 samples of cotton goods of interest in this connection.

**Dyestuff Situation in the United States, November, 1915.** THOMAS H. NORTON. Special Agents' Series 111, 19 pp. Paper, 5 cents.

#### GEOLOGICAL SURVEY

**Origin of the Zinc and Lead Deposits of the Joplin Region, Missouri, Kansas, and Oklahoma.** C. E. SIEBENTHAL. Bulletin 606. 283 pp. "A valuable contribution to the study of the lead and zinc deposits of the Mississippi Valley, which are not only of great economic importance but have long been intensely interesting to students of ore deposits because they constitute a conspicuous example of the occurrence of sulfide ores in a region where plutonic or volcanic activities can have had no part in their genesis. The author holds that the Joplin ores were segregated from disseminated zinc and lead minerals in the Cambrian and Ordovician rocks of the Ozark uplift, by circulating artesian alkaline-saline sulfureted waters, and his careful observations and cogent reasoning have gone far to establish the general conclusion that ordinary cold artesian water may under some circumstances be a very efficient agent in the solution, transportation, and deposition of the constituents of certain sulfide ores. The illustrations include topographic and geologic maps and cross-sections of the Ozark uplift, diagrams showing early and late stages in Ozark artesian circulation, and halftone plates showing the manner of occurrence of the ores in certain of the mines."

**Recent Alunite Developments near Marysvale and Beaver, Utah.** G. F. LOUGHLIN. Bulletin 620-K, from Contributions to Economic Geology, 1915, Part I, pp. 237-70. Published December 3, 1915.

**Notes on the Fine Gold of Snake River, Idaho.** J. M. HILL. Bulletin 620-L, from Contributions to Economic Geology, 1915, Part I, pp. 271-94. Published December 21, 1915. "Under the present conditions of distribution, character of the gold, and methods of its recovery, it seems very doubtful if any ventures of a size large enough to expect success can be commercially profitable."

**The Aztec Gold Mine, Baldy, New Mexico.** WILLIS T. LEE. Bulletin 620-N, from Contributions to Economic Geology, 1915, Part I, pp. 325-30. Published January 15, 1916.

**Cassiterite in San Diego County, California.** WALDEMAR T. SCHALLER. Bulletin 620-P, from Contributions to Economic Geology, 1915, Part I, pp. 351-4. Published January 15, 1916. Further prospecting in this district has not revealed any general deposits nor the source of the cassiterite which has recently been found in small quantity. Further prospecting is contemplated.

**Geology and Coal Resources of Northern Teton County, Montana.** EUGENE STEBINGER. Bulletin 621-K, from Contributions to Economic Geology, 1915, Part II, pp. 117-56. Published January 5, 1916. The scope of this paper is limited to the geologic and economic features of this district which have a bearing on the value and quantity of coal resources.

**Natural Gas Resources of Parts of North Texas.** Bulletin 629. 126 pp. This bulletin includes the following three articles which have been prepared by representatives of the Geologic Survey in cooperation with the cities of Dallas and Ft. Worth, Texas: (1) Gas in the Area North and West of Fort Worth. EUGENE W. SHAW. (2) Gas Prospects South and Southeast of Dallas. GEORGE C. MATSON. (3) Notes on the Gas Fields of Central and Southern Oklahoma. CARROLL H. WEGEMANN.

**Gold, Silver, Copper, Lead, and Zinc in Arizona in 1914.** V. C. HEIKES. Separate 15, from Mineral Resources of the United States, 1914, Part I, pp. 427-75. Published December 14, 1915. In 1914 Arizona mines produced these metals valued

at \$60,000,000 which represented a decrease of \$11,000,000 in value from the previous year. The decrease was principally in copper but slight decreases were noted also in lead and zinc. Gold and silver showed slight increase. The output of zinc increased in quantity but declined in value.

**Gold, Silver, Copper, Lead and Zinc in Idaho and Washington in 1914.** C. N. GERRY. (Mines Report.) Separate 18, from Mineral Resources of the United States, 1914, Part I, pp. 597-654. Published December 17, 1915. "The value of the mine production of gold, silver, copper, lead and zinc in Idaho in 1914 was \$24,645,848, an increase of \$496,799 over the value in 1913. This was not a large increase, as the metal market was dull during half the year, but the total value was greater than in any previous year. Marked increase, and, in fact, a record production, was made in silver, lead and zinc, but there was a decrease in gold, in copper, and in the quantity of ore marketed or treated."

**Gold, Silver, Copper, Lead and Zinc in Nevada in 1914.** V. C. HEIKES. (Mines Report.) Separate 19, from Mineral Resources of the United States, 1914, Part I, pp. 655-716. Published December 21, 1915. The mine production from 4,500,000 tons of ore, including the placer output, was valued at \$29,300,000, representing a decrease of nearly \$8,000,000 in value as compared with 1913. The number of producers was about the same as the previous year. The production of copper was nearly 28 per cent of the total value but represented a decrease of \$6,000,000 in the previous year. Each of the other metals also decreased slightly in value.

**Gold, Silver, Copper, Lead and Zinc in Utah in 1914.** V. C. HEIKES. (Mines Report.) Separate 20, from Mineral Resources of the United States, 1914, Part I, pp. 717-56. Published December 23, 1915. The mine production in 1914 was valued at \$37,000,000 or \$7,700,000 below the previous year. Fifty-four per cent of the production was copper, but this was valued at \$5,000,000 less than the previous year. Gold, silver and zinc showed decreases, but lead increased in quantity though decreased slightly in value.

**Gold, Silver, Copper, Lead and Zinc in Montana in 1914.** V. C. HEIKES. (Mines Report.) Separate 21, from Mineral Resources of the United States, 1914, Part I, pp. 757-97. Published December 24, 1915. The mine production of this state amounted to approximately \$48,000,000 but showed a decrease of \$14,000,000 in value compared with the previous year, due principally to the reduced output of copper, although silver and lead also decreased slightly.

**The Production of Iron Ore, Pig Iron and Steel in 1914.** ERNEST F. BURCHARD. Separate 16, from Mineral Resources of the United States, 1914, Part I, pp. 477-539. Published December 9, 1915. "The quantity of crude iron ore mined in the United States in 1914 amounted to 41,439,761 long tons, as compared with 61,980,437 long tons mined in 1913, a decrease of 20,540,676 long tons, or 33.14 per cent. . . . The average price of ore per ton for the whole country in 1914 was \$1.81, as compared with \$2.19 in 1913. These quantities of ore, both mined and marketed, include the iron ore used for fluxing other metallic ores at smelters in the Western States, but the marketed ore does not include the iron ore sold for the manufacture of paint. The quantity of iron ore for paint marketed in 1914, which is reported in detail in another chapter of Mineral Resources, amounted to 18,452 long tons, valued at \$46,995. The ore reported as sold for fluxing purposes other than in the manufacture of pig iron amounted to 42,677 long tons, valued at \$114,985, in 1914."

The statistics also include data of imports, exports, the Cuban iron industry, and the production of iron ore in the principal countries of the world. There is also included a new section on beneficiated iron ores which include those iron ores which are improved in quality by some physical or chemical

treating such as hand-picking, drying, roasting, washing, jigging, magnetic separation or agglomeration.

"The production in 1914 of all kinds of pig iron, including such ferro-alloys as spiegeleisen, ferromanganese, ferrosilicon, and ferrophosphorus, produced in blast furnaces as well as some that were electrically produced, was 23,332,244 long tons, compared with 30,966,152 tons produced in 1913, a decrease of 7,633,908 tons, or 24.65 per cent.

"The marketed production of pig iron in 1914 amounted to 22,263,263 long tons, valued f. o. b. at the furnaces at \$298,777,429, a decrease in quantity of 26.74 per cent, and in value of 34.81 per cent. The average price per ton in 1914 was \$13.42, a decrease in 1914 of \$1.66 a ton. These values represent the approximate price per ton f. o. b. at the furnaces; this approximate price eliminates freight costs, selling commissions, and other items, which are included in the market prices of certain grades of pig iron as published in the trade journals."

PRODUCTION OF PIG IRON IN 1914, BY GRADES (LONG TONS)	
Bessemer and low phosphorus.....	7,859,127
Basic (mineral fuel) (a).....	9,670,687
Forge pig iron.....	361,651
Foundry and ferrosilicon.....	4,533,254
Malleable.....	671,771
Spiegeleisen.....	79,935
Ferromanganese.....	106,083
White, mottled, direct castings, etc.....	49,736

Total..... 23,332,244

(a) Includes a small quantity of basic iron made with charcoal.

MARKETED PRODUCTION OF FERRO-ALLOYS IN 1914 (LONG TONS)		
	Quantity	Value
Ferromanganese.....	100,731	\$4,440,253
Spiegeleisen.....	76,625	1,386,139
Ferrosilicon and ferrophosphorus.....	77,182	1,621,830
Ferromolybdenum, ferrovanadium and ferro-tungsten.....	986	1,702,023
Total.....	255,524	\$9,350,245

**Copper in 1914.** B. S. BUTLER. (General Report.) Separate 17, from Mineral Resources of the United States, 1914, Part I, pp. 541-96. Published December 8, 1915.

"The following statistical statement summarizes the copper industry in the United States in 1914:

Production of copper	
Smelter output.....	1,150,137,192 lbs.
Mine production.....	1,148,431,437 lbs.
Refinery production of new copper:	
Electrolytic.....	991,573,073 lbs.
Lake.....	138,009,748 lbs.
Casting and pig.....	60,840,368 lbs.
Total domestic.....	1,210,423,189 lbs.
Total domestic and foreign.....	1,533,781,394 lbs.
Total new and old copper.....	1,790,000,000 lbs.
Total ore produced.....	35,187,118 short tons
Copper ore produced.....	35,175,341 short tons
Average yield of copper.....	1.60 per cent
Imports.....	306,350,827 lbs.
Exports.....	840,080,922 lbs.
Consumption:	
Total new copper.....	711,624,158 lbs.
Total new and old copper.....	968,000,000 lbs.
Value of production in the United States.....	\$ 152,968,246

"The smelter production of copper in 1914 showed a considerable decrease from that of 1913. The refinery production, like that of the smelters, showed a reduction from that of 1913, due to the same causes.

"Regardless of the unfavorable conditions, the average cost of producing copper in 1914 was doubtless considerably less than in 1913. The average cost per pound in 1914 of producing electrolytic and casting copper, as compiled from the annual reports of companies giving this item, was 8.62 cents, as compared with 9.49 cents in 1913 and with 8.74 cents in 1912. This cost for electrolytic and casting copper is probably somewhat below the average cost of the entire output, but doubtless represents the general trend of costs for the three years. The average cost per pound for Lake copper, as compiled from the reports of companies giving this item, was 10.94 cents in 1914, as compared with 13.44 cents in 1913 and with 10.28 cents in 1912. The cost figures for the year are somewhat surprising, in view of the marked curtailment of output for a part of the year, which might be supposed to raise the cost.

"The demonstration of this elasticity and ability to meet

varying conditions should be a source of satisfaction to all interested in the copper industry.

"The average selling price of electrolytic copper, as compiled from the reports of companies giving that item, was 13.4 cents in 1914, and that of Lake copper was also 13.4 cents. This was not quite 2 cents a pound lower than the selling price for 1913, and it is evident that the profits of the industry were considerably less in 1914 than in 1913, regardless of the lowering of the cost price."

**Lead in 1914.** C. E. SIEBENTHAL. (General Report.) Separate 22, from Mineral Resources of the United States, 1914, Part I, pp. 799-827. Published January 14, 1916. "The output of refined lead produced in the United States from domestic ores in 1914 was 512,794 short tons, valued at \$39,997,932, based on the average New York price of refined lead."

**The Production of Natural Gas in 1914.** JOHN D. NORTHPROP. Separate 32, from Mineral Resources of the United States, 1914, Part II, pp. 747-818. Published December 15, 1915. "The quantity of natural gas commercially utilized in the United States in 1914 exceeded that so utilized in any previous year in the history of the natural-gas industry. The quantity produced and used, which amounted to approximately 591,866,733,000 cu. ft., constitutes a new record, exceeding by nearly 10,000,000,000 cu. ft., or 1.7 per cent, the former record established in 1913.

"Of the record-breaking production of natural gas credited to 1914, it is estimated that a total of 203,104,358,000 cu. ft., or about 34 per cent, was supplied to domestic consumers at an average price of 28.04 cents per 1,000 cu. ft., and that 388,762,375,000 cu. ft., comprising the remaining 66 per cent, was supplied to industrial consumers at an average price of 9.56 cents per 1,000 cu. ft. During the last four years the ratio of domestic to industrial consumption has varied but slightly. Formerly, a relatively greater proportion of the annual yield was supplied to industrial consumers."

**The Stone Industry in 1914.** G. F. LOUGHLIN. Separate 33, from Mineral Resources of the United States, 1914, Part II, pp. 819-91. Published December 31, 1915.

**Petroleum in 1914.** JOHN D. NORTHPROP. Separate 34, from Mineral Resources of the United States, Part II, pp. 893-1098. Published January 12, 1916. "The combination of the figures for marketed production and of the estimated quantity of oil placed in producers' storage gives more than 290,000,000 bbls. as the total yield of the oil wells of the United States in 1914."

**The Public Interest in Mineral Resources.** GEORGE OTIS SMITH. Separate from Part I, Mineral Resources of the United States. 9 pp. Published December 31, 1915.

# DEPARTMENT OF AGRICULTURE

**Methods for the Examination of Bituminous Road Materials.** PREVOST HUBBARD AND CHARLES S. REEVE. Department Bulletin 314. 48 pp. "Its object is to present a description of methods now in use by the Office of Public Roads and Rural Engineering for the examination of bituminous road materials in such form that, with a little practice and proper equipment, such examinations may be made by an intelligent person. The various tests have, therefore, been described rather more in detail than would be necessary if they were intended for the use of chemists only, and illustrations of practically all of the apparatus required have also been included."

The tests included are the following: Specific gravity, specific viscosity, float test, penetration test, melting point, flash and burning points, volatilization test, distillation test, dimethylsulfate test, bitumen soluble in carbon disulfide, bitumen insoluble in paraffin naphtha, bitumen insoluble in carbon tetrachloride, fixed carbon, paraffin scale, extraction of bituminous aggregates, grading the mineral aggregate, voids in the mineral aggregate and bituminous emulsions.



## BOOK REVIEWS

**Engineering as a Career.** A series of papers edited by PROFESSOR F. H. NEWALL, University of Illinois, and C. E. DRAYER, Railroad Engineer, Cleveland, O.: D. Van Nostrand Co. 214 pages. Price, \$1.00, net.

The enormous strides made by engineers and engineering in recent years, at rates that are themselves increasing year by year, and in fields often not even suspected by the general public, have made engineering probably the most promising of all careers for the young man of proper calibre. This being the case, it would seem as if a book devoted to an exposition of engineering as a career would be a valuable contribution not only to engineering literature as a statement of the status of engineering at the present time, but to every prospective student and his family.

One would expect to find in a true story of this sort an irresistible lure, attracting any boy with a spark of ambition in him, for what boy has not dreamed of doing great things? With such a possibility in view this book is a most disappointing product. In the first place, it fails utterly in giving a representation of engineering activities as they are, and it is just about attractive enough to drive any prospective students of engineering into the ministry where, if report is to be believed, there is plenty of room. Twenty-two different authors, in 214 pages, have contributed essays averaging 10 pages each, and yet, to use the language of the stage, they have utterly failed to "put it over," collectively speaking.

C. E. LUCKE

**The Rare Earth Industry.** By SIDNEY J. JOHNSTONE, B.Sc. D. Appleton & Co., 1915. Royal 8vo., vii + 136 pp. Price, 7s 6d, net.

This book is the second of a series of Manuals of Chemical Technology edited by Geoffrey Martin. In its text content of 126 pages, 33 are devoted to the Thorium and Cerium Industry, while the remainder of the book consists of a technological description of Titanium, Zirconium, Tantalum and Niobium, Tungsten, the Incandescent Electric Glow Lamp Industry, Uranium, and Vanadium, with a final chapter of 16 pages on the Industry of Radioactive Substances, which has been written by Alexander S. Russell, M.A., D.Sc.

The book is designed to be essentially of a practical character, and limits itself to the commercial aspects of the elements and subjects enumerated in the nine chapters.

The salient points of each element and its uses are brought into prominence, though in many cases in only the most general way. The impression of a compilation is brought to the attention of the reader rather than that of first-hand knowledge on the part of the author.

On the whole, the most important methods for extraction of the earths and the rare metal compounds are outlined, and the preparation of the elements and their uses are noted. Attention is drawn throughout the book to the manufacture and uses of the various rare elements in whatever form they are adaptable to the problems of modern artificial illumination.

The final chapter on the Industry of Radioactive Substances is a brief résumé of these bodies, their sources, separations, methods of testing their strength, and their medicinal and general uses.

The work is a general description of the technological uses of the more commercially important rarer elements, together with brief descriptions of certain phases of the industries to which these elements are allied.

VICTOR LENHER

**Guide to the Reports, Evidence and Appendices of the Royal Commission of Sewage Disposal.** By G. B. KERSHAW. New York: D. Van Nostrand Co. 8vo. 178 pp. Price, \$2.00.

As is stated in the preface, the object of preparing this synopsis has been to provide a handy reference book or guide to the subject matter of the various reports and appendices presented by the Royal Commission on Sewage Disposal.

These documents terminated with the issue of the tenth report: their total number (published under separate covers) amounts to some thirty volumes, and it is no easy matter for the reader interested in a special subject to find the particular volume he requires, and even when the volume has been found, to isolate the special section required.

In this synopsis, the Commission's reports have been dealt with seriatim, the plan followed being to extract from each report, appendix, etc., all the headings and sub-headings, thus giving in condensed form the subject matter contained in them.

Opposite to each heading or sub-heading will be found the page or pages of the Report in which they occur, while the number of the Report is given at the top of each page.

The index is in three divisions, covering "Names," "Places" and "Subjects," respectively. Each one of the several Reports is treated separately and headings are given which permit ready reference to the ground covered by the Report, so that a minimum of time is required to find data dealing with such subjects as "Sewage Pollution of Tidal Waters," "Contamination of Shell Fish," "Land Treatment of Sewage," "Sewage Tanks," "Sewage Filters," "Contact Beds," "Sewage Sludges," "Nuisances," "Standards for Sewage Effluents," "Disposal of Distillery Refuse," "Excessive Growth of Green Sea Weeds," "Disposal of Manufacturing Wastes" and the like.

The bulky volumes of The Reports of the Royal Commission are exceedingly difficult to properly use without assistance such as is offered by this valuable guide.

W. P. MASON

**Farben und Farbstoffe.** By A. ZART. Illustrated with 31 figures. B. G. TEUBNER, Leipzig, 1915. 100 pp. Price, 1.25 M.

This is a small volume forming part of a series of monographs in popular science, being a collection "aus Natur und Geisteswelt," a form of technical literature which is both common and popular in Germany. The present little handbook deals with the theory of color and the history of dyestuffs. It then briefly discusses the nature of inorganic pigments together with the general methods of their preparation and manufacture. Chapters on the natural dyestuffs and the coal-tar dyes are also given, together with considerable matter relative to the commercial preparation of synthetic dyes. The uses of the various dyes in dyeing and printing is also described, and the general methods of testing the nature and fastness of dyestuffs.

The book is remarkably up-to-date, and while the descriptions are necessarily brief and rather sketchy, yet the examples are well chosen and exhibit a good grasp of the subject. The matter is presented in a simple and clear manner in keeping with the popular scientific character of the book. The volume is especially apropos just now in view of the wide-spread and popular interest in dyestuffs, and is even well worthy of being read by any chemist who is at all interested in this subject and who has a fair reading knowledge of German.

J. MERRITT MATTHEWS

# NEW PUBLICATIONS

By IRENE DeMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

- CORRECTION: Painting by Immersion and by Compressed Air.** A. S. JENNINGS. The price of \$2.75 quoted in THIS JOURNAL, 7 (1915), page 1094, should read \$3.50.
- Alternating Currents, Laboratory Manual.** L. C. EDDY. 12mo. 21 pp. Price, \$0.50. D. Van Nostrand Co., New York.
- Analytical Chemistry. Vol. 2. Quantitative Analysis.** F. P. TREADWELL. 4th Ed. 8vo. Price, \$3.75. Chapman & Hall, London.
- Analytic Mechanics.** J. A. MILLER AND L. B. LILLY. 8vo. 297 pp. Price, \$2.00. D. C. Heath & Co., New York.
- Analytical Mechanics.** H. M. DOUDOURIAN. 2nd Ed. 8vo. 431 pp. Price, \$3.00. D. Van Nostrand Co., New York.
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- Cellulose: Die Hydrolyse der Zellulose und des Holzes.** ERIK HÄRGLUND. 8vo. 52 pp. Price, \$0.35. F. Enke, Stuttgart.
- Chemistry: Handwoerterbuch der Chemie.** 122 Lfg. Price, \$0.65. F. Vieweg & Sohn, Braunschweig.
- Colloid-Chemistry.** WOLFGANG OSTWALD. 8vo. Price, \$3.00. P. Blakiston's Son & Co., Philadelphia.
- Colloids: An Introduction to the Physics and Chemistry of Colloids.** EML. HATSCHKE. 2nd Ed. 8vo. 118 pp. Price, \$0.75. J. & A. Churchill, London.
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- General Laboratory Apparatus and Supplies.** Catalogue (1916). Lenz & Naumann, Inc., 17 Madison Ave., New York.
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- Inorganic Chemistry: Gmelin and Kraut's anorganische Chemie.** 190-194 Lfg. FRIEDHEIM AND PETERS. 7th Ed. Price, \$0.40. Karl Winter, Heidelberg.
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- Chrome-Iron Ore as Lining for Reverberatory Furnaces.** EDGAR HILL. *Engineering and Mining Journal*, Vol. 101 (1916), No. 6, pp. 267-268.
- Coal and Coke Efficiency in Blast Furnace Operation.** B. F. BURMAN. *Metallurgical and Chemical Engineering*, Vol. 14 (1916), No. 3, pp. 137-140.



WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON FEBRUARY 19TH.

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Acetate of Lime, gray.....	100 Lbs.	7.00	@	7.25
Alum, lump.....	100 Lbs.	4.25	@	4.75
Aluminum Sulfate, high grade.....	100 Lbs.	5.00	@	5.25
Ammonium Carbonate, domestic.....	Lb.	9	@	9 1/4
Ammonium Chloride, gray.....	Lb.	8 1/2	@	9
Ammonium Phosphate, commercial, 98-100%.....	Lb.	11	@	11 1/4
Aqua Ammonium, 16°, drums.....	Lb.	2 1/2	@	—
Arsenic, white.....	Lb.	5 1/4	@	5 1/2
Barium Chloride.....	Ton	110.00	@	120.00
Barium Nitrate.....	Lb.	15	@	16
Barytes, prime white, foreign.....	Ton	19.00	@	23.00
Bleaching Powder, 35 per cent.....	100 Lbs.	13.50	@	14.50
Blue Vitriol.....	Lb.	20 1/2	@	21
Borax, crystals, in bags.....	Lb.	7	@	7 1/4
Boric Acid, powdered crystals.....	Lb.	12 1/4	@	14
Brimstone, crude, domestic.....	Long Ton	22.00	@	22.50
Bromine, technical, bulk.....	Lb.	5.00	@	6.50
Calcium Chloride, lump.....	Ton	—	@	11.78
Calcium Chloride, granulated.....	Ton	—	@	14.78
Caustic Soda, 74 per cent.....	Lb.	6 1/4	@	6 1/2
Caustic Soda, 76 per cent.....	Lb.	6 1/4	@	6 1/2
Chalk, light precipitated.....	Lb.	4 1/4	@	5 1/3
China Clay, imported.....	Ton	11.00	@	16.00
Feldspar.....	Ton	8.00	@	12.00
Fuller's Earth, foreign, powdered.....	100 Lbs.	80	@	1.05
Glauber's Salt, in bbls.....	100 Lbs.	60	@	75
Green Vitriol, bulk.....	100 Lbs.	75	@	80
Hydrochloric Acid, commercial, 18°.....	100 Lbs.	2.50	@	3.00
Hydrochloric Acid, C. P., conc., 22°.....	100 Lbs.	3.00	@	3.50
Iodine, resublimed.....	Lb.	4.25	@	4.30
Lead Acetate, white crystals.....	Lb.	13 1/8	@	14
Lead Nitrate.....	Lb.	16 1/8	@	16 3/4
Litharge, American.....	Lb.	—	@	6 1/4
Lithium Carbonate.....	Lb.	90	@	1.00
Magnesium Chloride.....	Lb.	10	@	12
Magnesium Carbonate.....	Lb.	37.50	@	40.00
Magnesite, "Calcined".....	Ton	1.85	@	2.15
Mercuric Chloride, commercial.....	Lb.	7 1/2	@	8
Nitric Acid, 36°.....	Lb.	9	@	9 1/2
Nitric Acid 42°.....	Lb.	30	@	32
Phosphoric Acid, sp. gr. 1.750.....	Lb.	35	@	1.00
Phosphorus.....	Lb.	1.50	@	1.70
Plaster of Paris.....	Bbl.	65	@	—
Potassium Bichromate, casks.....	Lb.	5.50	@	—
Potassium Bromide.....	Lb.	1.00	@	1.15
Potassium Carbonate, calcined, 80 @ 85%.....	Lb.	65	@	—
Potassium Chlorate, crystals, spot.....	Lb.	30	@	35
Potassium Cyanide, bulk, 98-99 per cent.....	Lb.	55	@	60
Potassium Hydroxide.....	Lb.	3.70	@	3.75
Potassium Iodide, bulk.....	Lb.	—	@	—
Potassium Nitrate.....	Lb.	2.00	@	—
Potassium Permanganate, bulk.....	Lb.	325.00	@	—
Quicksilver, flask, 75 lbs.....	Lb.	7 1/4	@	—
Red Lead, American, dry.....	Lb.	55	@	65
Salt Cake, glass makers'.....	100 Lbs.	36	@	38
Silver Nitrate.....	Oz.	10.00	@	12.00
Soapstone in bags.....	Ton	—	@	—
Soda Ash, 48 per cent.....	100 Lbs.	10 3/4	@	11
Sodium Acetate.....	Lb.	1.60	@	1.70
Sodium Bicarbonate, domestic.....	100 Lbs.	3 1/2	@	3 3/4
Sodium Bicarbonate, English.....	Lb.	45	@	50
Sodium Bichromate.....	Lb.	3.75	@	4.00
Sodium Carbonate, dry.....	100 Lbs.	40	@	50
Sodium Chlorate.....	Lb.	15	@	—
Sodium Fluoride, commercial.....	Lb.	3.00	@	3.25
Sodium Hyposulfite.....	100 Lbs.	3.10	@	—
Sodium Nitrate, 95 per cent, spot.....	100 Lbs.	85	@	1.10
Sodium Silicate, liquid.....	100 Lbs.	2	@	2 1/2
Sodium Sulfide, 30%, crystals, in bbls.....	Lb.	7	@	8
Sodium Sulfite, crystals.....	Lb.	38	@	—
Strontium Nitrate.....	Lb.	2.30	@	2.70
Sulfur, flowers, sublimed.....	100 Lbs.	1.90	@	2.20
Sulfur, roll.....	100 Lbs.	2.00	@	2.50
Sulfuric Acid, chamber, 60°.....	100 Lbs.	2.50	@	3.00
Sulfuric Acid, conc., sp. gr. 1.842.....	100 Lbs.	2.50	@	3.00
Sulfuric Acid, oleum (fuming).....	100 Lbs.	9.00	@	13.00
Talc, American.....	Ton	75	@	80
Terra Alba, American, No. 1.....	100 Lbs.	14	@	—
Tin Bichloride, 50°.....	Lb.	47	@	49
Tin Oxide.....	Lb.	6 1/3	@	—
White Lead, American, dry.....	Lb.	24	@	25
Zinc Carbonate.....	Lb.	12	@	18
Zinc Chloride, commercial.....	Lb.	9	@	18
Zinc Oxide, American process.....	Lb.	7 1/4	@	7 1/2
Zinc Sulfate.....	Lb.	—	@	—

## ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.....	Lb.	1.15	@	1.20
Acetic Acid, 28 per cent, in bbls.....	Lb.	7 1/2	@	8
Acetic Acid, glacial, 99 1/2%, in carboys.....	Lb.	32	@	36

Acetone, drums.....	Lb.	35	@	40
Alcohol, denatured, 180 proof.....	Gal.	50	@	52
Alcohol, grain, 188 proof.....	Gal.	2.62	@	2.64
Alcohol, wood, 95 per cent, refined.....	Gal.	55	@	57
Amyl Acetate.....	Gal.	4.50	@	5.50
Aniline Oil.....	Lb.	90	@	1.00
Benzoic Acid, ex-toluol.....	Lb.	4.00	@	4.60
Benzol, 90 per cent.....	Gal.	80	@	90
Camphor, refined in bulk, bbls.....	Lb.	44	@	—
Carbolic Acid, U. S. P., crystals, drums.....	Lb.	1.25	@	1.30
Carbon Bisulfide.....	Lb.	6	@	15
Carbon Tetrachloride, drums, 100 gals.....	Lb.	16	@	17
Chloroform.....	Lb.	70	@	75
Citric Acid, domestic, crystals.....	Lb.	65	@	70
Cresol, U. S. P.....	Gal.	1.15	@	1.25
Dextrine, corn (carloads, bags).....	100 Lbs.	3.10	@	3.20
Dextrine, imported potato.....	Lb.	12	@	13
Ether, U. S. P., 1900.....	Lb.	18	@	20
Formaldehyde, 40 per cent.....	Lb.	9 1/2	@	10
Glycerine, dynamite, drums included.....	Lb.	45	@	—
Oxalic Acid, in casks.....	Lb.	58	@	60
Pyrogallie Acid, resublimed bulk.....	Lb.	1.25	@	1.45
Salicylic Acid.....	Lb.	4.00	@	4.15
Starch, cassava.....	Lb.	3 1/4	@	4 1/3
Starch, corn (carloads, bags).....	100 Lbs.	2.25	@	2.36
Starch, potato.....	Lb.	6	@	6 1/2
Starch, rice.....	Lb.	8	@	10
Starch, sago.....	Lb.	3 1/4	@	3 3/4
Starch, wheat.....	Lb.	5	@	6
Tannic Acid, commercial.....	Lb.	75	@	76
Tartaric Acid, crystals.....	Lb.	55	@	57

## OILS, WAXES, ETC.

Beeswax, pure, white.....	Lb.	47	@	55
Black Mineral Oil, 29 gravity.....	Gal.	13	@	14
Castor Oil, No. 3.....	Lb.	17 1/4	@	18 1/4
Ceresin, yellow.....	Lb.	10	@	14
Corn Oil, crude.....	100 Lbs.	9.25	@	—
Cottonseed Oil, crude, f. o. b. mill.....	Gal.	63	@	64
Cottonseed Oil, p. s. y.....	Lb.	9 3/4	@	10
Creosote, beechwood.....	Lb.	8.50	@	9.00
Cylinder Oil, light, filtered.....	Gal.	20	@	25
Fusel Oil, crude.....	Lb.	4.00	@	4.50
Japan Wax.....	Lb.	13	@	—
Lard Oil, prime winter.....	Gal.	92	@	96
Linseed Oil, raw (car lots).....	Gal.	72	@	—
Menhaden Oil, crude (southern).....	Gal.	—	@	—
Naptha, 68 @ 72°.....	Gal.	30	@	35
Neat's-foot Oil, 20°.....	Gal.	95	@	97
Paraffine, crude, 117 & 119 m. p.....	Lb.	3 1/2	@	4
Paraffine Oil, high viscosity.....	Gal.	24 1/2	@	25
Rosin, "F" Grade, 280 lbs.....	Bbl.	—	@	5.80
Rosin Oil, first run.....	Gal.	—	@	32
Shellac, T. N.....	Lb.	22	@	23
Spermaceti, cake.....	Lb.	25	@	26
Sperm Oil, bleached winter, 38°.....	Gal.	74	@	75
Spindle Oil, No. 200.....	Gal.	19 1/2	@	20
Stearic Acid, double-pressed.....	Lb.	14 1/4	@	15
Tallow, acidless.....	Gal.	78	@	80
Tar Oil, distilled.....	Gal.	30	@	31
Turpentine, spirits of.....	Gal.	55	@	56

## METALS

Aluminum, No. 1, ingots.....	Lb.	53	@	55
Antimony, ordinary.....	Lb.	—	@	44
Bismuth, New York.....	Lb.	—	@	—
Copper, electrolytic.....	Lb.	28 1/2	@	—
Copper, lake.....	Lb.	28 1/2	@	—
Lead, N. Y.....	100 Lbs.	6.30	@	—
Nickel, electrolytic.....	Lb.	50	@	—
Nickel, shot and ingots.....	Lb.	45	@	—
Platinum, refined.....	Oz.	87.50	@	90.00
Silver.....	Oz.	—	@	56 1/8
Tin.....	100 Lbs.	—	@	42.12 1/2
Zinc, N. Y.....	Lb.	—	@	21 1/2

## FERTILIZER MATERIALS

Ammonium Sulfate.....	100 Lbs.	4.25	@	—
Blood, dried.....	Unit	3.35	@	—
Bone, 4 1/2 and 50, ground, raw.....	Ton	37.50	@	—
Calcium Cyanamid.....	Unit of Ammonia	2.45	@	—
Calcium Nitrate, Norwegian.....	100 Lbs.	—	@	—
Caster Meal.....	Unit	—	@	—
Fish Scrap, domestic, dried, f. o. b. works.....	Unit	3.85	@	10
Phosphate, acid.....	Unit	80	@	85
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	2.75	@	3.00
Tennessee, 70-80 per cent.....	Ton	5.00	@	5.50
Potassium "muriate," basis 80 per cent.....	Ton	490.00	@	—
Pyrites, furnace size, imported.....	Unit	14 1/4	@	14 3/4
Tankage, high-grade; f. o. b. Chicago.....	Unit	3.15	@	10

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## EDITORIALS

### PREPAREDNESS

In all this ebullition of preparedness for defense, there is at least one prime component which it is the duty of every American chemist to understand. We should not have written this note had we not found by experience that the facts are not generally appreciated. We plan a greater navy and a larger army, but we apparently have no assurance that either could be of use in time of war. We are not only failing to keep our powder dry, but we are not even surely planning to have any powder.

It is not generally realized that no useful explosive for any military use whatever can be made without nitric acid. From black powder and smokeless, through fulminates, nitroglycerine, dynamite, gun-cotton, picric acid, to trinitrotoluol and the latest more complex benzol derivatives, not a pound can be made without nitrates. These are now obtained from Chili exclusively. In the event of any interference with that supply, we should have to revert to the pea shooter, the sling, or the air gun. Can we be sure that Chili will always be willing and able to supply us, and also shall we be able to transport it in face of foreign opposition of conceivable kinds? These are points which chemists in particular should consider.

We have but one other considerable source of fixed nitrogen, the ammonium sulfate from by-product coke-ovens, and this is limited by the coke requirements of the iron industry. Carry the recovery of this salt as far as possible, as should of course be done in the interests of conservation, and the supply would still be quite insufficient.

Without discussing in detail particular sources of power like the Niagara, Tennessee, and Columbia Rivers, the low-grade coals of the culm heaps and of certain mines which do not pay for transportation but can be utilized on the spot, and without referring to

special processes of nitrogen fixation like the arc or cyanamid, it can be stated with certainty that we have all the requisites for a nitrate industry. America has plenty of idle, available power, such as other countries have known enough to use for this and similar purposes, and we have processes capable of economically producing all our needed supply of nitrates, ammonia and nitric acid, while consuming nothing whatever but a little of our limitless air and a small part of the wasting energy of some of our moving waters.

Furthermore, the plant and apparatus for this work can, during times of peace, turn out this same fixed atmospheric nitrogen in the forms which are most demanded by fertilizer requirements. If a manufacturing organization owned the farms and the water rights, it could and would certainly produce nitrogen fertilizer at half the present cost and would produce explosives with but little added equipment in times of war. This would mean that fertilizers would be used where now, though badly needed, they are prohibitively expensive. Can we not, as a nation, accomplish the same end? In spite of all the valuable work of improving the yields of corn in such states as Kansas, by breeding to large grains and big ears, the yield per acre is continually and rapidly falling off. Wheat yields in the northwest have fallen from 40 to 13 bushels per acre as the natural fertilizer has become exhausted. As this decrease continues, a point will be reached where fertilizers at any cost will have to be used. This has been the experience of older countries.

The time for planning work which takes years to bear fruit is at least years before the fruit is expected. We need cheaper fertilizers now and we may need our own explosives at any time. If these words are true, pass them along. If they are not, correct them.

## ORIGINAL PAPERS

### THE REMOVAL OF THE NATURAL IMPURITIES OF COTTON CLOTH BY THE ACTION OF BACTERIA

By B. S. LEVINE

Received January 6, 1916

The ordinary process of bleaching cotton cloth consists of: (1) a treatment for the removal of certain of the natural impurities which may be present; and (2) a bleaching proper, which decolorizes any impurities left after the preliminary treatment. The natural impurities of the cotton fibers have been studied by several investigators with no apparent relation to the processes of purification of cotton cloth, and by the writer of this paper in connection with a study of the bleaching process. According to the results obtained, the impurities of cotton fibers can be classified for practical purposes as follows:

*water-soluble, alcohol-soluble, mineral, ether-soluble impurities and nitrogenous coloring matters.*

Not all of the above named impurities, as has been shown by Hebden,<sup>1</sup> are responsible for the yellowing of cloth during the steam test or during storage. According to his opinion, the presence of the alcohol-soluble and of the nitrogenous substances only is responsible for a bleach being imperfect. From a study of the ether-soluble, alcohol-soluble and nitrogenous constituents of the growing cotton fibers,<sup>2</sup> we were able to corroborate the conclusion of Hebden with regard to the significance of the nitrogenous constituents of the cotton fibers in bleaching, but our unpublished results of a study of cloth in different stages of the bleaching process and of the nature of

<sup>1</sup> Hebden, *This Journal*, **6** (1914), 714.

<sup>2</sup> Levine, *Sci. N. S.*, **XLI**, 1058 (1915), 543-545.

the alcohol-soluble and ether-soluble impurities of cotton showed that the first, contrary to the opinion of Hebden, have no connection with the yellowing of cloth, whereas the presence of the latter, to which Hebden had ascribed no significance, bears in the yellowing of bleached cloth a share fully equal to that of the nitrogenous substances.

In connection with the determination of a convenient index of purity of cotton cloth, the question has come up whether the present processes of bleaching do not effect any structural differences in the cellulose molecule, thus making it possible to suppose that the quality of a bleach might be due to structural rearrangements. Accordingly, samples of cotton cloth in different stages of bleaching processes obtained from several bleacheries were analyzed for the percentages of carbon, hydrogen, and of oxygen, and tested for their reactivity to certain chemical reagents. From the results obtained, the conclusion was drawn that no structural differences were brought about in the fiber molecule, and that a bleach may be considered to be "good," when all or most of the nitrogenous and ether-soluble substances have been removed from the fibers. Thus, it may be said that the impurities which the bleaching process is supposed to remove or decolorize are the non-cellulose constituents of the cotton fibers, and that they are apparently in no chemical union with the molecules of the fibers. As they are of an organic nature, it seems possible that they might be rendered soluble by the action of certain enzymes of animal or vegetable origin, and that the action of any of these biological agencies upon cotton cloth would result in an efficient and perhaps cheaper method of purification of fabrics.

For some time the writer has been engaged in a study of the principles underlying the action of different enzyme preparations, of moulds, and of bacteria upon the impurities of cotton. The present paper deals with the study of the bacterial treatment of cotton cloth for the purpose of removing its impurities preliminary to bleaching.

# PRELIMINARY INVESTIGATION

The analysis of cloth in different stages of the bleaching process and a knowledge of the nature of the non-cellulose constituents of the cotton fiber make it clear, as summarily indicated in the introduction, that if bacteria are to be used for the purification of the cloth preliminary to bleaching, only those which can bring about all or some of the following transformations can be employed:

I—Those which render soluble or otherwise removable the coagulated non-soluble nitrogen-containing constituents of the fibers.

II—Those which render soluble or otherwise removable the alkali-resistant waxes and the fixed fats of the fibers which are represented by the ether extracts.

III—Those which render easily removable the substances which are related to the pectoses.

Most of the soil bacteria and also some of the bacteria which cause certain plant diseases fulfil some

or all of the above conditions. The ammonifying and denitrifying bacteria of the soil, as is well known at present, decompose a large amount of organic matter in the form of fat, waxes, oils, pectins, gums, and celluloses in order that they may get the necessary energy for the metabolism of the living cell. The bacteria which cause the root-rots of certain plants produce strong pectin decomposing enzymes. The cellulose-destroying bacteria, as was pointed out by Herbert<sup>1</sup> in 1892, do not attack the cellulose molecule proper before the pectins, gums, tannins, and other non-cellulose substances have been utilized by them. Thus, the number of bacterial species possessing one or more of the properties required for our purpose is very large, and the question which arose in connection with our problem was not "Can the fibers be purified by bacteria," but, "Which species of bacteria shall we employ for the solution of our problem?"

To answer the above question a number of bacterial species were secured, some of which were soil bacteria, some intestinal bacteria, and some plant pathogens. These were obtained from the collection at the Museum of Natural History in New York, from the Vermont Agricultural Experiment Station, and some were isolated by us. In all cases the identity of the species was established by determining their morphological and physiological characteristics. The selection of those best suited to our purpose was made in the following way: Flasks of standard broth and of synthetic medium (to be described later) were inoculated with the different strains and incubated at 37.5° C. from 10 to 14 days. Cotton yarn, which was thoroughly "wetted out" and sterilized in the autoclave, was introduced into the flasks and they were again incubated for periods not exceeding 10 days. The yarn was then taken out, properly labeled, washed in hot water, and boiled for 5 min. in a 1 per cent solution of caustic soda. It was then subjected to the bleach and sour as in the ordinary bleaching process, washed, dried, and steam-tested. The cultures which gave the best results were selected for further experiment. They were the following:

<i>Bacillus amyloctenans</i> .....	n. s.
<i>Bacterium lenti</i> .....	n. s.
<i>Bacillus bibulus</i> .....	n. s.
<i>Bacillus carotovorus</i> .....	n. s.
<i>Bacillus subtilis</i> (Ehrenberg).....	Cohn

All these bacterial species produce enzymes by means of which they perform the transformation of such substances as sugars, starches, gums, pectins, celluloses, and various proteins into substances, the molecules of which are much smaller than and possess chemical properties differing from those of the original substances, so that they can be easily distinguished from them. Thus the starches are broken down to dextrins and to dextrose, the pectins are changed to pectic acid, the celluloses to carbon dioxide, methane, various organic acids, and water. The proteins are broken down to carbon dioxide, water, ammonia, nitric and nitrous oxides, free nitrogen, and perhaps some other compounds. These bacterial enzymes

<sup>1</sup>Ann. Agron., 18 (1892), 536-550.



diffuse in the surrounding media to an extent which depends upon the amount and diffusibility of the enzyme produced. Hence, from the amount of substrate transformed, the enzymic strength of the bacteria may be determined by plating the bacteria out on agar containing a known per cent of the substrate and incubating for a few days. The enzyme excreted by the organism usually diffuses equally in all directions, and the circular zones around the colonies may be made visible by treating the plates with suitable reagents. The diameter of the circle can be measured and compared with that of zones produced by other organisms on the same substrate and their relative efficiency may thus be ascertained. The zone formed by a bacterial colony has been called the "enzymic zone" and its diameter expressed in millimeters or fractions thereof.

To further test the suitability of the strains previously selected, the bacteria were grown on cellulose-agar plates, starch-agar plates, pectin-agar plates, and their enzymic zones measured. The starch- and the cellulose-agar were prepared as follows:

CELLULOSE-AGAR	STARCH-AGAR	PECTIN-AGAR	AMOUNTS
Cellulose Solution	Starch Solution	Pectin Solution	500 cc.
Nutrient Solution	Nutrient Solution	Nutrient Solution	500 cc.
Agar	Agar	Agar	10 g.

The cellulose and the starch solutions were made up according to the directions given in *Bulletin 266*, United States Department of Agriculture, Bureau of Plant Industry, page 28. The pectin solution was

	ENZYMIC ZONES		
	STARCH	CELLULOSE	PECTIN
<i>B. hibulus</i> .....	1.0 to 2.0 mm.	0.1 to 0.3 mm.	1.0 to 1.5 mm.
<i>B. fimi</i> .....	2.0 to 3.0 mm.	0.5 to 1.0 mm.	0.5 to 1.0 mm.
<i>B. amylolyticus</i> .....	0.5 to 1.0 mm.	0.5 to 1.0 mm.	?
<i>B. carotovorus</i> .....	1.5 to 2.0 mm.	?	1.5 to 2.5 mm.
<i>B. subtilis</i> .....	?	0.2 to 0.5 mm.	0.7 to 2.0 mm.

It may be seen from an examination of this table that the transforming strength of the enzymes produced by the bacterial strains selected was great in all cases, and that their suitability to our work, as determined by the previously described flask-incubation method, was confirmed.

#### ACTION OF BACTERIA UPON THE IMPURITIES OF COTTON CLOTH

The bacterial strains selected as previously described were employed further in the study of the action of their enzymes upon the impurities of cotton cloth. Five hundred cc. of the nutrient solution described above and 50 g. of coarse cotton cloth containing about 5 per cent by weight of starch as a "sizing" material were put in each of 15 flasks and sterilized in the autoclave for 30 min. Sets of 3 flasks were then inoculated with the liquid cultures of the bacteria employed and incubated at 37.5° C. Control flasks with the nutrient solution and cloth were sterilized as described above and incubated without having been inoculated. One sample from each of the cultures was then taken out 1 mo., 2 mo., and 3 mo. after inoculation. The samples were thoroughly washed in boiling water to remove all the solu-

TABLE I—TESTS OF CLOTH SAMPLES AFTER 1 MONTH'S INCUBATION

No.	CULTURE	Starch Test	Transformation to a Dextrin	Softening of Cloth	Condition of "Motes"
A <sub>1</sub> .....	<i>B. amylolyticus</i>	Violet-blue	Probable	Slight	Merely swollen
A <sub>2</sub> .....	<i>B. hibulus</i>	Violet	Probable	Less than A <sub>1</sub>	Swollen and slightly discolored
A <sub>3</sub> .....	<i>B. fimi</i>	Greenish	Decided	Considerable	Swollen and slightly discolored
A <sub>4</sub> .....	<i>B. carotovorus</i>	Greenish	Decided	Considerable	Swollen and slightly discolored
A <sub>5</sub> .....	<i>B. subtilis</i>	Greenish violet	Less than above	Moderate	Swollen and discolored

TABLE II—TESTS OF CLOTH SAMPLES AFTER 2 MONTHS' INCUBATION

No.	CULTURE	Starch Test	Change beyond 1 Mo. Condition	Softening of Cloth	Condition of "Motes"
B <sub>1</sub> .....	<i>B. amylolyticus</i>	Violet	Not marked	More than A <sub>1</sub>	Same as A <sub>1</sub>
B <sub>2</sub> .....	<i>B. hibulus</i>	Greenish	Marked	Much more than A <sub>2</sub>	Almost completely gone
B <sub>3</sub> .....	<i>B. fimi</i>	Light green	Decided	Much	Barely colored and partly gone
B <sub>4</sub> .....	<i>B. carotovorus</i>	Light green	Decided	Moderate	Swollen and slightly discolored
B <sub>5</sub> .....	<i>B. subtilis</i>	Greenish violet	Not marked	Slight	Swollen and slightly discolored

TABLE III—TESTS OF CLOTH SAMPLES AFTER 3 MONTHS' INCUBATION

No.	CULTURE	Starch Test	Starch Transformation Indicated	Softening of Cloth	Strength of Cloth	Condition of "Motes"	BLEACHED SAMPLES (a)	MOTES
C <sub>1</sub>	<i>B. amylolyticus</i>	Faint violet	Partial removal of amyloextrins	Considerable	Unimpaired	Strongly discolored	White	None
C <sub>2</sub>	<i>B. hibulus</i>	Very faint green	Change or solution of dextrins	Decided (b)	Weakened (c)	Mostly gone	Very white	None
C <sub>3</sub>	<i>B. fimi</i>	Negative	Changed to sugars or achrodextrins	Decided (d)	Impaired (c)	Mostly gone	Whitest of all	None
C <sub>4</sub>	<i>B. carotovorus</i>	Very light green	Removal of dextrins	Considerable	Unimpaired	Mostly gone	Very white	None
C <sub>5</sub>	<i>B. subtilis</i>	Violet (greenish)	Further change in amyloextrins	Some	Unimpaired	Swollen and discolored	White	None

(a) See text for method of bleaching.

(b) Pinkish tint. (c) Signs of disintegration where the cloth was not wholly submerged and came in contact with the air.

(d) Pink tint lighter than C<sub>5</sub>.

prepared from the water-soluble substances of cotton in the following way: Unspun non-absorbent cotton was percolated with water for 24 hrs., the cotton pressed out and the solution filtered to clearness; it was then evaporated to dryness on a steam bath, and 10 g. of the dried extract were dissolved in 500 cc. of water. The nutrient solution consisted of 1 g. each of dibasic potassium phosphate and magnesium sulfate, 2 g. each of sodium chloride, ammonium sulfate and calcium hydrate, and 1000 cc. of water.

The bacteria were plated out on each of the media described and incubated at 37.5° C. in a chamber saturated with moisture so as to prevent drying of the plates. After 10 to 14 days' incubation, the enzymic zones were measured. The results were as follows:

ble products of the bacterial metabolism and the adhering chemical reagents of the medium, and the samples taken from the flasks incubated for 1 and 2 mo. were tested for starch; the samples taken from the flasks incubated for 3 mo. were tested for starch, nitrogen, and ether- and alcohol-soluble substances. The strength of the cloth, its softness, and the disappearance of the "motes" were also noted. The results appear in Tables I, II and III.

Samples from all the 3-mo. incubations were bleached for 4½ hrs. in a solution of freshly prepared calcium hypochlorite of 2° Tw. They were then thoroughly washed in cold water and put into a solution of sodium bisulfite (4° Tw.) for another 4½-hr. period. After this, the cloth was thoroughly washed, dried, ironed,

and compared as to whiteness, with the results noted in the last two columns of Table III.

The bleached samples were then subjected to the steam test under a pressure of 10 lbs. per sq. in. for 45 mins. None of the samples were yellowed by such treatment, and we assumed, therefore, that all the substances which cause yellowing of the bleached cloth during steaming or during storage were removed.

In order to determine whether the removed substances were the same as determined by the analysis of cloth in the different stages of the bleaching process, the bleached samples from the bacterial treatments were analyzed for the determination of the percentages of the ether-soluble, alcohol-soluble, and nitrogen-containing substances which were left in or on the fibers after the "chemick" and the "sour." The results are given in Table IV.

The cloth incubated in the control flasks after the 3-mo. incubation showed no starch transformation, very slight reduction in the percentage of the ether-soluble and nitrogen-containing substances, and no change in the percentage of the alcohol-soluble substances.

In all the bacterial treatments, the nitrogen-containing substances were removed from the cloth completely, the ether-soluble substances were removed

The transformation of nitrogenous substances which is usual in the case of decomposition of organic matter in the soil, suggests a way in which the answer might be given. To determine whether the case in our experiment was similar to that of the above mentioned condition in the soil, we tested several samples of media, taken out at various times of incubation, for the presence of ammonia. The quantity of cloth and the small percentage of the nitrogenous substances in it rendered our attempts fruitless. We were about to give up further investigation along that line, when we found in some of the flasks a very slight, white precipitate. On testing, it proved to be calcium carbonate, and it at once occurred to us that in the presence of calcium hydroxide the decomposition of the nitrogen-containing substances may be accompanied by the formation of calcium carbonate, free nitrogen or ammonia, and water.

The nitrogenous coloring substances of cotton in the American and the Egyptian varieties were studied by Dr. Schunk,<sup>1</sup> and according to his analysis the formula for the substances found in the American variety would be  $C_{10}H_{12}O_4N$ , and that of the substances found in the Egyptian variety  $C_{26}H_{30}O_9N_3$ . In the presence of calcium hydroxide the reactions brought about during the decomposition of the first

TABLE IV—TESTS SHOWING REMOVAL OF IMPURITIES FROM CLOTH SAMPLES BY INCUBATION FOR 3 MONTHS AND SUBSEQUENT BLEACHING

CULTURE	NITROGEN (OR PROTEIN)					ETHER EXTRACT					ALCOHOL EXTRACT							
	GRAMS		PER CENT REMOVED BY INCUBATION	PER CENT REMOVED BY "Sour"		Total	GRAMS		PER CENT REMOVED BY INCUBATION	PER CENT REMOVED BY "Sour"		Total	GRAMS		PER CENT REMOVED BY INCUBATION	PER CENT REMOVED BY "Sour"		Total
	ORIG-INAL	Incubation		Incubation	"Sour"		ORIG-INAL	Incubation		Incubation	"Sour"		ORIG-INAL	Incubation		Incubation	"Sour"	
<i>E. amylophilicus</i> .....	0.156	0.0032	None	75.8	24.2	100.0	0.392	0.059	0.015	78.8	9.3	88.1	0.5107	0.5107	0.4569	0.0	3.2	3.2
<i>E. bibulus</i> .....	0.156	Trace	None	100.0	..	100.0	0.392	0.0716	0.0446	78.6	9.3	87.9	0.5107	0.5107	0.472	0.0	3.0	3.0
<i>E. fimi</i> .....	0.156	0.038	None	97.9	2.1	100.0	0.392	0.117	0.041	85.0	11.2	95.2	0.5107	0.5107	0.4098	0.0	2.5	2.5
<i>B. carotovorus</i> .....	0.156	0.025	None	84.4	15.6	100.0	0.392	0.075	0.039	80.9	9.1	90.0	0.5107	0.323	0.306	35.9	5.2	41.1
<i>B. subtilis</i> .....	0.156	0.012	None	92.9	7.1	100.0	0.392	0.125	0.079	68.1	11.2	79.3	0.5107	0.465	0.457	8.9	2.5	11.4

more efficiently than they were after the chemical process of bleaching, the alcohol-soluble substances remained unchanged, except in the case of the cloth subjected to the action of cultures of *B. carotovorus* and of *B. subtilis*.

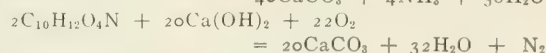
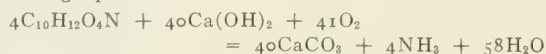
The weakening of the cloth in the samples subjected to the action of cultures of *B. bibulus* and of *B. fimi* may have been due to the action of the oxygen of the air on those parts of the cloth saturated with the calcium hydroxide of the media which were not completely submerged. It is possible also that during the long period of incubation to which the cloth was subjected, the bacteria may have acted upon it to such an extent that a slight general disintegration was caused.

But as the reactivity of the cloth remained apparently unchanged, we feel safe in concluding that a more thorough investigation of the action of some of the bacteria upon the impurities of cotton cloth would determine the conditions under which the bacteria would remove the nitrogenous and ether-soluble substances of the fibers without impairing the body of the fabric.

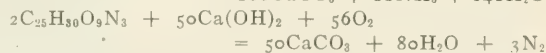
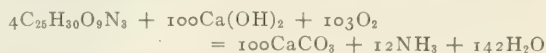
#### THEORETICAL CONSIDERATIONS

The question may be asked in connection with the disappearance of the insoluble nitrogen-containing substances of the cotton fibers: "How have they been removed to such an extent by the action of bacteria?"

by means of oxidation may be represented by the following equations:



and for the oxidation of the latter in the presence of calcium hydroxide the reactions may be represented as follows:



Free ammonia and free nitrogen are thus formed which could not be detected by us on account of their small amounts. As there was no precipitate found in some of the flasks, it may be supposed that mere liquefaction of the protein substances took place which rendered possible their complete removal after the strong oxidation during the "chemick" which had most probably converted the peptones and amino acids formed into nitrates and nitrates.

The reactions just given are of the nature of oxidations and result in liberation of energy. It therefore seems probable that the nitrogenous substances of the cotton fibers form some sources of energy to the

<sup>1</sup> Memoirs, Manchester Literary and Philosophical Society, Vol. IV, 3rd Series



bacteria. The pectins, gums, and waxes, no doubt, are used up by them first, the nitrogen-containing substances next, and, as the medium used in our experiments was devoid of carbohydrates, the cellulose finally was drawn upon by the bacteria as a source of energy. This probably would not be the case in the practical application of bacteria to the treatment of cotton cloth before bleaching, as the period of incubation would have to be reduced to a minimum. The weakening of the cloth would be eliminated entirely, and a cheaper, safer, and more convenient process for the purification of cotton cloth preliminary to its bleaching would thus be obtained.

Since the conclusion of the above described preliminary experimental investigations, studies have been carried on with a view to applying bacteria to practical purification of various cellulose fibers. By using different combinations of bacterial species, different media, different reactions of the media to start with, and different temperatures during the period of incubation, the latter was reduced to 72, 48, 36, and in some cases even to 24 hrs., all depending upon the nature of the fibers used.

A number of tests on a large scale were also performed for the purification of paper-making stock in connection with one of the eastern paper making factories, and for the purification of cotton yarn and cotton cloth in connection with some of the Rhode Island bleacheries. In all cases the results obtained were very encouraging.

#### SUMMARY

I—Of all the natural impurities of cotton cloth only the nitrogen-containing and the ether-soluble substances, when insufficiently removed from the cloth previously to the "chemick," cause yellowing of bleached cloth in the steam test or during storage.

II—The nitrogenous substances of the fibers were broken down by bacteria so that they were completely removed from the cloth. This transformation in the presence of the calcium hydroxide has probably resulted in some cases in the formation of either free ammonia or nitrogen, calcium carbonate, and water, and in some in the reduction of the nitrogenous substances to peptones and amino acids which are easily oxidized to nitrates and nitrites.

III—The ether-soluble substances of the cloth were removed in our experiments by bacterial treatment more efficiently than is the case in the ordinary bleaching process.

IV—The alcohol-soluble substances were very little attacked by the bacteria, probably because of the formation of a calcium salt in the presence of the calcium hydroxide of the media.

V—None of the bacteria experimented with have transformed the starch of the cloth any further than to dextrins.

VI Bacteria may be profitably employed as a substitute for the present method of purifying cloth preliminary to its bleaching.

The present paper records a part of the work done by the author along similar lines for Mr. J. C. Hebden of Providence, R. I., in connection with and under the auspices of the Biological Laboratory of Brown University. The author wishes to express his gratitude to the instructing staff of the Brown University Biological Laboratory and to Mr. Hebden for their general and generous assistance in the work and for permission to publish the results.

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#### PHYSICAL PROPERTIES OF DENTAL CEMENTS

By PAUL PORTSCHKE

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The principal types of dental cement which occupy a useful place in dentistry at the present time are known technically as the silicate, zinc oxyphosphate and copper cements. All of these products reach the dentist in the form of a powder and liquid to be combined, as occasion requires, by a special process of mixing. The constituents and applications of the three types and the various properties upon which their uses in applied dentistry depend, are given in Table I.

In order to determine the "fitness" of a dental



FIG. 1.—GENERAL ARRANGEMENT OF APPARATUS

From left to right, apparatus includes: Pail for overflow from mixing slab, clock, stop watch, thermos bottles (arranged for conducting feed water to mixing slab), Gilmore needles (for ascertaining the setting time), container for used spatulas, pipette, electrically controlled incubator, balance, hygrometer and setting device.

cement, due consideration must be given to its various properties, individually and collectively. A silicate cement which does not possess the required color and translucency would be lacking in the essential requirements of this type of cement, and no matter how perfect in other respects, it would fail to fulfil its main purpose—its ability to match the tooth structure in appearance. Likewise, germicidal efficiency is essential in a copper cement. It is obvious that

an investigation of the various dental cements, as regards the properties enumerated in Table I, is of great importance to the dental profession.

The chemical composition of a dental cement re-

cement has a definite and uniform effect does not warrant generalizations with respect to that same constituent when present in another cement. In other words, the effect of various constituents of

TABLE I—CONSTITUENTS, APPLICATIONS AND IMPORTANT PROPERTIES OF DENTAL CEMENTS									
TYPE OF CEMENT	POWDER CONSTITUENTS			LIQUID CONSTITUENTS			USE IN APPLIED DENTISTRY		
	PRINCIPAL	Modifiers and those not generally used		PRINCIPAL	Modifiers and those not generally used				
SILICATE	SiO <sub>2</sub> Al <sub>2</sub> O <sub>3</sub> CaO	ZnO BeO MgO	Na <sub>2</sub> O K <sub>2</sub> O	H <sub>2</sub> O H <sub>3</sub> PO <sub>4</sub> Al <sub>2</sub> (OH) <sub>3</sub>	ZnO		Fillings in anterior and posterior teeth simulates natural dentific enamel	Only type of dental cement which	
ZINC OXY-PHOSPHATE	ZnO	MgO Bi <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub> SiO <sub>2</sub>	H <sub>2</sub> O H <sub>3</sub> PO <sub>4</sub> Al <sub>2</sub> (OH) <sub>3</sub>	ZnO				
COPPER	ZnO CuO Cu <sub>2</sub> O Cu <sub>2</sub> I <sub>2</sub>	CO <sub>2</sub> O <sub>3</sub> Fe <sub>2</sub> O <sub>3</sub> MgO	Bi <sub>2</sub> O <sub>3</sub> CuSiO <sub>3</sub> CuHPO <sub>4</sub>	H <sub>2</sub> O H <sub>3</sub> PO <sub>4</sub> Al <sub>2</sub> (OH) <sub>3</sub>	ZnO Fe <sub>2</sub> (PO <sub>4</sub> ) <sub>2</sub> Ni <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> CuHPO <sub>4</sub>		Posterior fillings.	Treatment of deep-seated caries in children's teeth. Generally for posterior fillings where thorough cavity preparation is impracticable. Cementation of caps, crowns and bridges. Indicated wherever increased germicidal action is required and possibility of discoloration is unimportant	
PHYSICAL PROPERTIES									
PERMANENT				TEMPORARY		PHYSIOLOGICAL PROPERTIES			
Thermal conductivity	Tensile strength			Hydraulicity	Hardness	Time of setting	Germicidal efficiency		
Constancy of volume	Translucency			Porosity	Density	Heat generation	Toxic action on pulp		
Crushing strength	Permeability			Adhesion	Color	Plasticity	Discoloration		

veals but meager information with respect to its physical and other properties. Nevertheless, the dental literature is replete with articles in which opinions are freely expressed with reference to the ultimate effects of a given constituent on all classes of dental cements. Systematic investigation of every

dental cements cannot be predicted and must be individually determined, since these effects depend largely upon the physical condition and the peculiar association of all of the constituents.

All tests of dental cements must be conducted in accordance with a fixed and uniform procedure, and

TABLE II—CRUSHING STRENGTH OF DENTAL CEMENTS														
Liquid used with silicates, 0.20 cc.; liquid used with zinc + copper cements, 0.25 cc.														
No.	NAME OF PRODUCT	Room Temp. °F.	Relative Humidity Per cent (a)	Grams Powder Required	Setting Time Min. 20° C.	CRUSHING STRENGTH (Lbs. per 5 mm. cylinder)								
						CHL.				SALIVA				
						15 Min.	1 Day	7 Days	28 Days	1 Day	7 Days	28 Days		
SILICATES—SHOWING NO RETROGRESSION IN STRENGTH IN SALIVA														
1	De Trey's Synthetic Porcelain	72.2	45	0.800	7 1/2	628	1235	1385	1445	1230	1295	1448		
2	New Asher's Artificial Enamel	81.0	65	0.550	6 3/4	548	915	970	888	1210	1243	1350		
3	New Harvard'd Translucent Enamel	76.3	70	0.500	10	505	788	975	993	705	745	990		
4	Dr. Abraham's Translucine	85.1	55	0.750	12 1/4	330	733	918	1073	788	835	838		
5	Dental Porcelain Cement	78.7	80	0.625	5 1/4	380	760	955	878	225	240	270		
SILICATES—SHOWING RETROGRESSION IN STRENGTH IN SALIVA														
6	Ames' Berylite (No. 7 Slow-Setting Liquid)	78.1	85	0.700	10 (b)	563	1120	1338	1388	1073	1243	1200		
7	Schoenbeck's Silicate Cement	81.4	60	0.600	6 1/4	353	932	1130	1120	743	890	830		
ZINC OXYPHOSPHATES—SHOWING NO RETROGRESSION IN STRENGTH IN SALIVA														
8	Petrol Improved	66.1	15	0.900	22	768	980	1230	1185	833	908	968		
9	Harvard Cement	72.3	25	0.800	23	660	1063	1053	1233	853	945	955		
10	Caulk's New Diamond Cement	75.5	75	0.600	24	450	675	873	1023	730	778	943		
1	Caulk's Crown & Bridge & Gold Inlay Cement	77.0	50	1.150	22	440	703	798	883	658	780	810		
2	Vyvek	73.6	45	0.800	16	440	623	663	819	608	653	772		
3	D. C. C. Hydraulic Inlay Crown & Bridge Cement	76.8	65	0.800	10	328	615	688	697	583	633	685		
4	Ames' Special Crown & Bridge Cements (Liquid "C")	70.4	20	0.800	11	493	600	605	630	565	555	652		
5	J. B. Moyer's Imp. Crown & Bridge Cement	75.0	35	0.800	23	343	393	425	757	382	368	427		
ZINC OXYPHOSPHATES—SHOWING RETROGRESSION IN STRENGTH IN SALIVA														
6	Lithos Oxyposphate of Zinc Cement	81.7	65	0.750	16	383	700	848	898	700	988	895		
7	A-Jax Crown & Bridge Cement	58.0	20	0.800	10	498	945	998	1123	795	895	867		
8	Dunn's Cement	57.7	20	0.800	17	510	840	860	1010	748	683	674		
9	Fellowship Cement	76.5	80	0.900	18	433	510	773	630	680	720	660		
10	Fleck's Cement for Crown & Bridge & Inlay Work	74.5	75	0.800	9	378	655	778	757	723	765	648		
11	Akme Special Crown & Bridge Cement	82.4	70	0.650	9	223	420	660	663	545	583	560		
12	Alston Phosphate Cement	83.6	50	0.800	10	280	385	643	658	353	540	440		
13	Goldsmith's C. & B. & Inlay Cement	74.4	35	0.800	15	298	468	665	702	375	378	340		
14	Miller's C. & B. & Inlay Cement	76.2	65	0.800	78	88	190	165	218	190	255	218		
COPPER CEMENTS—SHOWING NO RETROGRESSION IN STRENGTH IN SALIVA														
15	Petrol Improved with Copr-Zinc	82.0	60	0.900	21	635	920	1190	1183	955	833	955		
16	Caulk's Black Copper Cement	81.5	60	1.000	24	430	693	928	1030	685	920	940		
17	Copr-Zinc with Caulk's C. & B. & Gold Inlay Cement	75.5	35	1.150	15	563	785	825	963	870	799	930		
18	Caulk's Red Copper Cement	80.3	50	1.000	11	473	808	885	1000	788	800	918		
19	Caulk's New Diamond Cement with Copr-Zinc	78.2	65	0.600	24	448	735	970	1035	683	750	840		
20	Caulk's C. & B. Gold & Inlay Cement with Copr-Zinc	73.8	45	1.150	18	507	660	698	845	595	755	833		
21	Fleck's Red Copper Cement	81.2	65	0.900	17	418	653	763	950	640	773	804		
22	Fellowship Oxyposphate of Copper Cement, Black	83.4	70	0.600	20	213	540	658	775	530	570	705		
23	D. C. C. Zinc Copper Cement, Black	78.5	65	0.700	16	255	480	695	780	430	540	660		
24	Fellowship Copper Cement, White	84.5	55	0.750	24 1/2	105	100	95	145	180	263	350		
COPPER CEMENTS—SHOWING RETROGRESSION IN STRENGTH IN SALIVA														
25	Smith's Copper Cement	65.5	25	0.900	22	628	970	923	1027	970	903	797		
26	Ames' New Process Oxyposphate of Copper Cement	82.0	65	1.400	17	465	983	930	1125	935	1000	788		
27	Amalgam Cement (c)	74.3	70	0.900	8	405	655	755	768	718	803	730		
28	J. B. Moyer's White Copper Cement	86.3	55	0.800	19	275	363	468	553	398	503	430		
29	Decido Copper Cement, Black	79.6	70	1.000	25	230	458	468	538	280	270	000(d)		

(a) Obtained from wet and dry bulb hygrometer readings, in still air, using the Bureau of Standards Psychrometer charts (B of S, *Cro.* 55, 117).

(b) Average of eight determinations. Setting not constant.

(c) This product is not a true copper cement, but is included among the copper cements because the liquid contained copper. It does not contain the metals present in dental amalgams and the name is therefore an illusion.

(d) Disintegrated.

property of merely one dental cement, in order to determine the precise effect of various additions to the basic constituents, is an immense undertaking. The mere fact that a certain constituent in one dental

this must be in harmony with mouth conditions. The object of laboratory tests is to secure trustworthy evidence regarding the behavior of these materials in the mouth, and it is precisely this requirement



which complicates the work and makes it exceedingly difficult to devise suitable methods of testing. The object of this paper is to present a method for determining the crushing strength of dental cements; a study of various factors related thereto; the results obtained on forty commercial dental cements, repre-

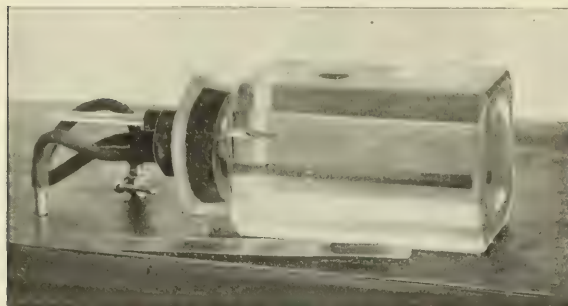


FIG. 2—CONSTANT TEMPERATURE MIXING SLAB WITH THERMOMETER AND CONNECTIONS FOR WATER FROM THERMOS BOTTLES

senting the silicate, zinc oxyphosphate, and copper types; and finally, the utility of the apparatus, described in this paper, for the study of the various properties of dental cements, is discussed.

#### METHOD FOR DETERMINING CRUSHING STRENGTH OF DENTAL CEMENTS

##### APPARATUS AND ACCESSORIES REQUIRED (SEE FIGS. 1-8)

- |   |  |
|---|--|
| I—POWDER AND LIQUID                                 | IV—STORAGE OF CYLINDERS                      |
| 1—Pipette graduated to 0.01 cc.                     | 14—Saliva                                    |
| 2—Balance sensitive to 0.5 mg.                      | 15—Oil                                       |
| 3—Camel's hair brush                                | 16—Vials                                     |
| II—MIXING CEMENT                                    | 17—Glass beads                               |
| 4—Constant temp. mixing slab                        | 18—Chloroform                                |
| 5—Agate spatula                                     | 19—Incubator for storing vials at 37° C.     |
| 6—Alcohol   | V—CRUSHING CYLINDERS                         |
| 7—Stop-watch  | 20—Forceps for removing cylinders from vials |
| 8—Hygrometer  | 21—Machine for crushing cylinders            |
| III—MOLDING CYLINDERS                               |  |
| 9—Molds   |  |
| 10—Clamps   |  |
| 11—Incubator for heating molds and clamps to 37° C. |  |
| 12—Setting device                                   |  |
| 13—Clock  |  |

##### NOTES ON APPARATUS

MOLDS—A great deal of experimental work was required to



FIG. 3—MOLDS—DISCARDED FORMS

develop a suitable form of mold for making perfect cylinders. Fig. 3 shows different types of gang-molds which were found to be unsatisfactory. The mold was placed on a glass plate, the openings filled to slight excess with the cement, and another glass plate pressed onto the mold and held in place by a 2-kg.

weight. The main difficulty encountered was that a film of cement (the excess) attached itself to the cylinder and this threw the opposite faces out of parallel. This was especially the case with the first molds, the two shown to the left of Fig. 3. An attempt to correct this defect was made by cutting a ridge around the openings (to receive the excess of cement) as shown in the third mold from the left. This also failed to accomplish the purpose. The next change in the molds is shown in the mold at the right in Fig. 3. In this case

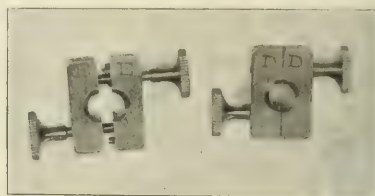


FIG. 4—MOLDS—ADOPTED FORM

the openings were brought to a knife edge even with the flat faces of the mold. This gave fairly perfect cylinders. It was soon found, however, that uniform results could not be obtained by using a gang-mold of this type, and also, the conditions under which the cement was allowed to set did not conform to customary dental practice.

The form of mold finally adopted (Fig. 4) makes an individual cylinder, 5 mm. high and 5 mm. in diameter. The mold is gold plated so as to avoid corrosion by the cement liquid. The opening is filled to slight excess and immediately secured in the clamps shown in Fig. 5. The faces of the clamp, which come in contact with the cement, are also gold plated.

SETTING DEVICE—A good deal of difficulty was encountered in securing some means by which the temperature of the cylinder could be kept at 37° C. during its initial setting. The setting device finally adopted (Fig. 6) consists of a water-jacketed vessel containing a neutral, colorless, hydrocarbon oil, kept at a temperature of 37° C. by electrically heating the surrounding water. The clamps are secured in the wooden support shown above the jacketed vessel. A cord, with a 2-kg. weight attached, passes through the wooden support just over the groove which fits the handle of the clamp and then passes over a pulley at the back of the support. The lower portion of the clamp



FIG. 5—CLAMPS FOR MOLDS

and the entire mold are submerged in the oil when fixed in place.

SALIVA is collected in the manner described by the author in a previous publication.<sup>1</sup> About 1 cc. of

<sup>1</sup> THIS JOURNAL, 7 (1915), 198.

chloroform is added to every 100 cc. of saliva as a preservative. The mixture is thoroughly shaken before transferring to the corked vials used for storing

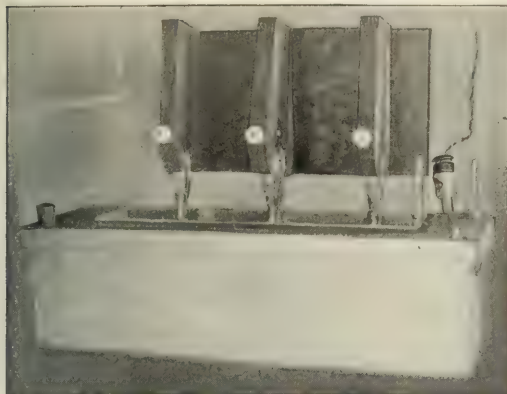


FIG. 6—SETTING DEVICE

clamps (also at  $37^{\circ}$  C.). The clamp and mold are then transferred to the setting device, the time recorded, and allowed to remain exactly 15 min. in the oil at  $37^{\circ}$  C. Readings of the hygrometer are recorded at the same time. The slab is cleaned and prepared for the next mix. Three mixes can be made in about the time the first will be ready for removal from the setting device. After 15 mins.' setting the clamp is removed and the binding screws of the mold released, to remove the cylinder, as shown in Fig. 4 (EE). If the cylinder is to be stored under saliva, it is immediately washed<sup>1</sup> in pure petroleum ether and then dropped into a vial containing saliva (see above), previously warmed to  $37^{\circ}$  C. If it is to be stored in oil, it is placed, without washing, in a vial containing oil, also warmed to  $37^{\circ}$  C. The cylinders are then stored for the required time in the large incubator (Fig. 7) and the strength determined by crushing in the machine (Fig. 8). Three cylinders are prepared for each test and the average of at least two agreeing results accepted as the crushing strength. Tests are made for periods of 15 min., 1, 7, and 28 days in oil, and for 1, 7, and 28 days in saliva,

the cylinders. Approximately 5 cc. of saliva are placed in each vial, which is also provided with a layer of glass beads, about 1 cm. deep, so as to keep the cylinder supported from the bottom of the vial and thus avoid accumulations of sediment on the surface of the cylinder.

#### TECHNIQUE

The mixing slab is adjusted to a temperature of  $20^{\circ}$  C.; the incubator for heating the molds and clamps to  $37^{\circ}$  C.; and the oil in the setting device to  $37^{\circ}$  C. The slab is then cleaned with alcohol and the weighed powder is transferred, with the aid of a small camel's hair brush, to the right end of the mixing slab. The liquid is then measured with the pipette and delivered onto the left end of the mixing slab, as shown in Fig. 2. The mix is made immediately, starting the stop watch on the first addition of powder to the liquid so as to time the mix. As soon as the mix is completed it is filled into the closed



FIG. 7—INCUBATOR FOR STORING VIALS

Note the turbidity of the saliva and that the cylinders can be seen at the bottom of the vials containing oil. Incubator is heated by gasoline gas. Temperature is controlled by the author's thermoregulator. See *J. Am. Chem. Soc.*, 31 (1909), 1218.

The mold is filled to slight excess and immediately clamped in position between the jaws of the

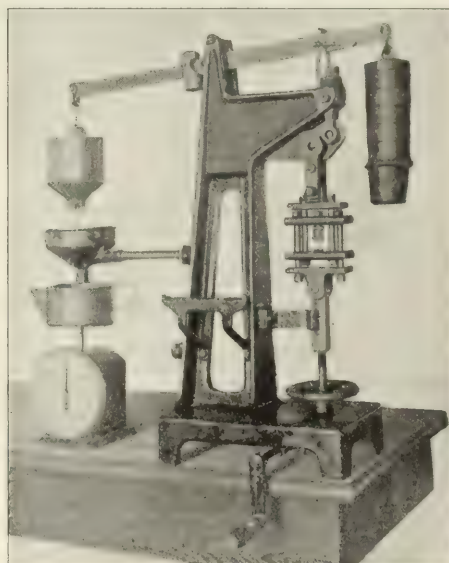


FIG. 8—MACHINE FOR CRUSHING CYLINDERS

The customary machine used for tensile strength tests of Portland cement, provided with special attachment for crushing. The cylinder sets on a small removable anvil in the center of the crushing device. Pressure is applied at the rate of 1000 lbs. per min.

which requires 21 cylinders for each cement tested. Working with an assistant, it is possible to make from 42 to 63 cylinders in one day.

#### NOTES ON TECHNIQUE

**MEASUREMENT OF LIQUID AND POWDER**—It is essential in these tests to use definite amounts of powder and liquid, especially in view of the fact that only one cylinder is made from a mix. Every cylinder, to be strictly comparable, must be made from identical quantities of powder and liquid. In this work the

<sup>1</sup> The object of washing is to remove all traces of oil so that the saliva may come in direct contact with the cylinder.



amount of liquid taken was 0.25 cc. for the zinc oxyphosphate and copper cements, and 0.20 cc. for the silicates. The amount of powder used naturally varied with the cement. A fixed amount of liquid was decided upon for convenience, and to secure a mix of sufficient bulk.

**CONSISTENCY OF MIX** Assuming that the temperature of the mixing slab is constant, the consistency of the mix will depend upon the amount of powder introduced into a fixed amount

mixing the silicates. In this work, the weighed zinc oxyphosphate or copper cement powder was approximately divided with the end of the spatula into four parts, and the first and last quarter subdivided equally. The first addition of powder  $\frac{1}{8}$  of the total required powder, the next addition  $\frac{1}{8}$ , then two  $\frac{1}{8}$  portions, and finally two  $\frac{1}{8}$  portions. The mix was made in  $1\frac{1}{2}$  min. spatulating thoroughly between additions, and working with a rotary motion liberally over the slab, thus permitting the heat of reaction to be conducted to the slab. Every particle of powder was thoroughly incorporated. During the mixing, the mass was "worked" by a rotary motion of the spatula, followed by scraping the mass together with the spatula and depositing it upon the slab by several turns of the spatula held close to the slab.

The silicate cements were mixed by approximately dividing the weighed powder into 2 parts, subdividing one of these parts again into 4 parts. On the first addition,  $\frac{1}{2}$  of the total powder required was added, followed by four  $\frac{1}{8}$  portions. Spatulation in this case was the same as for the zinc oxyphosphate and copper cements, but the mix was completed in  $1\frac{1}{4}$  min.

**TEMPERATURE OF MIXING SLAB**—A temperature of  $20^{\circ}\text{C}$ . was chosen because this is the accepted normal temperature for physical measurements and is a desirable average room temperature. There are comparatively few days on which the humidity and temperature is such that  $20^{\circ}\text{C}$ . would be below the dew point, and thus permit condensation of moisture on the slab. A temperature of  $15^{\circ}\text{C}$ . was found to be undesirable on this account, during the summer months. As mentioned under "consistency of mix," the mixing temperature exercises a marked influence on the consistency and thus on the amount of powder required for a given consistency. It is therefore obvious that a standard temperature must be used for mixing a dental cement for physical tests.

**TEMPERATURE FOR MOLDING, SETTING AND STORING**—The body temperature,  $37^{\circ}\text{C}$ ., was adopted for these operations and it is obvious that the filling of a tooth or the setting of a crown or bridge is conducted under precisely the same thermal conditions.

**TIME OF SETTING**—Fifteen min. at  $37^{\circ}\text{C}$ . was considered to be ample time for setting. A cement should harden sufficiently at this temperature to permit access of saliva without detriment.

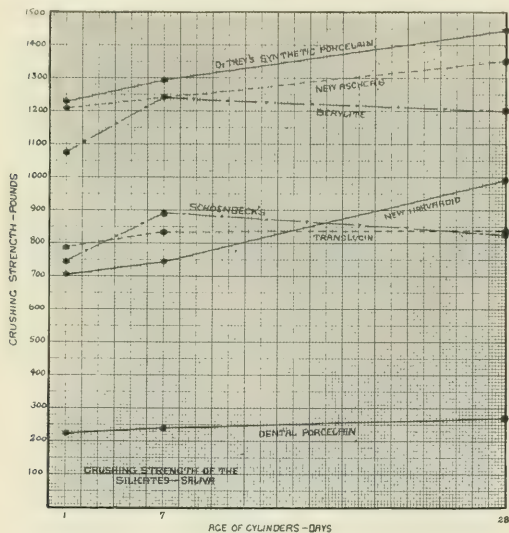


CHART I

of liquid. The rate of addition of the powder and manner of spatulation also affects the consistency and must be controlled. Different dental cements, even of the same type, will require varying quantities of liquid for a mix of definite consistency. In this paper, the silicate cements were all mixed to "filling" consistency and the zinc oxyphosphate and copper cements to "crown and bridge" consistency.

**MIXING**—In a few instances, the manufacturers of dental cements give detailed instructions for mixing, but in the majority of cases the instructions are very meager. Whenever detailed instructions are given, these should be rigidly observed on the assumption that the manufacturer knows or should know the character of his own product. However, in those instances where vague instructions are given, customary practice in manipulation must be followed.

Usually, copper cements may be mixed in the same manner as the zinc oxyphosphates, but silicates are mixed differently than either of these.

Owing to the increased "reactivity" of the zinc oxyphosphate and copper cements over the silicate cements, it is necessary to add the first portions of powder much more slowly when mixing the zinc oxyphosphate and copper cements than when

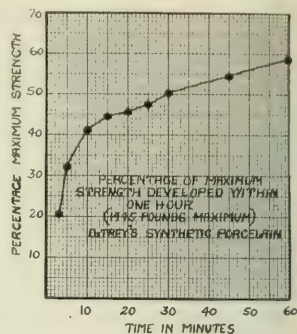


CHART III

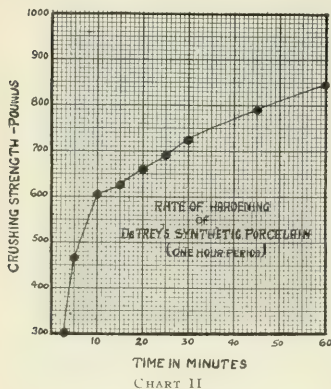


CHART II

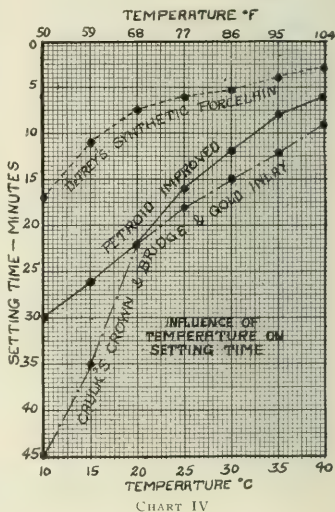
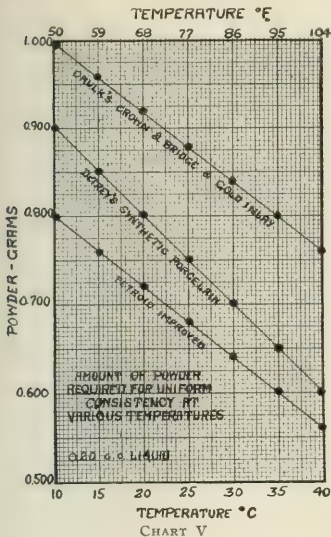


CHART IV

TEST PERIODS AND STORAGE—A uniform period for storage is absolutely essential. In this work periods of 15 min., 1, 7, and 28 days were adopted. The 15-min period is important in showing the progress of hardening of the cement and the strength actually developed before placing in saliva or oil. The 1-, 7-, and 28-day periods are important in showing the



of water in the course of time does affect the cylinder. However, the results in oil are interesting and will be discussed later.

IMPORTANCE OF CRUSHING STRENGTH OF DENTAL CEMENTS

The ability of a filling material to sustain the force of mastication<sup>1</sup> is one of the prominent requirements for permanence. This depends upon the inherent strength of the material and the destructive influences which tend to undermine that strength.

The size of the filling, its location in the mouth, and the force of each bite during mastication, cannot be predetermined, and it follows that high crushing strength is of fundamental importance.

A dental cement should not be weakened on contact with saliva and should show a progressive increase in strength until its maximum strength is reached, which should then be maintained. Retrogression in strength under saliva indicates that the cement is being dissolved or penetrated by the saliva, and therefore less able to withstand masticatory pressure.

Measurements of masticatory pressure have been made by different observers with the aid of gnatho-dynamometers. Black ("Operative Dentistry," Vol. 1) found that the force of the bite, or the pounds force with which the jaws may be closed upon any object, varied greatly among different persons. In 1000 persons the average force exerted was 171 lbs. on the molar teeth, and considerably less on bicuspsids and incisors. The variation was from 25 to 275 lbs. (the limit of the instrument). The instrument constructed by Black measured the force exerted in pressing the teeth together. Eckermann (Ragnar Eckermann, "Mastication and Tooth Structure," *The Dental Record*, 35, 726) constructed a gnatho-dynamometer which measured the power required to open the tightly-pressed jaws, and found that the masticatory pressure of women only in exceptional cases exceeds 66 and 132 lbs., and of men 88 and 176 lbs., respectively, at the incisors and wisdom tooth. The normal masticatory pressure of men is not under 55 lbs. at the incisors; of women, not under 44 lbs. The maximum pressure recorded by Eckermann was 119 lbs. at the incisors and 238 lbs. at the wisdom tooth.

maximum strength developed and also any retrogression in strength. Saliva and a neutral hydrocarbon oil were used as fluid media.

Obviously, the tests in saliva are of first importance because this is the natural medium for a dental cement. The oil was used in order to determine the strength developed in an inert medium. Unfortunately a slight evaporation of water takes place from the cylinders confined under oil at 37° C. and while the oil itself does not affect the cylinder, yet the slight evaporation

Exposure of the test cylinders to saliva gives an added significance to the results.

CRUSHING STRENGTH OF COMMERCIAL DENTAL CEMENTS

Table II gives the results obtained on forty dental cements offered for sale to the dental profession. They are arranged according to the crushing strength after 28 days in saliva.

DISCUSSION OF RESULTS

The wide variation in the crushing strength of commercial dental cements noted is more clearly shown in Table III. The crushing strength of some of the cements is so low that they can hardly be expected to withstand masticatory pressure for even a limited time.

TABLE III—AVERAGES FROM TABLE II

	OIL				SALIVA		
	15 min.	1 day	7 days	28 days	1 day	7 days	28 days
SILICATE							
Minimum	330	733	918	878	225	240	270
Maximum	628	1235	1385	1445	1230	1295	1448
ZINC OXYPHOSPHATE...							
Minimum	88	190	165	218	190	255	218
Maximum	768	1063	1230	1235	965	1070	968
COPPER							
Minimum	105	100	95	145	180	263	0
Maximum	635	983	1190	1183	970	1000	955

The silicate cements show greater resistance to saliva than the other types, only 2 out of 7 (28 per cent) showing retrogression in strength under saliva.

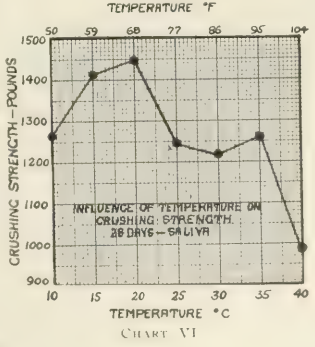
Chart I shows graphically the results obtained on the silicates in saliva. The effect of saliva, and the variation in strength of the different silicates, is of particular interest, since this type of cement is depended upon for permanence. Obviously, a low-strength material cannot be expected to resist masticatory pressure and one showing retrogression in strength will be gradually weakened in the mouth.

The zinc oxyphosphate cements tested show retrogression in strength in saliva in 55 per cent of the cements. Of the copper cements, only 33 per cent show retrogression in strength in saliva.

The value of tests in oil is strikingly shown in several instances. Silicate No. 5 develops a strength of 878 lbs. in oil in 28 days and only 270 lbs. in the same time under saliva. On the other hand, silicate No. 2 shows 888 lbs. in oil in 28 days and 1350 lbs. in the same time under saliva.

These results show opposite effects; with No. 5 saliva reduces the strength on account of lack of resistance, and with No. 2 slight dehydration weakens the material. Copper cement, No. 40, which shows 538 lbs. in oil in 28 days, completely disintegrates in saliva in the same time. These results show the fallacy of tests for crushing strength which disregard the question of a suitable medium.

Referring to the results obtained on the copper





cements, it is interesting to compare the germicidal efficiency<sup>1</sup> of these cements with the crushing strength and retrogression in strength.

Many statements have appeared in the dental literature with reference to the cement-making property of the cuprous and cupric oxides, but these statements have never been based upon experimental evidence. The results on the copper cements, given in Table II, show that high crushing strength and resistance to saliva are obtained with copper cements entirely free from cuprous and cupric oxides. It is hazardous to predict the ultimate effect of any constituent on a dental cement.

#### UTILITY OF APPARATUS FOR CRUSHING-STRENGTH TESTS IN STUDYING OTHER PROPERTIES OF DENTAL CEMENTS

**RATE OF HARDENING**—Ease of manipulation is largely dependent upon the rate of hardening of a dental cement. The rate of hardening can be readily determined by following the technique already given, crushing the cylinders at suitable intervals of time.

Chart II shows the rate of hardening of silicate No. 1 for time intervals up to one hour at a temperature of 37° C. and Chart III shows percentage of maximum strength developed throughout the same periods of time.

A tremendous amount of work would have been re-

corded as the setting time. The setting time is influenced slightly by unusually wide differences in temperature between the slab and the atmosphere. Two results, in thorough agreement, were obtained in every case with the exception of cement No. 6, in which case the setting time of different mixes varied considerably. The range in setting time, of the three types of cement, is as follows:

TYPE OF CEMENT	CONSISTENCY
Silicate..... 5 1/4 to 12 1/4 min.	"Filling"
Zinc Oxyphosphate..... 9 to 78 min.	"Crown and Bridge"
Copper..... 8 to 25 min.	"Crown and Bridge"

These results are interesting in showing the relative setting qualities of the different cements. They do not show how soon the cement will set in the mouth, since the tests were made at 20° C. (average room temperature), but they serve admirably in grading the cements as to setting time, which is important from the standpoint of manipulation in dental practice.

**INFLUENCE OF MIXING TEMPERATURE ON SETTING TIME**—The temperature at which a dental cement is mixed markedly affects the setting time. Chart IV shows the influence of mixing temperature on the setting time of one silicate and two zinc oxyphosphate cements. The temperatures of mixing and setting were identical. These experiments show that the setting time of a dental cement can be controlled

TABLE IV

NAME OF PRODUCT	Per cent Germicidal Efficiency after Exposure of			Crushing Strength in Saliva after Exposure of			Per cent Retrogression in Strength in Saliva
	5 min.	15 min.	1 hr.	1 da.	7 da.	28 da.	
Smith's White Copper Cement.....	0	66.6	83.3	970	903	797	17.8
Caulk's Crown & Bridge & Gold Inlay Cement with Copr-Zinc.....	99.4	100.0	100.0	595	755	833	0
Caulk's Red Copper Cement.....	97.1	100.0	100.0	788	800	918	0
Ames' New Process Oxyphosphate of Copper Cement.....	96.0	100.0	100.0	935	1000	788	21.2
Decido Copper Cement.....	10.0	96.0	98.0	280	270	0	100.0
Fellowship Oxyphosphate of Copper Cement.....	0	96.4	97.1	530	570	705	8

quired to determine the rate of hardening of the forty dental cements studied. For practical purposes, the rate of hardening is indicated by the crushing strength after 15 min., as given in Table II. These data are important in their relation to dental practice, in that they show the necessity of allowing a filling to harden for a definite time before commencing the operation of "finishing." The hardening of any dental cement can be accelerated by an increase of temperature, but further investigation is required to determine the effect of local application of heat to a "filling." In actual practice, the heat cannot be applied equally to all parts of the filling, and this would result in unequal setting at different parts of the filling. Whether this effect would result in diminished strength and resistance remains to be determined.

**TIME OF SETTING**—The results given in Table II were obtained with the aid of the Gilmore needle shown in Fig. 1. The large needle, weighing 1 lb. and having a point 1/24 in. in diameter, was used. A pat of the freshly mixed cement, about 1 mm. thick, 10 mm. wide, and 20 mm. long, is allowed to set at 20° C. on the mixing slab, shown in Fig. 2. The interval of time which elapses from the time the mix is started to the time that the needle fails to make a perceptible indentation on 5 sec. application

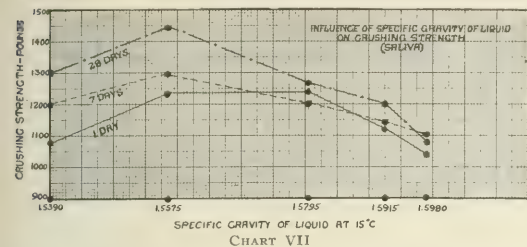
by the temperature at which it is mixed. In crown and bridge work, it is often desirable to retard the setting of a zinc oxyphosphate in order to give more working time, and on exceptionally warm days it is frequently necessary to retard setting, especially in the case of the silicates.

**INFLUENCE OF MIXING TEMPERATURE ON AMOUNT OF POWDER REQUIRED FOR UNIFORM CONSISTENCY**—Chart V shows the amount of powder required for uniform consistency at different mixing temperatures. The silicate cement was mixed to "filling" consistency and the two zinc oxyphosphates to "crown and bridge" consistency. The amount of powder required varies inversely with the temperature. This effect is also of practical importance.

**INFLUENCE OF MIXING TEMPERATURE ON CRUSHING STRENGTH**—Chart VI shows the effect of mixing temperature on the crushing strength of silicate No. 1 (28 days in saliva). The best results for crushing strength are obtained when this material is mixed at a temperature of 20° C. (68° F.). Contrary to general opinion, too low a temperature causes an overloading of the liquid with powder, resulting in decreased strength. Too high a temperature, on account of the fact that less powder is required for the mix, overloads the mass with liquid, this again resulting in diminished strength.

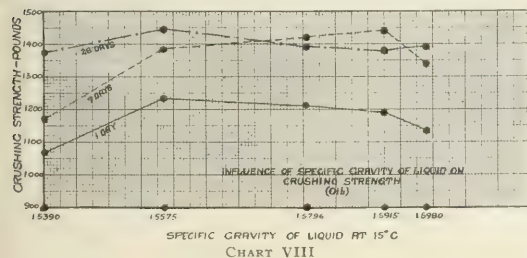
<sup>1</sup> THIS JOURNAL, 7 (1915), 195, 1000.

**INFLUENCE OF SPECIFIC GRAVITY OF LIQUID ON CRUSHING STRENGTH**—Alteration in the specific gravity of a dental cement liquid may be occasioned by the addition or subtraction of water. In actual practice, carelessness in capping the liquid bottle will result



in evaporation of water, thus increasing the specific gravity of the liquid. Chart VII shows the influence of specific gravity of the liquid on the crushing strength of silicate No. 1.

It will be noted that a certain specific gravity, in this case 1.5575 at 15° C., gives the highest crushing strength, and that a decrease (an addition of water) or increase (abstraction of water) results in diminished resistance to saliva. The importance of this observation is that the method may be utilized in determining the proper "balance" of a dental cement. The specific gravity of a liquid is an index of its concentration, and if the constituents of the liquid are properly proportioned with relation to the powder of a dental cement, it is possible to "balance" the liquid by determining the effect of a given liquid adjusted to different specific gravities. It is evident from these results that liquid of different settings, if supplied for use with one and the same powder of a silicate cement, would yield varying results as regards saliva resistance, and that only one standard liquid can be expected to yield the best results.



Reference to Chart VIII shows that liquids higher in specific gravity than the standard liquid do not show the characteristic loss in strength in oil, although liquids of lower specific gravity show the same effect as in saliva. Excessive concentration of liquid apparently results in increased solubility of the material with a corresponding loss in strength in saliva.

#### SUMMARY

I—In order to establish the "fitness" of a dental cement, it is necessary to consider, individually and collectively, its various physical, physiological and chemical properties. The composition of a dental

cement has no definite relation to its ultimate properties, nor can *a priori* conclusions be drawn with reference to the effect of a given constituent in a dental cement. This must be arrived at experimentally.

II—A method for determining the crushing strength of dental cements is described in detail. The conditions under which the tests are made have been standardized so as to conform, as nearly as possible, to mouth conditions.

III—Crushing strength is of fundamental importance in establishing the relative value of commercial dental cements with respect to their ability to resist masticatory pressure. Tests conducted under saliva have an added significance, in that the effect of the saliva is incidentally determined.

IV—Forty commercial dental cements were tested and found to vary considerably in crushing strengths. Retrogression in strength under saliva occurred in a large percentage of the cements tested. There is no relation between germicidal efficiency and resistance to saliva in the case of the copper cements. Those showing retrogression in strength in saliva may show either high or low germicidal efficiency.

V—Several properties of dental cements, of importance in applied dentistry, may be studied with the aid of the apparatus described in this paper.

Further investigations relating to the crushing strength of dental cements and other properties are being conducted in this laboratory and will be published in future papers.

Acknowledgment is due Frank L. Grier for many valuable suggestions and aid in conducting the experimental work; also to Paris T. Carlisle, 4th, for assistance in conducting the tests.

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MILFORD, DELAWARE

#### COLOR STANDARDS AND COLORIMETRIC ASSAYS

By H. V. ARNY AND C. H. RING

Received September 13, 1915

#### INTRODUCTION

Entrusted by the Committee on Revision of the National Formulary with the task of standardizing the coloring agents, cudbear and caramel, recipes for tinctures of which are given in that book, one of us (in 1908) became interested in color standardization. Finding that no rational system of color-matching obtained, other than the Lovibond tintometer, the standard glasses of which are arbitrarily chosen, study suggested the use of a standard red solution made from a cobalt salt, a standard yellow solution made from a ferric salt, and a standard blue solution made from a copper salt. Such solutions were prepared, and by mixing the three, blends were obtained that gave a variety of hues limited only by the character of the colors of the original fluids. This line of colored fluids, the "Co-Fe-Cu" blends—which were demonstrated and described at the Eighth International Congress of Applied Chemistry<sup>1</sup>—gave a fine line of green, yellow and orange shades, but were lacking in deep blues and reds; so further work?

<sup>1</sup> See Proceedings, Vol. 26, p. 319.

Arny and Pickardt, *Process Chemistry*, 57 (1914), 131.



was performed in 1913 and during the past year by the present writers. The result of this work was the preparation of a supplemental set of colors, designated as the "Co-Cro-Cu" blends, which furnish the needed blues and some of the reds. To secure the purplish reds, blends of volumetric solutions of potassium dichromate and of potassium permanganate have been devised as indicated in Table 1. These two

TABLE 1 SOLUTIONS USED FOR MAKING STANDARD BLENDS

NAME OF SERIES	COLOR	SUBSTANCES USED Formula	Grams	SOLVENT USED	STRENGTH OF SOLUTIONS
"Co-Fe-Cu"	Red	CoCl <sub>2</sub> ·6H <sub>2</sub> O	59.49	1 Per cent	
	Yellow	FeCl <sub>3</sub> ·6H <sub>2</sub> O	45.05	Hydrochloric	N/2
	Blue	CuSO <sub>4</sub> ·5H <sub>2</sub> O	62.43	Acid(a)	
"Co-Cro-Cu"	Red	CoCl <sub>2</sub> ·5NH <sub>3</sub> ·H <sub>2</sub> O	2.7	2.8 Per cent	
	Yellow	(NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0.42	Ammonia	N/50
	Blue	CuSO <sub>4</sub> ·5H <sub>2</sub> O	2.496	Water(b)	
"Cro-Manganate"	Purple	KMnO <sub>4</sub>	0.0413	(b)	N/1000
	Yellow	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	0.487	(b)	N/100

(a) Made by adding 25 cc. concentrated hydrochloric acid to 975 cc. water.

(b) Standard U. S. P. solutions are diluted as required.

lines of colored fluids are described at length in the *Journal of the Franklin Institute* for August, 1915, p. 199. Some of the matches obtained by the use of these solutions are given in Table 2.

TABLE 2—MATCHES OBTAINED WITH STANDARD COLORS

SOLUTION MATCHED	BLEND USED FOR MATCHING
Standard Caramel (1 g. sugar heated to 180° C., then diluted to 500 cc. with water).....	"Co-Fe-Cu, 4-7-1"
Nessler Test (ammonia dilution equivalent to 1:500,000).....	"Co-Fe-Cu, 3-9-0, 50%"
Phenol-Sulfonic Acid Test (1:500,000).....	"Co-Fe-Cu, 0-12-0, 66%"
Molybdate Assay for Phosphoric Acid (1:20,000).....	"Co-Cro-Cu, 0-12-0, 15%"
Folin's Vanillin Test (1:100,000).....	"Co-Cro-Cu, 3-3-10"
Riegler's Uric Acid Test (1:40,000).....	"Co-Cro-Cu, 2-2-8"
Salicylic Acid (1:50,000) + proper amount FeCl <sub>3</sub> Solution.....	"Co-Cro-Cu, 7-1-5, 65%"
Naphthylamine Methylamine-Sulfanilic Acid Test for Nitrites (1:10,000,000).....	"Cro-Manganate, 15-1, 55%"

The blending of the acidulated fluids or of the ammoniacal fluids can, of course, be performed in any proportion that fancy suggests.

**NOMENCLATURE**—The original red fluid is "R. Y. B., 12-0-0;" the original yellow is "R. Y. B., 0-12-0;" and the original blue is "R. Y. B., 0-0-12." The sample designated as "R. Y. B., 6-6-0" will, of course, be an orange hue; that called "R. Y. B., 0-6-6" will be green, while "R. Y. B., 6-0-6" has a purplish tint. That the intensity of the three basic fluids is about the same is shown by the fact that "R. Y. B., 4-4-4" closely approaches, both in the "Co-Fe-Cu" and in the "Co-Cro-Cu" series, the "neutral gray" which is the closest that blended reds, yellows and blues can approach to water-white condition.

**PERMANENCY OF FLUIDS**—The original acidulated cobalt, iron and copper solutions and their blends neither fade nor precipitate to a perceptible degree until at least two years old; the ammoniacal cobalt and chromium solutions have, now been under observation for over a year without any fading being detected. The ammoniacal copper, on the other hand, precipitates, and consequently undergoes color change within a few weeks, but our experiments so far show that the blends keep satisfactorily when sealed in ampuls or kept in well filled, rubber-stoppered bottles which are not opened. In practice, however, the ammoniacal copper solution is prepared by diluting the permanent N/2 acidulated copper solution to N/50 strength by the addition of ammonia water

and water; hence the preparation of the "Co-Cro-Cu" blends is merely a matter of mixing solutions that can be kept in stock for months without deterioration.

#### USE OF COLORED FLUIDS IN COLORIMETRIC ASSAY

The article in the *Druggists Circular* mentioned above showed that the prescribed methods of colorimetric assays were far from perfect. This year, however, we are able to report that practically every tint desired in colorimetric work can be obtained from either the "Co-Fe-Cu," the "Co-Cro-Cu" or the "Cro-Manganate" blends; and that under certain conditions the colorimetric assays themselves can be made uniform.

#### CAUTIONS

Unless a colorimetric assay is performed with proper regard to the amount and proportion of the reagent employed, the test is very liable to be inaccurate when the color is matched against a solution containing a known quantity of the substance under examination; and it is practically worthless when matched against a rigid standard of either colored glass or colored fluids, unless this fact is understood. The data given further along show that: (1) in some cases, a difference of only a few drops of the reagent may make a vast difference in the color of the two samples, each having the same volume and the same amount of substance under assay; (2) several lots of a given reagent, made by slightly different recipes, may fail to produce uniform color results, even though exact duplication of work is performed in each test (e. g., Nessler's solution).

On the other hand, if the reagents are carefully prepared and if the test itself is carried out with proper regard to the exact quantities of the reagents and to the sequence of mixing, the color results are, as a rule, uniform. This also holds good in regard to different samples of the chemical being used, provided, of course, that only chemicals of tested purity are employed. Such being the case, our plan of color standardization is shown to be entirely feasible, and its use will greatly facilitate colorimetric assays by obviating the preparation of standard solutions of the chemicals under assay.

#### AMMONIA COLORIMETRIC TESTS

Four different recipes<sup>1</sup> are available for the preparation of Nessler's reagent, the universally recognized method for the determination of ammonia in minute quantities. These four recipes differ only in the proportional amounts of the ingredients and the manner of mixing them. In another recipe, suggested by Frerichs and Mannheim,<sup>2</sup> mercuric iodide is used in place of mercuric chloride in the preparation of this reagent. We tested each of these reagents on standard samples of ammonium chloride solution prepared from "Kahlbaum-Reagent-Ammonium Chloride," following the usual method of adding 2 cc. of the reagent to

<sup>1</sup> The recipes were obtained from the following books: (1) *The United States Pharmacopeia*; (2) "Standard Methods for the Examination of Water and Sewage," American Public Health Association; (3) "Examination of Water," William P. Mason; (4) "Sanitary and Applied Chemistry," E. H. S. Bailey.

<sup>2</sup> *Apoth. Zeit.*, 29 (1914), 972.

50 cc. of the solution containing a known quantity of nitrogen in the form of ammonia. The strikingly discordant results obtained are shown in Table 3.

Besides the six different Nessler solutions used in Table 3, we also used a solution prepared according to the U. S. P., but made up freshly. A precipitate formed at every trial, just as when solutions made by the Mason or Bailey recipes were used.

It is, of course, well known that an "aged" Nessler solution, at least 6 mo. old, should be used when possible, since freshly prepared solutions produce an entirely different color value from that obtained with an aged sample made from the same recipe. As far as we can see, no matter what recipe is followed, the older the solution the less likelihood there is of its causing precipitation. The only freshly prepared solution that has been at all satisfactory is that prepared according to the recipe of Frerichs and Mannheim, and in our judgment, this recipe should be chosen as the official one for all Nessler tests. Although an old Nessler solution should be used when possible, this is sometimes out of the question and we recommend the Frerichs and Mannheim modification as the best, since it can be used immediately. This recipe is as follows: Potassium iodide 2.5 g., mercuric iodide 3.5 g., 15 per cent solution of KOH 100 g.; dissolve the potassium iodide in 3.0 g. of water, add the mercuric iodide and, when dissolved, add the solution of

to make a second Lovibond reading of any value; the exception was the reagent prepared by the Frerichs and Mannheim recipe, and with this sample readings were made an hour after mixing. The blends were then kept in rubber-stoppered bottles and were read again the next day, with the following results:

NITROGEN CONTENT	Reading	Red	Yellow	Blue
1 : 500,000	1st	1.0 + 0.1	3.0 + 0.1	0.1
	2nd	1.0 + 0.2	3.0 + 0.2	-0.2
1 : 1,000,000	1st	0.7	1.6	None
	2nd	0.7	2.0 + 0.2 + 0.1	-0.2

For some reason, at present unknown to us and which will require further investigation, the stronger solution ( $N = 1 : 500,000$ ) was the more stable.

We next made comparative readings of five tests, each treated with the Nessler reagent "U. S. P. Old Solution" and representing a nitrogen content of 1 : 500,000. The first readings were made within an hour or two after mixing. The tests were kept in rubber-stoppered bottles and read again the following day.

Soln. No.	About 1 Hr. after Mixing			1 Day after Mixing		
	Red	Yellow	Blue	Red	Yellow	Blue
1	1.0	2.0 + 0.2	-0.1	1.0 + 0.1	1.0 + 1.5	-0.1
2	1.0 + 0.1	2.0 + 0.4 + 0.1	-0.1	1.0 + 0.1	1.0 + 1.5	-0.1
3	1.0 + 0.2	1.0 + 1.5	-0.1	1.0 + 0.1	1.0 + 1.6	-0.1
4	1.0 + 0.1	1.0 + 1.8	-0.1	1.0 + 0.1	1.0 + 1.5	-0.1
5	1.0 + 0.1	1.0 + 1.5	-0.1	1.0 + 0.1	1.0 + 1.6	-0.1

While these five comparative readings show such slight changes in tint in the course of several hours that the color can be said to remain almost stable

TABLE 3 CONDITION AND LOVIBOND READINGS OF TESTS OF AMMONIUM CHLORIDE USING DIFFERENTLY PREPARED SOLUTIONS OF NESSLER'S REAGENT

Proportional Part of N: NESSLER SOLUTION USED	Tests with Various Nessler Reagents					
	1 to 100,000	1 to 200,000	1 to 500,000	Lovibond Readings with Various Nessler Reagents		
				1 to 200,000	1 to 500,000	
U. S. P. Old (1 yr. old)	Fairly clear	Clear	Clear	Red	Yellow	Blue
U. S. P. Stock (6 mo. old)	Precipitate	Clear	Clear	1.9 + 0.2	5.0 + 1.6	-0.2
F. & M. Fresh	Not clear	Clear	Clear	1.0 + 1.6	5.0 + 1.9 + 1.0	-0.5
A. P. H. A. Fresh	Precipitate	Clear	Clear	2.0 + 0.2	5.0 + 2.0 + 1.3	-0.8
Mason Fresh	Precipitate	Precipitate	Precipitate	2.0 + 0.7	5.0 + 3.0 + 0.2	0.3
Bailey Fresh	Precipitate	Precipitate	Precipitate			

potassium hydroxide; let stand until perfectly clear and decant. If needed at once, filter through sand.

The next problem was to see if a definite reagent applied in exactly the same manner to solutions of different samples of ammonium chloride, all of the same strength, would give the same color value. We prepared standard solutions from Kahlbaum's reagent, from stock salt, and from a concentrated standard solution that had been on the shelf for over 6 mo. As shown in Table 4, the results were practically the

during the time between the two readings, still, it is never safe to Nesslerize and then await one's convenience before making color comparison. We cannot lay too much stress on the fact that in this kind of work it is as necessary to have an exact standard method of procedure as it is to have a standard of color.

We next tried the tests with a larger amount of the reagent, but results were not satisfactory. We prepared 40 cc. of an ammonium solution and added 10 cc. of Nessler's (Frerichs and Mannheim) reagent, so that in the total volume of 50 cc. the proportion of nitrogen was 1 in 500,000. Another test was made in the same way with the nitrogen content 1 in 1,000,000. In both cases the liquid was a little cloudy, but we managed to get the following Lovibond readings of them, though the colors did not last long and had to be read quickly.

NITROGEN CONTENT	Red	Yellow	Blue
1 : 500,000	2.0	5.0 + 2.0 + 0.3	0.1
1 : 1,000,000	0.7	1.5 + 0.7 + 0.2	0.1

In the paper in the *Druggists Circular* for March, 1914, there is given a color match with our standard fluids for Nessler's test where nitrogen equals 1 part in 100,000, which is "Co-Fe-Cu, 5-7-0." This means that the color produced by this Nessler test was of the same shade and intensity as resulted when the

TABLE 4—LOVIBOND READINGS ON AMMONIUM CHLORIDE SOLUTIONS

SALT USED IN SOLUTION	NITROGEN 1 : 250,000		
	Red	Yellow	Blue
Kahlbaum.....	1.9	4.0 + 2.0 + 0.1	-0.2
Stock.....	1.9	4.0 + 2.0 + 0.2	-0.2
Old Standard Solution.....	2.0 + 0.1	5.0 + 1.6	0.3

same in every trial. Only very slight differences were shown by the Lovibond readings, while, when compared by the eye, no difference at all could be discerned.

It is well known that the tints produced by the action of Nessler's reagent on a solution of ammonium chloride are far from permanent. A solution treated with a freshly prepared sample will show precipitation on standing much sooner than will a solution of the same strength treated with an aged Nessler. With but one exception, the tests made with the various freshly prepared reagents were too unstable in tint



"Co-Fe-Cu" standard  $N/2$  acidulated colored solutions were blended in the proportion of 5 cc. of the cobalt solution, 7 cc. of the iron solution, and none of the copper solution.

Recently we repeated color matches for the Nessler test of nitrogen 1 : 200,000 and 1 : 500,000 with our "Co-Fe-Cu" standard fluids. We made these tests with the "U. S. P. Old" Nessler reagent and found that the color of the solution containing 1 part of nitrogen to 200,000 matched our blend of "Co-Fe-Cu, 4-8-0, 70%," while the one having a nitrogen content of 1 : 500,000 matched our blend of "Co-Fe-Cu, 3-9-0, 50%."

This means that to match the tint produced in the Nessler test where nitrogen is present in a proportion of 1 to 200,000 it was necessary to first obtain the best match in *color quality*, which we found to be a blend consisting of 4 cc. of  $N/2$  acidulated cobalt solution, 8 cc. of  $N/2$  acidulated iron solution and none of the copper solution. The color *intensity* of this blend was too great to match the Nessler test, so we finally obtained a perfect match by diluting the original  $N/2$  "Co-Fe-Cu, 4-8-0" blend with water to 70%. In other words, we took 14 cc. of the  $N/2$  "Co-Fe-Cu, 4-8-0" blend and added 6 cc. of water, making a total of 20 cc. of colored fluid. In the same way we matched the Nessler test with a nitrogen content of 1 : 500,000 and found it to be "Co-Fe-Cu, 3-9-0, 50%," that is, the  $N/2$  blend "Co-Fe-Cu, 3-9-0" was prepared and then 10 cc. of it was mixed with 10 cc. of water. The Lovibond readings of these two matches were:

"Co-Fe-Cu"		Red	Yellow	Blue
4-8 0	70%	1.9 + 0.2	5.0 + 1.3	-0.3
3-9-0	50%	1.0 + 0.1	1.5 + 1.0	-0.2

If these readings are compared with those of the corresponding Nessler tests ("Co-Fe-Cu, 4-8-0, 70%" with  $N = 1 : 200,000$  and "Co-Fe-Cu, 3-9-0, 50%" with  $N = 1 : 500,000$ ), it will be seen that they are very good matches by the Lovibond method as well as by the eye.

While prosecuting this line of work, we investigated the system of standard color matches for Nessler reactions as laid down in the "Standard Methods of Water Analysis," American Public Health Association, 1913, which consist of two empiric solutions made up as follows: RED—12 g. of cobalt chloride dissolved in distilled water, add 100 cc. strong hydrochloric acid and make up to 1 liter with water. YELLOW—2 g. potassium platonic chloride dissolved in water, add 100 cc. strong hydrochloric acid and make up to 1 liter with water. These two solutions are blended and diluted in varying proportions, each finished sample being of a tint which is supposed to represent the color shade and intensity of a certain corresponding Nessler test. We tested this, following the directions in every respect with the utmost care, but we could get no satisfactory results whatever. It is only fair to state that in the book where this method is given no claim is made for its accuracy.

## NITRATE DETERMINATION

In the work on determination of nitrates we have employed the methods as directed in the "Standard Methods for Examination of Water and Sewage," A. P. H. A., 1913; Mason's "Examination of Water," and other reference books. As is well known, the yellow color of the nitrate test is as stable as could be desired. After proving this stability sufficiently, three different lots of potassium nitrate—"Kahlbaum reagent," an average sample in crystal form, and still another in powder, that were taken from stock—were submitted to comparative tests. Standard solutions were prepared, according to directions, with phenol-sulfonic acid, *i. e.*, a standard solution was evaporated to dryness, phenol-sulfonic acid added to the residue, and then water added in sufficient amount to make a standard solution that would be of a strength appropriate to our use. When the final standard solutions, or portions thereof diluted, were treated with ammonia water, uniform color intensity was obtained from solutions of the same strength as Lovibond readings in Table 5 show.

SALT USED IN SOLUTION	Nitrogen 1 : 1,000,000		Nitrogen 1 : 2,000,000	
	1st Reading	2nd Reading	1st Reading	2nd Reading
Kahlbaum.....	2.0 + 0.05	2.0 + 0.07	1.0 + 0.04	1.0 + 0.07
Crystal.....	2.0 + 0.05	1.9 + 0.1	1.0 + 0.05	1.0 + 0.04
Powder.....	2.0 + 0.1	2.0 + 0.1	1.0 + 0.05	1.0 + 0.04

The very slight differences shown are much more likely caused by changes in the vision of the person reading than by any change of color in the liquid. This color was of such a pure yellow that it was found only necessary to use yellow Lovibond glasses when making the readings. In some of the tests the amounts of phenol-sulfonic acid and of ammonia water employed were varied from the regulation quantities, in order to note the influence of such deviation; variations within reasonable bounds made no difference in the resulting color, all tests of equal strength of nitrogen producing equal color values.

We also found that while most authorities direct the use of 100 cc. of volume for each test, 50 cc. of nitrate solution and half the usual quantity of ammonia water gave practically the same color value as the usual amounts. To facilitate diffusion we used glass-stoppered cylinders in place of Nessler tubes.

In all cases where the matching of colored fluids was not carried out with the Lovibond tintometer, we used 1-oz. Blake bottles, these being filled, from the glass cylinders used for making the determinations. Rubber stoppers were used for alkaline solutions and corks for acid mixtures.

In Table 6 are given the Lovibond readings obtained on another line of tests which were kept in Blake bottles. Only the stronger solutions showed any considerable color change.

In looking for blends of our standard fluids that matched the color produced by these nitrate tests, we found that  $N/2$  acidulated ferric chloride solution was of exactly the right tint, making blending unnecessary. We merely diluted this with water, according to the strength of the nitrate tint that was to be matched. Only three nitrate tints (nitrogen content 1 : 500,000, 1 : 1,000,000, and 1 : 2,000,000) were

thus matched. From several trial dilutions of the  $N/2$  ferric chloride solution, we selected three to compare with each nitrate test, making, in all, nine samples of iron solution. These were placed in 1-oz. Blake bottles, as were the three nitrate tests, and the twelve fluids were matched as "unknowns." The ferric chloride matching fluids were made by diluting the  $N/2$  solution to the following percentage strengths:  $16\frac{2}{3}\%$ , 20, 25,  $28\frac{1}{2}\%$ ,  $33\frac{1}{3}\%$ , 40,  $66\frac{2}{3}\%$ , 75 and 80; i. e., "20%" fluid was made by diluting 1 part of the  $N/2$  solution with 4 parts of water.

The twelve fluids, each bearing a key number, were then submitted to three observers for matching and the results were as follows: Nitrate solution containing 1 N to 2,000,000 was found by all observers to stand between the "25%" and "20%"  $N/2$  ferric chloride solution, with the "25%" as a better match.

NITROGEN CONTENT	READ SHORTLY AFTER MIXING	
	Red	Yellow
1 : 2,000,000	None	1.0 + 0.05
1 : 1,000,000	0.1	2.0 + 0.1
1 : 500,000	None	5.0
1 : 250,000	None	5.0 + 2.0 + 1.6
1 : 200,000	None	5.0 + 3.0 + 1.6
1 : 150,000	None	5.0 + 4.0 + 1.6
1 : 125,000	None	5.0 + 4.0 + 2.0 + 0.1

The 1 N to 1,000,000 was found by all observers to stand between the "40%" and the " $33\frac{1}{3}\%$ "  $N/2$  ferric chloride, without being able to decide which was the better match. The nitrate solution containing 1 N in 500,000 proved more difficult to match; while all observers agreed that the " $66\frac{2}{3}\%$ "  $N/2$  ferric chloride solution was closest, the other two ferric chloride solutions picked out as nearly matching—"75%" and "80%" of  $N/2$  strength—were so similar in hue to the " $66\frac{2}{3}\%$ " dilution that the observers could not agree on the proper sequence.

In the order dark to light, Observer A reported "75%, 80%, nitrate solution,  $66\frac{2}{3}\%$ ." Observer B reported "80%, nitrate solution,  $66\frac{2}{3}\%$ , 75%," and Observer C "75%, 80%,  $66\frac{2}{3}\%$ , nitrate solution." This confirms the statement made in a previous paper, that the average eye cannot discern, in ordinary cases of matching color, differences of less than 5 per cent. Lovibond readings were made of all 12 samples and the results are shown in Table 7: since

TABLE 7—LOVIBOND READINGS OF DILUTED FeCl <sub>3</sub> SOLUTIONS					
1 N in 2,000,000		1 N in 1,000,000		1 N in 500,000	
Yellow 1.0 + 0.05		Yellow 2.0 + 0.1		Yellow 5.0	
FeCl <sub>3</sub> Yellow		FeCl <sub>3</sub> Yellow		FeCl <sub>3</sub> Yellow	
$16\frac{2}{3}\%$ 0.7 + 0.2		$28\frac{1}{2}\%$ 1.5 + 0.1		$66\frac{2}{3}\%$ 3.0 + 1.3 + 0.1	
20% 1.0 + 0.1		$33\frac{1}{3}\%$ 1.9 + 0.1		75% 5.0 + 0.1	
25% 1.0 + 0.2		40% 2.0 + 0.4		80% 5.0 + 0.7	

all were matchable with the yellow Lovibond glasses alone, the "red" and "blue" columns are omitted. These results prove that the simple bottle readings agree so closely with the Lovibond readings that for practical purposes our  $N/2$  acidulated ferric chloride, properly diluted, can be used as a standard for the quantitative determination of nitrogen as nitrates in minute quantities. Thus if the color of a nitrate test matches the color of a  $N/10$  acidulated ferric chloride standard fluid, such a solution contains nitrogen, as nitrates, in the proportion of 1 : 2,000,000. If the color of the test matches the color of the  $N/6$  standard fluid, the proportion of nitrogen will be 1 : 1,000,000.

The scope of this plan of assay is limited only by the ability of the eye to discern the yellow tint in the solution. In tests where nitrogen is present in less than 1 : 2,000,000, the tint is too light to read satisfactorily with the Lovibond tintometer, unless a layer of fluid several inches through is employed. In very tenuous solutions, it would, of course, be necessary to examine and compare the color through a considerable layer of fluid, as is done regularly in water analysis by using Nessler tubes; but in these cases, dilutions of the standard ferric chloride fluid can be used for comparison in such tubes.

In the foregoing paragraphs we have shown that the nitrate colorimetric test of nitrogen content 1 : 500,000, 1 : 1,000,000, and 1 : 2,000,000 match our standard acidulated ferric chloride solutions of " $66\frac{2}{3}\%$ ," "40%," and "25%" of  $N/2$  strength,

LOVIBOND READINGS, USING BLAKE BOTTLES					
READ 1 OR 2 DAYS AFTER MIXING		READ 3 WEEKS AFTER MIXING			
Red	Yellow	Blue	Red	Yellow	Blue
None	1.0 + 0.07	None	None	1.0 + 0.05	None
None	2.0 + 0.1	None	None	1.9 + 0.2	None
None	5.0	None	None	3.0 + 1.5	None
None	5.0 + 2.0 + 1.5	None	None	5.0 + 3.0 + 0.2	None
None	5.0 + 3.0 + 1.6	None	None	5.0 + 3.0 + 0.7	None
None	5.0 + 4.0 + 1.8	-0.1	None	5.0 + 4.0 + 2.0	-0.2
None	5.0 + 4.0 + 2.0	0.1	None	5.0 + 4.0 + 1.6	-0.5

respectively, and this, we believe, demonstrates the fact that any other readable nitrate fluid, so treated, has an exact counterpart in a dilution of our acidulated ferric chloride standard fluid.

NITRITES

The accepted colorimetric method for the determination of nitrogen in the form of nitrites in an extremely dilute solution of sodium nitrite, with sulfanilic acid and a naphthylamine salt, was then investigated. We found that the color produced could not be directly matched by any combination of the red, yellow and blue Lovibond glasses. Of course, the red color predominated; but when red Lovibond glasses were compared with the solution, the tint of the latter was so much more brilliant than the tint of the red glasses, that both yellow and blue glasses had to be placed against the cell containing the fluid in order to obtain a satisfactory match, thus subduing the real color of the nitrite solution. We were thus able to use the tintometer as a basis of comparison and thus we also secured perfect color matches with some of our standard colored fluids, as will be presently shown.

In this test we used two different sets of reagents. The first, which is sanctioned by the A. P. H. A. book on water methods, was prepared by dissolving each of the two reagents in 5 N acetic acid: 2 cc. of each of the reagents were added to 100 cc. of solution containing the sodium nitrite. The second set, prepared according to "Examination of Water," by W. P. Mason, was made by dissolving the proper amount of sulfanilic acid in hot water, and the naphthylamine hydrochloride in boiling water. Two cc. of each of these reagents were added to 100 cc. of solution containing the nitrite which was first acidulated with a drop of concentrated hydrochloric acid.

Comparing the effects of these two sets of reagents, it was found that with hydrochloric acid present a slightly darker tint was usually obtained. We also



tried acidulating the solutions with a small amount of a mixture of acetic and hydrochloric acids when using the acetic acid reagents. This produced about

NITROGEN CONTENT	REAGENT	Red	Yellow Blue
1: 1,000,000	A. P. H. A.	5.0 + 4.0 + 3.0 + 2.0 + 1.0 + 1.9	1.9 1.5
	A. P. H. A. (a)	5.0 + 4.0 + 3.0 + 2.0 + 1.0 + 1.6	-2.0 -1.3
	Mason	5.0 + 4.0 + 3.0 + 2.0 + 1.0 + 1.9	-1.9 -1.5
1: 2,000,000	A. P. H. A.	5.0 + 4.0 + 3.0 + 0.7	1.5 0.9
	A. P. H. A. (a)	5.0 + 4.0 + 3.0 + 1.0	1.5 0.7
	Mason	5.0 + 4.0 + 3.0 + 1.0	-1.5 -1.0
1: 5,000,000	A. P. H. A.	4.0 + 1.6	0.3 + 0.1
	A. P. H. A. (a)	5.0 + 1.6	0.4 None
	Mason	5.0 + 1.5	-0.3 + 0.1
1: 10,000,000	A. P. H. A.	3.0 + 0.4	None + 0.3
	A. P. H. A. (a)	4.0	None + 0.3
	Mason	4.0 + 0.2	-0.1 + 0.2
1: 14,000,000	A. P. H. A.	1.0 + 1.3	None + 0.2
	A. P. H. A. (a)	1.0 + 1.8	None + 0.2
	Mason	3.0	None + 0.2
1: 18,000,000	A. P. H. A.	1.9	None + 0.2
	A. P. H. A. (a)	2.0 + 0.1	None + 0.2
	Mason	2.0	None + 0.1
1: 20,000,000	A. P. H. A.	1.5 + 0.2	None + 0.2
	A. P. H. A. (a)	1.9	None + 0.2
	Mason	1.9	None + 0.1

(a) Acidified by the addition of mixture of acetic and hydrochloric acids to the tests.

the same color results as were obtained with the hydrochloric acid reagents and also seemed to effect greater permanency in the tint, as is indicated in Table 8. We found that slight variations in the amounts of reagents used made no perceptible differ-

NITROGEN CONTENT	1/2 HOUR AFTER MIXING	2 OR 3 HOURS AFTER MIXING
	Red Yellow Blue	Red Yellow Blue
1: 3,000,000	5.0 + 2.0 + 1.5	-0.7 -0.2 5.0 + 4.0 + 1.5
1: 5,000,000	5.0 + 1.6	-0.4 None 5.0 + 1.9
1: 10,000,000	4.0	None + 0.4 4.0
1: 12,000,000	3.0 + 0.2	None + 0.2
1: 14,000,000	1.0 + 1.8	None + 0.2
1: 16,000,000	1.0 + 1.5	None + 0.2
1: 18,000,000	2.0 + 0.1	None + 0.2
1: 20,000,000	1.9	None + 0.2

The second readings were identical with the first

ence in the color results, also that 50 cc. of the nitrite solution containing about half the quantity of reagents was always of the same color value as 100 cc. of the same solution containing the regular quantity of reagents. Making Lovibond readings of a few of the stronger nitrite solutions, we found that the strongest ones, particularly the one in which the nitrogen content was 1: 1,000,000, had to be read within 15 or 20 min. after mixing, although the ones to which both acetic and hydrochloric acids were added lasted longer than the others.

To study the effect of time on the tint produced, we repeated the experiment, using the acidified A. P. H. A. reagent, which we found the most satisfactory of the three. As solutions representing more than nitrogen 1: 3,000,000 were not permanent in color after two hours, the solutions read had strengths ranging from 1: 3,000,000 to 1: 20,000,000. The matching of the color of the nitrite tests with our standard colored fluids was not easy, since the color produced by the addition of naphthylamine and sulfanilic acid reagent to a solution of nitrite is in a class

by itself. In very dilute solutions it is a brilliant pink, while in stronger ones it is more like a shade of carmine. Since all of the nitrite tints have suggestions of blue or violet, none of the "Co-Fe-Cu" blends were like them. Fairly close matches were obtained with some of the "Co-Cro-Cu" fluids, and as a preliminary to matching, the appropriate blends of the standard N/50 "Co-Cro-Cu" fluids were diluted with water and then submitted to Lovibond readings.

These readings (Table 10) show that the color of some of the nitrite tests is very closely matched by some of the "Co-Cro-Cu" blends. Thus, the Lovibond reading for nitrogen 1: 18,000,000 in Table 9 is exactly the Lovibond reading of blend, "Co-Cro-Cu, 9-0-3, 40%" found in Table 10. Nitrite tests of other

"Co-Cro-Cu, 10-0-2"			"Co-Cro-Cu, 9-0-3"		
DILUTION	Red	Yellow Blue	DILUTION	Red	Yellow Blue
"20%"	1.5	None + 0.1	"20%"	1.3	None 0.2
"25%"	1.6	None + 0.1	"25%"	1.5	None 0.2
"30%"	1.9	0.2 None	"30%"	1.6 + 0.1	None 0.2
"35%"	1.9	0.1 0.1	"35%"	1.9	None 0.3
"40%"	2.0 + 0.2	None	"40%"	2.0 + 0.1	None 0.2
"45%"	2.0 + 0.3	None None	"50%"	1.0 + 1.8	None 0.3
"50%"	1.0 + 1.6 + 0.1	None None	"60%"	3.0 + 0.4	None 0.4
"60%"	2.0 + 1.3 + 0.1	None None	"70%"	4.0 + 0.2	None 0.4 + 0.1
"70%"	4.0 + 0.1	None 0.1	"85%"	3.0 + 1.8	None 0.7
"80%"	5.0 + 0.4	None 0.2	"100%"	5.0 + 1.3	None 0.7 + 0.1

strengths can also be matched as closely as this, as far as Lovibond readings are concerned, but, curiously, these fluids of equal Lovibond values do not necessarily match when compared in Blake bottles. When so compared the color quality does not appear to be the same, for a peculiar tinge which is characteristic of the nitrite test is lacking in the "Co-Cro-Cu" blends. For practical purposes of analysis, however, these matches would be entirely satisfactory, but for exact work they left something to be desired; we solved this difficulty by means of blends of the potassium permanganate and potassium dichromate standard colored fluids. These blends are not at all stable, and, as mentioned above, should be prepared freshly when needed. Preliminary to matching the color of these blends with the tints produced in the nitrite tests, we made Lovibond readings of them as soon as possible after mixing, read them again on the following day, and again on the third day.

Table 11 throws some light on the interesting character of these permanganate-dichromate blends. Because of their instability, we have so far employed them only when we found that the "Co-Fe-Cu" or "Co-Cro-Cu" blends did not furnish the desired shade of color. We hope, however, in the future to study them at greater length. At this time we merely point out that the results as shown in Table 11 proved that the blends required dilution before they would match the tints of the nitrite tests. These dilutions

MN-CR BLEND	READ SOON AFTER MIXING			READ 1 DAY AFTER MIXING			READ 2 DAYS AFTER MIXING		
	Red	Yellow	Blue	Red	Yellow	Blue	Red	Yellow	Blue
"1-11"	0.7 + 0.1	5.0 + 1.6	-0.5	0.7 + 0.1	5.0 + 1.6	-0.5	0.4 + 0.1	5.0 + 2.0	-1.0
"2-10"	1.0	5.0 + 0.7 + 0.1	-0.5	1.0 + 0.1	4.0 + 1.6 + 0.1	-0.5	1.0	5.0 + 1.6	-0.7
"3-9"	1.6	5.0 + 0.4 + 0.1	-0.2	1.6	4.0 + 1.6	-0.3	1.5	5.0 + 0.7 + 0.1	-0.5
"4-8"	2.0	5.0 + 0.1	-0.1	2.0 + 0.1	5.0 + 0.2	-0.3	1.9 + 0.1	5.0 + 0.1	-0.3
"5-7"	1.0 + 1.3	4.0	-0.1	1.0 + 1.5	4.0	-0.2	1.0 + 1.3	4.0 + 0.1	-0.3
"6-6"	1.8 + 1.0	1.8 + 1.0	-0.1	2.0 + 0.4	1.9 + 1.0	-0.6	1.6 + 1.0	3.0 + 0.2	-0.5
"7-5"	1.8 + 1.3	1.9 + 0.1	-0.1	3.0 + 0.2	2.0 + 0.2	-0.6	3.0 + 0.2	2.0 + 0.4 + 0.1	-0.4
"8-4"	2.0 + 1.6	1.3 + 0.1	-0.1	2.0 + 1.5	1.0 + 0.7	-0.4	3.0 + 0.4 - 0.2	1.9 + 0.1	-0.2
"9-3"	3.0 + 1.5	0.7	-0.1	4.0 + 0.4	0.7 + 0.1	-0.4	4.0 + 0.2	1.0	-0.4
"10-2"	5.0	0.1	None	5.0	0.4	-0.2	4.0 + 0.4	0.4 + 0.2	-0.3
"11-1"	5.0 + 0.4	-0.3	+0.1	5.0 + 1.0	-0.1	None	5.0	+0.2	None

were prepared by first making a blend from  $N/1000$  permanganate and  $N/100$  dichromate solution and then diluting to the desired intensity of color. The Lovibond readings appear in Table 12.

BLEND	DILUTION	Red	Yellow	Blue
"17-1"	"25%"	1.3	None	0.1
	"30%"	1.6	None	0.1
	"35%"	1.8	None	0.1 + 0.05
	"40%"	2.0 + 0.1	None	0.2
	"100%"	5.0 + 0.4	—0.4	0.1
"16-1"	"25%"	1.3	None	0.1
	"30%"	1.6	None	0.1
	"35%"	1.9	None	0.1
	"40%"	1.9 + 0.2	None	0.1
	"100%"	5.0 + 0.4 + 0.1	—0.4	0.1
"15-1"	"30%"	1.6	None	0.1
	"35%"	1.6 + 0.2	None	0.1
	"40%"	2.0 + 0.1	None	0.1
	"45%"	1.9 + 0.4	None	0.1
	"50%"	1.9 + 0.7	None	0.1
	"55%"	1.6 + 1.3	None	0.1
	"60%"	1.8 + 1.5 + 0.1	—0.1	0.2

Since the dilutions of the "Mn-Cr-15-1" blend seemed to us to be the best matches for the tint produced in the nitrite tests, we prepared four nitrite tests for final matches, using reagent No. 1 and obtained the Lovibond readings given in Table 13.

NITROGEN CONTENT	LOVIBOND	"Mn-Cr-15-1" MATCHES			
		Red	Yellow	1st Blue Observer	2nd Blue Observer
1: 20,000,000	1.8	None	None	0.1 "30%"	"30%"
1: 18,000,000	1.8 + 0.1	None	None	0.2 "35%"	"35%"
1: 14,000,000	2.0 + 0.2	None	None	0.2 "40%"	"45%"
1: 10,000,000	1.9 + 1.0 + 0.2	—0.2	None	"55%"	"55%"

Two observers independently matching as "unknowns" the colors obtained in these nitrite tests with the "Mn-Cr-15-1" dilutions, both sets being in Blake bottles, arrived at the concordant results given in Table 13.

Comparison of Tables 12 and 13 show clearly that matches in Blake bottles agree closely with those obtained by the Lovibond method. Curiously, however, there is rarely an absolute agreement between them, although the difference is within the limits of visual error.

### VANILLIN

We first tried the vanillin method given in *Bull. 107*, Bureau of Chemistry, U. S. Department of Agriculture; it may be outlined as follows: Fifty mg. of vanillin are dissolved in 25 cc. of alcohol and the solution is made up to 100 cc. with water; this solution, therefore, contains 1 part of vanillin in 2,000. Two cc. of this standard are diluted with 30 or 40 cc. of water, 3 or 4 drops of bromine water added and enough freshly prepared ferrous sulfate solution to produce a maximum bluish green color; thereupon enough water is added to make a total volume of 50 cc. This colored dilution, therefore, has a vanillin content of 1 : 50,000, and is supposed to be of the same tint as any other vanillin solution of the same strength prepared in the same way. We tried several solutions of various proportions of vanillin, and also treated them with varying amounts of reagents, but our experience with this test was highly unsatisfactory and we consider it unreliable.

We, therefore, confined ourselves to tests by this method of only two strengths of vanillin, 1 : 50,000 and 1 : 20,000, preparing the solutions from three different samples of vanillin which were on hand and

which are designated as Nos. 1, 2 and 3, in Table 14.

TABLE 14 LOVIBOND READINGS OF SOLUTIONS OF THREE SAMPLES OF VANILLIN

Sample No.	VANILLIN CONTENT	Readings taken 1/2 HOUR AFTER MIXING			2 OR 3 HOURS AFTER MIXING		
		Red	Yellow	Blue	Red	Yellow	Blue
1	1: 50,000	None	0.4 + 0.2	1.0 + 0.2	None	0.4 + 0.2	1.0 + 0.2
	1: 20,000	None	0.4 + 0.2	1.0 + 0.2	None	0.4 + 0.2	1.0 + 0.2
2	1: 50,000	None	0.4 + 0.2	1.0 + 0.1	None	0.4 + 0.2	1.0 + 0.2
	1: 20,000	None	0.4 + 0.2	1.0 + 0.3	None	0.4 + 0.2	1.0 + 0.3
3	1: 50,000	None	0.4 + 0.2	1.0 + 0.1	None	0.4 + 0.2	1.0 + 0.1
	1: 20,000	None	0.7	1.8 + 0.1	None	0.7	1.3 + 0.3

Endeavoring to see if solutions of three samples of equal strength would be of uniform color when all were treated in the same manner, we carried out one test of each solution in the two strengths 1 : 50,000 and 1 : 20,000. In each of these tests we used 4 drops of bromine water and 1 cc. of ferrous sulfate solution, excepting in the last test, when we used 5 drops of bromine water instead of 4. It is plainly seen that the vanillin tests produced uniformity of color, *only when identical amounts of reagents were used*, regardless of the amount of vanillin in solution. When the amount of bromine water was increased by only 1 drop, there resulted an increase in color value, as is shown by reading of sample No. 3, 1 : 20,000. The five tests that had been treated with 4 drops of bromine water and 1 cc. of ferrous sulfate solution were given to two observers as "unknowns" for the purpose of being arranged in the order of color intensity, but as all had the same tint, neither observer could tell which were the vanillin dilutions 1 : 20,000 and which the 1 : 50,000.

The effects of varying amounts of the reagents were then tested with the results given in Table 15,

TABLE 15—EFFECT OF VARYING AMOUNTS OF REAGENTS ON VANILLIN TESTS

TABLE 1. EFFECT OF VARYING AMOUNTS OF REAGENTS ON VANILLIN TESTS							
Drops Bromine Water	Ce FeSO <sub>4</sub> Solution	SHORTLY AFTER MIXING			1 OR 2 HOURS AFTER MIXING		
		Red	Yellow	Blue	Red	Yellow	Blue
VANILLIN SOLUTION 1 : 20,000							
5	1	None	0.7	1.6	0.2	0.7 + 0.1	1.5
6	1	None	0.7 + 0.1	1.0 + 0.7	0.2	1.0 + 0.1	1.9
7	1	None	1.0 + 0.1	2.0	0.2	1.0 + 0.1	1.9 + 0.2
5	2	None	0.7	1.6	0.2	0.7 + 0.1	1.5
6	2	0.2	0.7	1.6	0.2	0.7 + 0.1	1.0 + 0.7
7	2	0.2	1.0 + 0.1	2.0	0.2	1.0 + 0.1	2.0
VANILLIN SOLUTION 1 : 50,000							
5	1	None	0.6	1.0 + 0.1	None	0.6	1.0 + 0.1
6	1	None	0.6	1.0 + 0.2	None	0.6	1.0 + 0.1
7	1	None	0.6	1.0 + 0.2	0.2	0.6	1.3
5	2	None	0.6	1.3	None	0.6	1.3 + 0.1
6	2	None	0.6	1.3	0.1	0.7	1.6
7	2	None	0.6	1.3 + 0.1	0.2	0.7	1.0 + 0.7

which show that the intensity of color produced in the official vanillin test depends principally upon the amount of reagents used and not upon the amount of vanillin present. We, therefore, abandoned this method and turned to the one proposed by Folin.

FOLIN'S VANILLIN ASSAY—Directions for the preparation of the reagent used and for the manipulation followed in this assay were taken from *THIS JOURNAL*, 4 (1912), 670, and may be outlined as follows: The phosphotungstic-phosphomolybdic acid reagent used is made by placing in a flask with reflux condenser 100 g. pure sodium tungstate and 20 g. phosphomolybdic acid, followed by 100 g. 85 per cent phosphoric acid and 700 cc. water. The mixture is then boiled over the open flame during 1½ hrs. and is allowed to cool, after which it is filtered, if necessary, finally diluting to 1000 cc. with water. This solution has a vanillin content of 1 : 10,000. Five cc. of it are placed



in a glass-stoppered cylinder and 5 cc. of the phosphotungstic phosphomolybdic acid reagent are added. After mixing well and letting stand for 5 min. the fluid is diluted to 50 cc. with a saturated solution of sodium carbonate. After standing for 10 min., the blue color of the fluid, which contains 1 part of vanillin in 100,000, is observed.

We prepared standard solutions from two samples of vanillin. Each was diluted to three different strengths representing 1 : 100,000, 1 : 150,000, and 1 : 200,000, respectively. When these solutions were tested and read with the tintometer (Table 16) we found that the two original vanillin samples gave

TABLE 16—LOVIBOND READINGS OF FOLIN VANILLIN TESTS

VANILLIN CONTENT	SOLUTION No. 1			SOLUTION No. 2		
	Red	Yellow	Blue	Red	Yellow	Blue
1:200,000	0.3	0.2	2.0	0.3	0.3	1.9
1:150,000	0.4 + 0.2	0.4 + 0.1	1.6 + 1.0	0.4 + 0.1	0.4 + 0.1	1.5 + 1.0
1:100,000	1.0	0.7 + 0.05	3.0 + 0.7	1.0	0.7 + 0.1	2.0 + 1.5

the same color effects for equal strengths of dilution and that the color produced was proportional to the amount of vanillin present.

We found excellent color matches for these tests in blends from our *N*/50 "Co-Cro-Cu" standard colored fluids. These blends were then diluted and examined in the tintometer with the results given in Table 17.

TABLE 17—LOVIBOND READINGS OF *N*/50 "Co-Cro-Cu" BLENDS

BLEND	DILUTION	SOLUTION No. 1			SOLUTION No. 2		
		Red	Yellow	Blue	Red	Yellow	Blue
"2-2-8"	"50%"	0.2	0.2	1.0 + 0.4			
	"60%"	0.2 + 0.1	0.2	1.6			
	"70%"	0.2 + 0.1	0.2	1.9			
	"80%"	0.2 + 0.1	0.2	2.0 + 0.1			
	"90%"	0.2 + 0.1	0.2	1.5 + 1.0			
	"100%"	0.4	0.7	2.0 + 1.6			
"3-3-10"	"50%"	0.3	0.2	1.0			
	"55%"	0.3	0.2	1.0 + 0.05			
	"60%"	0.3	0.3	1.3			
	"70%"	0.3	0.3	1.6			
	"80%"	0.4	0.4	2.0 + 0.1			
	"90%"	0.4 + 0.1	0.4 + 0.1	2.0 + 0.4			
"2-2-10"	"100%"	0.4 + 0.1	0.4 + 0.1	1.9 + 1.0			
	"60%"	0.2	0.2	1.8			

Comparing the tests and the blends as "unknowns" in Blake bottles, we found that the vanillin dilution 1 : 100,000 matched the "Co-Cro-Cu" blend "3-3-10, 100%," that vanillin dilution 1 : 150,000 matched "Co-Cro-Cu" blend "2-2-8, 70%," and that vanillin dilution 1 : 200,000 matched "Co-Cro-Cu" blend "2-2-10, 60%." Second readings of the vanillin tests are not given, since the color, after half an hour, was so changed that the readings were worthless.

While the Folin vanillin test is more satisfactory than the Official Method, it leaves much to be desired. In either test, a slight variation in the amount of reagent added makes too great a difference in the color to permit it to be an accurate method of analysis. We believe the Folin test for vanillin to be a good one, but think it needs considerable experimental work before it can be called perfectly satisfactory.

#### URIC ACID

After experimenting on several proposed colorimetric tests for uric acid we found the most satisfactory one was that published by Riegler<sup>1</sup> in which phosphomolybdic acid is the reagent employed.

The standard solution was made by adding 0.1 g. of Kahlbaum uric acid to the same quantity of sodium bicarbonate and dissolving in water to make a total volume of 100 cc. This represented a uric acid con-

tent of 1 : 1,000. The test was carried out as follows: One cc. of the standard uric acid solution was mixed with 2 cc. of 10 per cent solution of phosphomolybdic acid in a glass-stoppered cylinder; after mixing thoroughly, 7 cc. of 5 per cent solution of sodium phosphate were added and then the well mixed liquid was diluted with water to make 30 cc., the uric acid content of the finished fluid being 1 : 30,000. We also made similar blue fluids containing uric acid, 1 : 40,000 and 1 : 50,000. The color produced in these tests was similar to that obtained in the vanillin tests, but much more permanent. It was no trouble to obtain a second reading with the tintometer after the lapse of 1 hr. The results of readings are given in Table 18.

TABLE 18—LOVIBOND READINGS

URIC ACID	Reading	SOLUTION No. 1			SOLUTION No. 2		
		Red	Yellow	Blue	Red	Yellow	Blue
1 : 50,000	1st	0.2	0.05	1.5 + 1.0			
	2nd	0.2	0.1	1.3 + 1.0 + 0.1			
1 : 40,000	1st	0.2	0.1	2.0 + 1.3			
	2nd	0.2 + 0.1	0.2	3.0 + 0.1			
1 : 30,000	1st	0.4 + 0.1	0.2 + 0.05	3.0 + 1.3			
	2nd	0.4 + 0.2	0.2 + 0.1	4.0 + 0.1			

Excellent color matches in Blake bottles were obtained for these tests with our standard "Co-Cro-Cu" colored fluids. The uric acid fluid 1 : 50,000 matched our blend of "Co-Cro-Cu, 2-2-8, 80%," the one diluted to 1 : 40,000 matched the straight *N*/50 blend of "Co-Cro-Cu, 2-2-8" without any dilution, while the one diluted to 1 : 30,000 had greater intensity of color than had the straight *N*/50 blend. We, therefore, prepared dilutions from our *N*/10 "Co-Cro-Cu" fluids and found a proper match for the uric acid 1 : 30,000 in a blend of "Co-Cro-Cu, 4-3-12, 30%," prepared from the *N*/10 standards.

As noted in some of the other tests, exact matches, when the fluids were viewed in Blake bottles, were not the same as the corresponding Lovibond readings. For comparison therefore we will state that the Lovibond readings of the "Co-Cro-Cu" matches were: *N*/10 "4-3-12, 30%"—red 1.0 + 0.2, yellow 0.4 + 0.1, blue 4.0; *N*/50 "2-2-8, 100%"—red 0.4, yellow 0.7, blue 2.0 + 1.6; *N*/50 "2-2-8, 80%"—red 0.2 + 0.1, yellow 0.2, blue 2.0 + 0.2.

#### SALICYLIC ACID

Colorimetric tests on solutions of salicylic acid were made according to directions given in *Bull.* 107, Bureau of Chemistry, U. S. Department of Agriculture. The standard solution is prepared by dissolving 0.1 g. of salicylic acid in 100 cc. of water, this representing a salicylic acid content of 1 : 1,000; 1 cc. of this solution is placed in a glass-stoppered cylinder and is diluted with water to 50 cc.; a few drops of ferric chloride solution (0.5 per cent) or ferric alum solution (2 per cent) are then added, and after mixing, the fluid takes on a bluish color suggestive of lavender. In experimenting with this test, we found that the ferric alum solution produced a deeper color than did the same amount of ferric chloride solution. This was to be expected, however, since a given amount of a 2 per cent ferric alum solution contains more iron than does the same amount of 1/2 per cent ferric chloride solution. In comparing tests of equal strength where the amount of metallic iron in each reagent used was

<sup>1</sup> *Z. anal. Chem.*, **51** (1912), 466.

equal, we obtained equal color values. To a solution containing salicylic acid 1 : 50,000 we added 9 drops of 0.5 per cent ferric chloride solution and compared the resulting color with that produced in a solution of the same salicylic acid content to which were added 4 drops of the 2 per cent ferric alum solution. The tints were exactly the same.

Desiring to determine the effects of various amounts of the ferric reagents on the salicylic acid reaction, Lovibond readings were taken as shown in Table 19.

TABLE 19 EFFECT OF VARYING REAGENTS ON SALICYLIC ACID TESTS									
FERRIC SOLN. Reagent	Drops	Salicylic Acid 1 : 50,000			Salicylic Acid 1 : 25,000			None	Blue
		Red	Yellow	Blue	Red	Yellow	Blue		
Alum.	4	2.0 + 0.1	0.1	0.7	3.0 + 1.8	0.1	1.6		
Chloride	4	1.6	None	0.4 + 0.1	2.0	0.1	0.7 + 0.1		
Chloride	9	2.0 + 0.1	None	0.7 + 0.1	3.0 + 1.8	0.1	1.6 + 0.1		

Finding that the color produced by the ferric chloride solution was more permanent than that of the ferric alum solution, we thereafter used only the former.

A standard solution was prepared from crystallized salicylic acid. A small quantity of this was dissolved in 1 cc. of alcohol and then diluted with water to 1 : 10,000. From this a 1 : 50,000 solution was prepared and to 50 cc. of the latter 9 drops of ferric chloride reagent were added. The Lovibond reading of the resulting fluid was: *red*, 2.0 + 0.1; *yellow*, none; *blue*, 0.7 + 0.1, which is exactly the same reading as that obtained from the standard solution of the other sample of salicylic acid, each test being of the same strength and treated with the same amount of the same reagent.

As subsequent tests showed that the minute quantity of alcohol present had no effect on the color results, we suggest that in preparing the salicylic dilution, the acid be dissolved in a small amount of alcohol, as directed above, in order to facilitate solution.

Two standard ferric chloride solutions of different strengths were then prepared—*N*/10 and *N*/20—and the colors produced on different volumes of salicylic acid solution 1 : 50,000 gave Lovibond readings as per Table 20. These figures suggested the use of

	TABLE 20					
	<i>N</i> /10 FERRIC	CHLORIDE	Blue	<i>N</i> /20 FERRIC	CHLORIDE	Blue
1 cc. in 50 cc.	2.0 None	0.7 + 0.1		2.0 None	0.7 + 0.05	
2 cc. in 50 cc.	2.0+ None	0.7 + 0.1		2.0 None	0.7 + 0.1	
1 cc. in 100 cc.	1.9 None	0.7 + 0.1		1.9 None	0.7 + 0.01	
2 cc. in 100 cc.	2.0 None	0.7 + 0.1		2.0 None	0.7 + 0.05	

1 cc. of *N*/10 ferric chloride reagent to 50 cc. of solution containing salicylic acid in tests of this kind, and we prepared to match the colors with our "Co-Cro-Cu" *N*/50 blends. Finding the "7-1-5" and "6-1-5" blends the best matches, these were diluted and examined in the tintometer with the results given in Table 21. Comparison of these results with those given in Table 19 shows that the "Co-Cro-Cu" blends

TABLE 21—LOVIBOND READINGS OF <i>N</i> 50 "Co-Cro-Cu" BLENDS									
DILUTION	"7-1-5" BLEND			"6-1-5" BLEND			None	Blue	
	Red	Yellow	Blue	Red	Yellow	Blue			
"60%"	1.8 + 0.1	None	0.4 + 0.1	1.6 + 0.2	None	0.4 + 0.2			
"65%"	2.0 + 0.1	None	0.4 + 0.1	1.9 + 0.1	None	0.7 + 0.1			
"70%"	2.0 + 0.2	None	0.4 + 0.2	2.0 + 0.2	None	0.7 + 0.2			

"7-1-5, 65%" and "6-1-5, 65%" have practically the same Lovibond readings as the colored fluids resulting from the salicylic acid dilution 1 : 50,000 being treated with the ferric chloride reagent, and

the identity in color of these three fluids was further established by matching as "unknowns" in Blake bottles.

### PHOSPHATES

We tried both phosphoric acid and sodium phosphate with the regular ammonium molybdate reagent used in qualitative analysis and studied the color produced. The standard phosphate solution represented a  $P_2O_5$  content of 1 : 2,000. To 5 cc. of this in a glass-stoppered cylinder were added 2 cc. of nitric acid and 4 cc. of a 5 per cent solution of ammonium molybdate and the mixture was then diluted with water to 50 cc. The finished fluid represented  $P_2O_5$  (1 : 20,000), and the color obtained was a pure yellow that was perfectly matched by our *N*/50 ammoniacal dichromate standard fluid diluted to "15%," *i. e.*, the color of a mixture of 15 cc. of the *N*/50 ammonium dichromate standard fluid and 85 cc. of water. The Lovibond reading of the  $P_2O_5$  solution (1 : 20,000) was: *red*, none; *yellow*, 1.0; and *blue*, 0.05, while that of the *N*/10 dichromate fluid ("15%") was: *red*, none; *yellow*, 1.0; and *blue*, 0.05. Solutions having a  $P_2O_5$  content of 1 : 10,000 were then tried with the same reagents, but the resulting solution became cloudy within 5 min. We then tried the test, using 4 cc. of nitric acid instead of 2 cc., but although the liquid remained clear, the color was lighter than it was in the previous tests with solutions have a  $P_2O_5$  content of 1 : 20,000. This is evidently another test in which exact quantities of reagent must always be employed.

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### THE GENERAL APPLICABILITY OF THE PAPER PULP FILTER TO QUANTITATIVE ANALYSIS<sup>1</sup>

By S. L. JODIDI AND E. H. KELLOGG  
Received February 21, 1916

In the course of an investigation into the chestnut blight disease the authors have made a number of phosphoric acid estimations of various chestnut barks according to Neumann's method. The latter was shown to yield somewhat inaccurate results because of the too low<sup>2</sup> factor used for calculating the phosphoric acid, the inaccuracy being due in part to the influence of the water<sup>3</sup> used for washing the ammonium phosphomolybdate precipitate. Inasmuch as the difficulties encountered in the filtration and washing of the yellow precipitate on a folded paper filter, as recommended by Neumann, were successfully overcome by the employment of the pulp<sup>4</sup> filter which was also found suitable for the filtration of calcium oxalate<sup>5</sup> and magnesium ammonium<sup>6</sup> phosphate, it was natural to suppose that the pulp filter may be generally applicable to quantitative analysis. This is actually the case, as will be seen from the data presented in this paper.

<sup>1</sup> Published by permission of the Secretary of Agriculture

<sup>2</sup> S. L. Jodidi, *J. Am. Chem. Soc.*, **37** (1915), 1708.

<sup>3</sup> S. L. Jodidi and E. H. Kellogg, *J. Frank. Inst.*, **180** (1915), 349

<sup>4</sup> S. L. Jodidi and E. H. Kellogg, *Biochem. Bull.*, **4** (1915), 87-94; see also *J. Am. Chem. Soc.*, **27** (1905), 287.

<sup>5</sup> S. L. Jodidi and E. H. Kellogg, *J. Frank. Inst.*, **181** (1916), 21.



## PAPER PULP USED FOR FILTRATION

If not otherwise stated, the paper pulp applied to the quantitative estimations given in this paper was prepared as follows: S. & S. filters (No. 590—from 9 to 12.5 cm. in diameter) were cut to pieces and placed in a strong round bottomed flask into which distilled water was poured, allowing 100 to 150 cc. for each filter added. The flask was now tightly stoppered with a rubber stopper and the whole vigorously shaken for a minute or two, when a pulp was obtained which was ready for immediate use. To prepare a pulp filter, a Gooch crucible placed in a suction flask (as in the case of an asbestos filter) is filled with the pulp emulsion, whereupon gentle suction is applied until all of the water is filtered off, when the suction is interrupted. The filling with the pulp emulsion, etc., is repeated once and, if necessary, twice.

For practical reasons we applied the pulp filter to the estimation of those bases and acids which the analyst and investigator alike are frequently called upon to determine. The strengths of solutions used and the results obtained appear in Table I.

TABLE I COMPARISON OF RESULTS OBTAINED WITH ORDINARY PAPER FILTERS AND PAPER PULP FILTERS

A—BaCl <sub>2</sub> ·2H <sub>2</sub> O—2 g. dissolved in water and made up to about 100 cc. B—Solution A diluted with about an equal volume of water. C—AgNO <sub>3</sub> —1 gram in 1 liter of water. D—Solution C diluted with about an equal volume of water. E—KCl—1 gram in 100 cc. of water. F—A 0.5 per cent solution of NH <sub>4</sub> Cl in water. G—N/5 H <sub>2</sub> SO <sub>4</sub> . H—N/5 HCl.					
Ten cc. portions of the above solutions were used except in the case of the silver nitrate (C), of which 200 cc. portions were taken.					
ESTIMATION	No.	Filter Used	Found Gram	Calculated Gram	
Barium as BaSO <sub>4</sub> .....	A1	Paper (a)	0.1878		
	A2	Pulp (a)	0.1886		
	A3	Pulp (a)	0.1883		
	B1	Paper (a)	0.0944		
	B2	Pulp (a)	0.0944		
	B3	Pulp (b)	0.0952		
Silver as AgCl.....	C1	Paper	0.1645		
	C2	Pulp	0.1641		
	D1	Paper	0.0942		
	D2	Paper	0.0945		
	D3	Pulp	0.0948		
	D4	Pulp	0.0943		
Potassium as K <sub>2</sub> PtCl <sub>6</sub> ..	E1	Paper	0.3257	0.3258	
	E2	Paper	0.3262	...	
	E3	Pulp	0.3259	...	
	E4	Pulp	0.3248	...	
	E5	Pulp	0.3253	...	
	E6	Pulp	0.3242	...	
Ammonium as (NH <sub>4</sub> ) <sub>2</sub> PtCl <sub>6</sub> .....	F1	Paper	0.2105		
	F2	Paper	0.2098		
	F3	Pulp	0.2095		
	F4	Pulp	0.2096		
Sulfuric acid as BaSO <sub>4</sub> ..	G1	Paper	0.2322	0.2334	
	G2	Paper	0.2316	...	
	G3	Pulp	0.2334	...	
	G4	Pulp	0.2333	...	
Hydrochloric acid as AgCl.....	H1	Paper	0.2858	0.2866	
	H2	Paper	0.2859	...	
	H3	Pulp	0.2856	...	
	H4	Pulp	0.2863	...	

(a) Filtrate clear.

(b) Filtrate cloudy, was refiltered.

BARIUM was precipitated as barium sulfate which was treated in the ordinary<sup>1</sup> way and filtered through an S. & S. filter, No. 590. In two portions in which the barium sulfate was obtained, as usual, the supernatant liquid was only once decanted on a Gooch provided with a pulp filter, when the barium sulfate was treated in the beaker with about 100 cc. of boiling hot water, and the whole quantitatively filtered and washed on the pulp filter. The Gooch crucible was

now placed in a somewhat larger platinum crucible (with which it was previously ignited, cooled and weighed) and the barium sulfate containing pulp filter was directly heated over the burner, at first cautiously to remove the moisture, then gradually increasing the flame until the pulp filter was completely burned. As the barium sulfate is hereby reduced in part to barium sulfide it is necessary to heat the precipitate in the inclined crucible for some time until it is oxidized again to barium sulfate, which is finally heated a few more minutes in the covered crucible.

From the concordant results obtained with good filter paper, on the one hand, and paper pulp on the other, it follows that the pulp filter quantitatively retains the barium sulfate precipitate despite the fact that its filtration and washing on the pulp filter takes but 10 min. as against 35 min. required for the repeated decantation, filtration and washing of the barium sulfate on a paper filter.

SILVER—In one portion of the solution the silver was estimated according to the standard<sup>1</sup> method, the silver chloride having been filtered on filter paper. In another equal portion the silver chloride obtained as above was determined as follows: A Gooch crucible placed in a suction flask was provided with a pulp filter as already described, the latter having been washed with distilled water until paper fiber no longer came through. Ordinarily, washing the pulp filter with from 300 to 500 cc. of distilled water suffices for this purpose. The Gooch crucible is now placed in a weighing bottle and dried to constant weight at 100° C. Next the crucible is placed in the suction flask and the silver chloride precipitate, after having settled, is stirred up with the supernatant liquid and the whole quantitatively filtered and washed on the pulp filter. The crucible containing the precipitate is now dried in the weighing bottle to constant weight at 100°, the increase in weight representing the silver chloride present. From the results in Table I it is evident that the pulp retains silver chloride completely. The filtration and washing of the silver chloride on paper pulp takes from 8 to 15 min. as against 30 to 40 min. required by the paper filter.

POTASSIUM was precipitated in the form of its chlorplatinate, which was filtered on filter paper and otherwise treated in accordance with the standard<sup>2</sup> method, with the only difference that the final potassium platonic chloride obtained was dried to constant weight at 130° C., instead of at 160°. In four portions of the solution, in which the potassium platonic chloride was obtained as above, the precipitate on receiving a few cc. of 90 per cent alcohol was carefully broken up into a fine powder which was allowed to settle, whereupon the supernatant liquid was decanted but once on a Gooch provided with a pulp filter. Now at least from 10 to 20 cc. of alcohol were added to the precipitate which was well stirred up with the alcohol, and the whole quantitatively filtered and washed

<sup>1</sup> Treadwell's "Analytical Chemistry," Vol. II (1907), p. 240; Fresenius' "Quantitative Analysis," Vol. I (1903), p. 298.

<sup>2</sup> Treadwell's "Analytical Chemistry," Vol. II (1907), pp. 41-2.

<sup>1</sup> Treadwell's "Analytical Chemistry," Vol. II (1907), p. 69. See also Fresenius' "Quantitative Analysis," Vol. I (1903), p. 229.

with alcohol on the pulp filter. The precipitate was now completely dissolved out by means of some boiling hot water into a weighed platinum dish, evaporated to dryness on the water bath at low temperature and finally dried at 130° C. to constant weight.

Examination of Table I shows that the decantation, filtration and washing of the chlorplatينات on paper pulp yielded results as accurate as those obtained with filter paper. When we consider that the work with the pulp filter is easier and more convenient than with the paper filter and that one decantation (which is here sufficient) together with the filtration and washing of each individual potassium platonic chloride precipitate on a pulp filter takes but 15 min., instead of from 40 to 50 min. required for the repeated decantations, filtrations and washings of the chlorplatinate on a paper filter, it is fair to state that the pulp filter is superior to the paper filter. This holds good not only for the separation of potassium platonic chloride, but also for the separation of the other precipitates treated in this paper.

AMMONIUM can be determined in a variety of ways, but its precipitation as chlorplatinate affords a quick and convenient means for ascertaining whether a substance contains, in addition to ammonia, organic volatile bases which may be present under certain conditions in vegetable and animal materials, in soils, etc. The organic chlorplatينات behave very much like ammonium platonic chloride, but differ from the latter in their platinum<sup>1</sup> content the more, the larger their molecule is.

The precipitation of ammonium platonic chloride and its treatment was accomplished essentially as described in the estimation of potassium as chlorplatinate. The results show that the pulp filter quantitatively retains the precipitate in spite of quite rapid filtration.

SULFURIC ACID—In order to be in a position to check up the gravimetric analyses we have used in each of the four estimations 10 cc. of carefully prepared *N*/5 H<sub>2</sub>SO<sub>4</sub> which on dilution was, in the presence of some hydrochloric acid, precipitated with an excess of boiling hot barium chloride solution. The decantation, filtration and washing of the barium sulfate precipitates (after they had settled on the water bath) either on paper filters or on pulp filters, as well as their further treatment, were executed exactly as described in the estimation of barium as sulfate.

HYDROCHLORIC ACID—This determination was suggested by the fact that the silver chloride obtained by precipitating a silver solution with excessive hydrochloric acid is somewhat different in its behavior from the silver chloride resulting from the precipitation of a chloride with an excess of silver nitrate solution. In order to have a check for the gravimetric analyses we used in each of the estimations 10 cc. of carefully prepared *N*/5 HCl which was diluted prior to its treatment in the cold with an excess of silver nitrate solution containing some free nitric acid. The further

treatment of the heated silver chloride precipitates, after they had been allowed to settle, was exactly as outlined in the estimation of silver as chloride.

The concordance of the analytical results, as well as their agreement with the theoretical value, proves that the pulp filter is very well adapted for the quantitative determination of sulfuric acid as barium sulfate or of hydrochloric acid as silver chloride.

#### CONCLUSIONS

I—The application of the pulp filter to the quantitative estimation of barium and sulfuric acid as barium sulfate, of silver and hydrochloric acid as silver chloride, and of potassium and ammonium as chlorplatينات, has been shown to give results as accurate as those obtained with standard filter paper.

II—The pulp filter which is convenient and easy to handle, when applied to the quantitative determination of the above acids and bases, enables one to save considerable time and labor.

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### THE FORMOLITE REACTION OF NASTUKOFF AS APPLIED TO OIL RESIDUALS AND NATURAL ASPHALTS

By CLIFFORD RICHARDSON

Received January 8, 1916

Nastukoff<sup>1</sup> has investigated the results of the reaction between lubricating oils derived from petroleum with formaldehyde and sulfuric acid as a means of differentiating them. He denominated the resulting product "Formolite" and determined the percentage obtained from oils of various origin. He has not extended his investigations to the heavier, more viscous and solid native bitumens which now have a constant application in the industries as, for instance, in the construction of asphalt pavements, in waterproofing, etc. It seemed to the writer that this formolite reaction might serve as a means of characterizing and differentiating these asphaltic materials in a satisfactory way.

The reaction as explained by Nastukoff involved the precipitation of a certain class of unsaturated hydrocarbons in the oils in the form of amorphous compounds through the action of sulfuric acid and formaldehyde upon them. In the method as originally presented, one part of the petroleum product is treated with one and a half or two parts by volume of concentrated sulfuric acid and then with one volume of 40 per cent formalin. The resulting brown precipitate is washed free from the reagents and from the oil not acted upon and then dried and weighed; the figure thus obtained, when multiplied by the factor 0.8, gives the *formolite number* of the material examined.

This method was tried out upon a heavy liquid petroleum residual of 0.962 gravity. The vigorous action of the acid, however, carbonized the material, so that no further action by the formalin was possible. In order to reduce the action of the acid, the residual was then dissolved in various solvents: carbon tetra-

<sup>1</sup> While (NH<sub>4</sub>)<sub>2</sub>PtCl<sub>6</sub> has 43.93 per cent Pt, the chlorplatينات of methylamine, ethylamine and triethylamine, *e. g.*, have 41.32, 39.01 and 31.86 per cent Pt, respectively

<sup>2</sup> J. Russ. Phys. Ges., 36 (1904) 881, J. Soc. Chem. Ind., 23 (1904), 1082.



chloride, carbon disulfide and chloroform. In these solvents the residuals gave upon reaction with sulfuric acid and formalin a heavy emulsion which it was impossible to break up so that the formolite could be separated from it.

The residual was next dissolved in light naphtha, which had been previously treated with strong sulfuric acid, and this solution (from which the insoluble portions had been removed), representing one gram of the material to be examined in 10 cc. of solvent, was then treated in a 250 cc. beaker with 10 cc. of concentrated sulfuric acid dropped in slowly from a burette, the solution being violently stirred at the same time; 3 cc. of 40 per cent formalin were then added slowly from a burette with constant stirring, and the solution allowed to stand for 30 min. It was then diluted with 100 cc. of water, made alkaline with ammonia and the precipitate filtered out with the aid of a vacuum pump, washed with water and with light naphtha and dried over sulfuric acid. It was found, however, that there was as large a difference as 5.5 per cent in duplicate analyses, due to the fact that the thorough washing of the precipitate was impossible, as it retained some sulfuric acid, and it was further demonstrated that the action of the acid and formalin was incomplete, an additional amount of formolite being obtained upon repeating the operation upon the oil.

An attempt was then made to apply a modification of the formolite reaction as described by Marcusson<sup>1</sup> for the differentiation and characterization of lubricating oils, but with the substitution of paraformaldehyde in fine powder for the liquid aldehyde. It was again found that the reaction by this method was incomplete and that an additional precipitate was obtained by successive treatment which rendered it useless as applied to such materials as were being examined, probably due to the large amount which was originally taken for the purpose. The method was, therefore, modified by using a-naphtha solution of only one gram of the bitumen to be examined. This solution was concentrated to the volume of 10 cc. after the removal of the insoluble portion. This was placed in a glass-stoppered bottle immersed in ice water while 10 cc. of concentrated sulfuric acid were gradually added from a burette, the solution being agitated with continual refrigeration, in the course of a minute, and shaken violently for 5 min. to insure complete action by the acid, the bottle being reimmersed in ice water if it became warm, and carefully opened from time to time to relieve pressure. After thoroughly cooling, 1 g. of finely powdered paraformaldehyde was introduced with agitation in the course of a minute. The bottle was then opened, the neck and stopper washed with a little sulfuric acid and allowed to stand for 30 min. at room temperature. It was again cooled in ice, 100 cc. of cold distilled water added and again shaken. Finally, the acid was neutralized with strong ammonia in excess and the mixture allowed to stand for several hours in order

to bring about complete neutralization of the acid retained by the formolite particles. The liquid and formolite were then poured on a 10 cm. Buchner funnel fitted with a double thick filter paper, allowed to stand for a short while to permit the formolite to rise to the surface, drained with suction and washed with water to remove ammonia and salts and then with 88° naphtha to remove the oil not acted upon. The filter paper and the material retained by it were then transferred to an oven and dried at 110° C. for an hour. The impure formolite was then removed from the paper and ground up with 88° naphtha to free it from residual oil. It was washed into a weighed Gooch crucible, again treated with naphtha and also with alcohol and water to remove soluble salts. It was then dried in an oven at 110° C. for 30 min. If a considerable quantity of formolite adhered to the filter paper it was dissolved in aniline from which it was reprecipitated by dilute hydrochloric acid and added to the precipitate first obtained.

By this method concordant results were first obtained upon a cylinder oil and then upon a Trinidad residual pitch, but they were not entirely satisfactory, while the manipulation called for is rather complicated.

MATERIAL	FORMOLITE			
	I	II	III	IV
Cylinder oil.....	26.0	26.8	26.2	
Trinidad residual (97° Pen.)..	82.2	83.1	81.6	81.7

It was suggested by the writer that the method could be more satisfactorily carried out by collecting and weighing the residual oil which was unacted upon. The formolite precipitate, obtained as previously described, and the filter paper holding it was, therefore, placed in a paper thimble and extracted for several hours with naphtha and combined with the naphtha solution obtained in the original washing. This naphtha solution was concentrated by distillation. The last of the solvent was removed by placing a flask containing it in an air bath at 100° C. for 30 min., a slight suction carrying off the vapor. The amount of residual oil thus obtained represents that portion of the material examined which was unacted upon by the formalin and acid. The results of triplicate determinations were satisfactorily concordant, as shown by the following data:

MATERIAL	RESIDUAL OIL FROM FORMOLITE REACTION			
	PER CENT	I	II	III
Cylinder residual	Residual oil.....	80.1	80.0	79.8
	Formolite (by diff.)..	19.1	20.0	20.2
Trinidad residual (97° Penetration)	Residual oil.....	34.2	34.4	34.1
	Formolite (by diff.)..	65.8	65.6	65.9

In view of these results a series of determinations was made upon six bituminous materials representing distinct types of asphalt and oil residuals of nearly the same consistency, the ordinary characteristics of which had been determined by standard methods of analysis. The results appear in Table I. The data show the percentage of saturated hydrocarbons unacted upon by ordinary and fuming sulfuric acids in the asphalts of various origin and of that unacted upon by sulfuric acid and paraformaldehyde. The results sharply differentiate the products derived from petroleum originating in different localities, and,

<sup>1</sup> "Mittheilungen aus dem Königlichen Materialprüfungsamt," 1913, p. 301.

TABLE I

MATERIAL	Penetration	Naphtha-Soluble Bitumen (Pure Basis)	PER CENT By Ordinary $\text{H}_2\text{SO}_4$	SATURATED HYDROCARBONS By Fuming $\text{H}_2\text{SO}_4$	PER CENT UNSATURATED HYDROCARBONS — Amount Removed by			
					Fuming over Ordinary $\text{H}_2\text{SO}_4$	$\text{H}_2\text{SO}_4 + (\text{HCOOH})_2$ over Fuming $\text{H}_2\text{SO}_4$	Total over Ordinary $\text{H}_2\text{SO}_4$	
Texas residual.....	20°	64.3	44.5	37.5	35.8	7.0	+1.3	8.3
California residual.....	22°	65.0	40.1	38.2	33.0	1.9	+5.2	7.1
Mexican residual.....	22°	72.2	37.5	31.3	25.2	6.2	+6.1	12.3
Trinidad residual.....	23°	73.1	32.7	28.4	24.0	4.3	+4.4	8.7
Bermudez refined asphalt.....	17°	71.9	28.3	22.6	21.1	5.7	+1.8	7.2
Trinidad refined asphalt.....	4°	64.9	23.7	22.3	22.7	1.4	—0.5	

again, the native asphalts from these. It appears that the more thoroughly asphaltic a bitumen is the smaller the amount of saturated hydrocarbons it contains, as evidenced by the residue left by the treatment of the total bitumen, not only with sulfuric acid and paraformaldehyde but likewise with fuming acid and even with concentrated sulfuric acid. In view of these facts it hardly seems necessary to extend, for the purpose of differentiating bitumen of this type, the treatment to the use of formaldehyde since they are, essentially, as well differentiated by the use of ordinary and fuming sulfuric acid.\* The differentiation by means of the formolite reaction is, however, of great value as confirming our previously conceived ideas that the more satisfactory form of bitumen, from its consideration as a cementing material, is the one containing the smaller proportions of saturated hydrocarbons.

The native or natural asphalts from the Trinidad and Bermudez deposits consist largely of unsaturated hydrocarbons, followed by the Trinidad residual pitch, whereas the residuals prepared from Mexican, California, and Texas oils contain very much higher percentages of saturated hydrocarbons, from which fact, in the light of practical experience, the deficiencies of the artificial asphalts in their industrial behavior, as demonstrated by service tests, may be considered to be satisfactorily explained.

The results here presented, as far as they relate to the amount of saturated compounds unacted upon by ordinary sulfuric acid for the various materials, may be compared with an earlier study of the same subject by the writer, the results of which were published in the *Engineering Record* of April 26, 1913. The comparison is shown by the following figures:

PER CENT OF MATERIALS UNACTED UPON BY ORDINARY  $\text{H}_2\text{SO}_4$ 

Year	Tex. Oil	Cal. Oil	Mex. Oil	Trinidad Asphalt	Bermudez Asphalt	Trinidad Refined Asphalt
1913.....	48.1	30.0	33.4	24.6	24.0	24.4
1914.....	44.5	40.1	37.5	32.7	28.3	23.7

From the earlier results the same conclusions can be and were drawn as to the nature of these materials as from the present data. The two show considerable differences, except in the case of the Trinidad refined asphalt. This may be accounted for by the fact that all oil products are extremely variable in character, owing to the variations in the character of the petroleum from which they are prepared and of the lack of regularity in the processes by which the preparation is carried out. The Trinidad asphalt alone, being a substance of a very uniform character, would be expected, as it does, to give uniform results, when examined at intervals.

In conclusion, the writer desires to thank Dr. Philip

Schneeberger, who has efficiently carried out the laboratory work which has supplied the data for this paper.

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### THE DETERMINATION OF CARBON IN STEELS AND IRONS BY DIRECT COMBUSTION IN OXYGEN AT HIGH TEMPERATURES<sup>1</sup>

By J. R. CAIN AND H. E. CLEAVES

Received January 6, 1916

The influence of temperature on the results obtained by the direct combustion of steel and iron in oxygen has been frequently investigated<sup>2</sup> and the general consensus of opinion seems to be that higher results for carbon are obtained with higher combustion temperatures. This conclusion, however, is rendered doubtful by a number of circumstances:

(1) Quite frequently, because of uncertainties in blanks, it is impossible to conclude whether the difference in results claimed is due to variation in blank or is real.

(2) The published work does not indicate that investigators have always assured themselves that the material used to support the drillings or that the fluxes sometimes used are completely free from carbon.

(3) Differences in carbon results with the same steel are frequently due to a variation in the size of drillings used.

Combustions of steel are ordinarily made in such a way that the oxides are in the fused condition for only a very short time: this is evident from work done here, which shows that the fusion point of the oxides themselves is above 1450° C.,<sup>3</sup> and that as soon as the fused material has combined with or permeated the bed material the melting point of the combination becomes much higher. The temperature of a combustion furnace as ordinarily operated does not exceed 1200° and usually lies between 950° and 1100°; hence it is evident that the oxides from 1 or 2 g. of steel must solidify very rapidly after the combustion period is over, for it is only during this time that the temperature is above the melting point of the oxides. Burning in the ordinary way, if the sample consists of very large particles, there is always the danger of incomplete combustion of all its parts; on the other hand, if the particles are very small the combustion may proceed so rapidly as to cause initial fusion of a portion of the oxides followed by quick solidifica-

<sup>1</sup> This paper is an amplification of a preliminary paper on this subject by the same authors. See *J. Wash. Acad. Sci.*, **4**, 1914, 893.

<sup>2</sup> See Lorenz, *Z. anorg. Chem.*, **6**, 313, 395, 411, 648, and Foerster, *Z. anorg. Chem.*, **8** (1895), 274, for work at high temperatures; for references to work at other temperatures, see article by Mueller and Diethelm, *Z. anorg. Chem.*, **27** (1910), 2114.

<sup>3</sup> By G. K. Burgess and R. G. Waltenburg, unpublished



tion of the fused part with resultant enclosure of yet unburned metal. There is some chance, too, that carbon dioxide or monoxide may be enclosed in the solidified mass, and that with certain alloy steels, difficultly oxidizable carbides (silicon, tungsten, chromium) may escape oxidation except at very high temperatures.

A consideration of these facts, together with previous experimental work here and elsewhere, which showed that oxides from apparently well-burned samples yielded additional carbon upon being finely pulverized and reburned, led to the development of the present method, in which the sources of error cited in the first paragraph are eliminated. The object of this work was to develop a procedure which would give the best possible chance for oxidation and liberation of all the carbon in the sample, regardless of the original size of drillings, and especially to ascertain by such method the order of the error, if any, which affected the carbon determinations reported on the certificates for the Bureau's series of standard analyzed irons and steels. The latter determinations were made as usual, either by direct combustion of the metal at temperatures of  $950^{\circ}$  to  $1200^{\circ}$ , or else by burning the carbon residue left after solution of the steel or iron in a suitable solvent.<sup>1</sup> Briefly, our method consisted in burning the metal directly in oxygen within the usual temperature range, then raising the temperature to a point above the fusion point of the oxides and maintaining this temperature long enough to insure that all parts of the sample had been brought in contact with oxygen or fused iron oxide. The sample was burned directly on platinum (with precautions described later) so that no carbon could be obtained from the support for the drillings; the carbon was estimated by the barium carbonate titration method devised by one of the authors,<sup>2</sup> and in such way that the blank was negligible.

It seemed first desirable to know whether carbon dioxide or monoxide were left enclosed in the oxides produced during the direct combustion process as ordinarily carried out. To determine this there was used an apparatus consisting of an evolution flask connected to a suitable purifying train followed by absorption tubes for carbon dioxide and monoxide.<sup>3</sup> In the evolution flask there was placed a large excess of concentrated hydrochloric acid together with the uncrushed oxides resulting from the combustion in the ordinary way (on pure alundum) of twenty-two 2-g. samples of steels known to yield carbon upon reburning after pulverizing. Boiling the contents of the flask for several hours resulted in complete solution of everything except the mechanically held alundum, and during this time a current of air purified from carbon dioxide and monoxide was passed through the apparatus. The carbon dioxide found in the absorption tube was 0.00104 g., which would correspond to 0.0007 per cent carbon on the basis of 44 grams of metal taken; the absorption tube for carbon

monoxide showed none of this gas to be present. It seems fair to conclude from this experiment that any error in ordinary combustions resulting from occlusion or inclusion of carbon dioxide or monoxide is quite negligible. The case might be different where silica is used as supporting material for drillings and there is consequently the possibility of forming viscous, slowly solidifying slags which might well retain large bubbles of gas. It should be noted in this connection that immediately after the combustion of metal has ceased the partial pressure of carbon dioxide and monoxide inside the combustion tube reaches a maximum because the incoming oxygen has been almost completely consumed by the metal, leaving but little excess to sweep on the products of combustion; the oxides begin to freeze very soon after, and, accordingly, conditions are then very favorable for retention of carbon dioxide or monoxide by the solidifying oxides. However, as stated, when non-viscous, quickly solidifying oxides result, as in our experiment, the error from this cause may be regarded as negligible.

For carrying out combustions under the conditions selected by us—initial temperatures of  $1050^{\circ}$  to  $1100^{\circ}$  followed by temperatures above  $1450^{\circ}$  and burning the metal directly supported on platinum—it was necessary either to start with low temperatures and

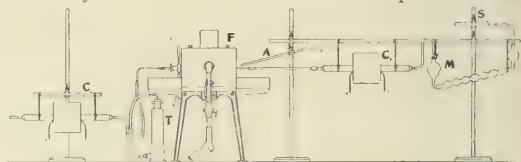


FIG. 1—DETAILS OF APPARATUS

C<sub>1</sub> and C<sub>2</sub>, porcelain tubes filled with copper oxide and wound with nichrome wire for heating; T, tower filled with stick KOH; F, gas furnace; A, tube for air-cooling; M, Meyer bulb; S, soda-lime guard-tube

slow oxygen current, increasing both as the skin of oxide on the grains became thick enough to protect the platinum, or else to burn initially in a furnace kept at the lower temperatures and then transfer the boat and contents to the high-temperature furnace. The first method was carried out in the gas furnace shown in Figs. I and II;<sup>1</sup> the second procedure was used with our usual nichrome-wound furnaces in conjunction with the platinum-wound furnace shown in Fig. III. In view of the failure to find notably higher results by our method (as will appear later) we did not deem it worth while to proceed to the next obvious step in apparatus—the construction of a single electric furnace suitable for both stages of the combustion. The electric furnace method is very much to be preferred. The required temperatures are reached and maintained with much greater regularity and convenience than when gas is used, the wear on the platinum is less and the chance for error from extraneous carbon dioxide is eliminated. The gas furnace is very destructive in its effects on the combustion tube; the boats seem to suffer very little by either method. If, however, the operation of the gas furnace is conducted carelessly so that the temperature initially is caused to rise too rapidly and the fusion tempera-

<sup>1</sup> Reproduced from our first paper on high temperature carbon combustions, above cited.

<sup>1</sup> In a few cases certificate results include the carbon obtained from reburning the oxides.

<sup>2</sup> J. R. Cain, Bur. of Standards, *Tech. Paper*, 33; *THIS JOURNAL*, 6 (1914), 465.

<sup>3</sup> Both palladium chloride and iodine pentoxide tubes were used.

ture of the oxides is reached before all the iron is burned, then a boat is soon destroyed by alloying with iron; this is also the case if the combustion of metal is incomplete in the first electric furnace when using that method. Temperatures were measured with a Wanner optical pyrometer and with a platinum-iridium thermoelement in conjunction with a millivoltmeter. The low temperature electric furnace

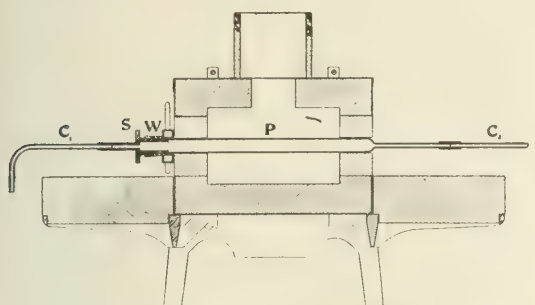


FIG. II—CROSS-SECTION OF GAS FURNACE

P, platinum tube; W, water-cooled jacket of German silver; S, stopper, German silver; C<sub>1</sub> and C<sub>2</sub>, copper tubes soldered to the platinum tube

was maintained at 1050° to 1100°, the high temperature electric furnace at 1475°; the gas furnace was started from room temperature and raised gradually to 1525°, at which temperature it was held during the fusion period. The copper oxide catalyzer following the furnace was found absolutely necessary when using the gas furnace, otherwise very large amounts of carbon monoxide were produced and escaped absorption; the low temperature electric furnace

was effected; then the temperature was raised to 1050° or 1100° and the combustion of the iron completed. As soon as absorption of oxygen by the burning metal had ceased the blow-pipe flame was turned on full, this stage of the combustion being continued 25 to 30 min. The Meyer tube was disconnected and the determination finished by filtering off and washing the precipitated barium carbonate and titrat-

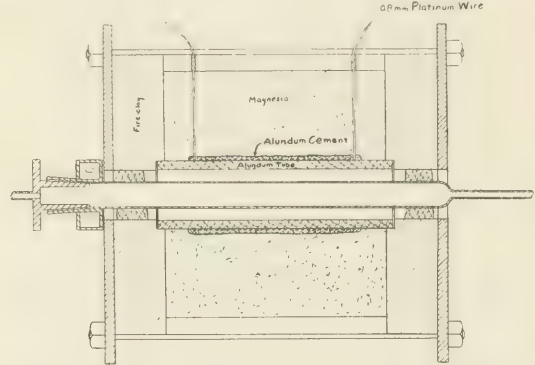


FIG. III—CROSS-SECTION OF ELECTRIC FURNACE FOR HIGH TEMPERATURES

ing it against standard acid as described in the cited paper on this method. The procedure when using the electric furnace method was to place the boat containing the sample in the already heated nichrome furnace, starting with a very slow current of oxygen, increasing gradually to the rate usually maintained and holding this condition until all the metal was burned and the carbon dioxide swept out of the combustion tube. Then the connection of the Meyer tube was

TABLE I—RESULTS ON CARBON IN BUREAU OF STANDARDS STANDARD IRONS AND STEELS

												Difference between average and certificate per cent	
Description and B. S. No. of Sample		Certificate value for C Average of all methods			PER CENT CARBON OBTAINED BY COMBUSTION AT HIGH TEMPERATURES Individual results obtained by Authors								Average
BESSEMER													
0.1% C No. 8a	0.084	0.088	0.086	0.088	0.086	0.086	...	...	...	...	0.087	+0.003	
0.4% C No. 10b	0.373*	0.370	0.371	0.374	0.374	...	...	...	...	...	0.372	-0.001	
0.8% C No. 23	0.805	0.806	0.800	0.805	0.805	0.804	0.809	0.805	0.804	0.805	0.805	0.000	
B. O. H.													
0.1% C No. 15a	0.111	0.116	0.116	0.118	0.116	0.118	...	...	...	...	0.117	+0.006	
0.4% C No. 12a	0.364	0.379	0.379	0.376	0.376	0.379	...	...	...	...	0.378	+0.014	
0.8% C No. 14a	0.815	0.816	0.819	0.816	0.816	0.812	...	...	...	...	0.816	+0.001	
A. O. H.													
0.2% C No. 19a	0.207	0.218	0.214	0.218	0.214	...	...	...	...	...	0.216	+0.009	
0.6% C No. 21	0.591	0.598	0.602	0.602	0.598	...	...	...	...	...	0.600	+0.009	
1.0% C No. 35	1.03	1.048	1.052	1.045	1.052	1.048	...	...	...	...	1.050	+0.020	
ALLOY STEELS													
Chrome Vanadium No. 30	0.373	0.375	0.382	0.379	0.379	0.381	0.381	0.379	...	...	0.379	+0.006	
Chrome Nickel No. 32	0.372	0.380	0.383	0.386	0.383	0.380	0.383	...	...	...	0.383	+0.011	
Chrome Tungsten No. 31	0.599	0.610	0.610	0.608	0.608	0.612	0.609	0.609	...	...	0.609	+0.010	
Nickel Steel No. 33	0.278	0.280	0.282	0.289	0.285	0.288	...	...	...	...	0.285	+0.007	
Vanadium Steel No. 24	0.348	0.350	0.350	0.354	0.353	...	...	...	...	...	0.352	+0.004	
IRONS													
Iron C No. 5b	2.726	2.75	2.74	2.74	...	...	...	...	...	...	2.743	+0.017	
Iron D No. 6a	2.46	2.48	2.48	2.48	...	...	...	...	...	...	2.480	+0.02	

\* Certificate value (direct combustion), 0.363.

also contained heated copper oxide in the forward portion of the (porcelain) combustion tube.

The routine followed in making a determination in the gas furnace consisted in inserting into the combustion tube the boat holding the sample and connecting up the Meyer tube containing barium hydroxide solution. While passing a slow current of oxygen the combustion tube was brought to 700° or 800° and kept within these temperatures for a minute or two until the superficial oxidation of the particles

changed to the near-by high temperature furnace through which oxygen was passing and the boat was transferred quickly to this furnace, which was maintained continuously at the proper temperature. After remaining in the high temperature furnace 15 to 20 min. the Meyer tube was disconnected and the filtration and titration finished as before. The oxides were usually found to be thoroughly fused and to have spread over the bottom of the boat; in some cases they even crept over the sides of the container. A



second fusion of such oxides gave no further carbon dioxide to a freshly filled and clear barium hydroxide tube. Great care was taken at all stages of the work to eliminate extraneous carbon dioxide or other substances that would cause a blank, so that, as already stated, the blank was always negligible. The frequent blanks which were made during this work were carried out (1) without any steel in the furnace; (2) when burning B. of S. Standard Steel No. 23, which, as shown in the table of results in this paper, gives identical values when burned in the ordinary way and by our modified method. The fused oxides were readily removed from the boats, in preparation for the next combustion, by digesting in strong hydrochloric acid for a few hours.

The results in the table show that some steels give higher results by the new method than are shown on the certificates, others yield only slightly higher figures and still others give the same results by both methods. We find it impossible to relate these three classes with the size of drillings used, with the carbon content of the sample, or especially, with the presence or absence of the usual alloying elements. In only two cases were the results by the modified method as much as 0.02 per cent higher than the certificate value; with most of the other samples the difference was of the order of 0.01 per cent. Our work does not cover the Bureau's complete series of standard analyzed steels and irons, but the results are deemed quite representative, and we believe they are complete enough to justify us in the conclusion that the certificate values for these steels cannot be affected with an error greater than 0.015 per cent (probably minus), and in most cases the error is much less. It is believed that such errors are negligible, considering the uses to which these standards are at present being put. The experimental difficulties and the inconvenience of this method of determining carbon place it beyond the reach of most industrial and works laboratories, and we do not, therefore, recommend its use to such, except in the case of products for which it may be found better adapted than other methods.

BUREAU OF STANDARDS, WASHINGTON

#### AN ACCURATE END-POINT IN THE VOLUMETRIC DETERMINATION OF SULFUR IN STEEL

By HERBERT ZSCHIEGNER

Received November 26, 1915

The following method was devised with the object of eliminating the inaccuracies due to the varying shades of the blue color of the starch iodide formed in the titration of hydrogen sulfide with iodine. While it depends primarily on the production of starch iodide, as does the former method, the actual blue color is disregarded.

In the experimental evolution of this end-point a standard solution of potassium iodide and iodate was used, together with an ammoniacal solution of cadmium chloride as an absorption medium and a solution of wheat starch as indicator. The iodine or iodate solution is made slightly stronger than usual and is standardized against a steel of known sulfur content.

This deviation from the usual method is in use in our laboratory and yields very good results.

The starch solution found to give the best results is made by rubbing to a paste with water, 12 g. of wheat starch and pouring the mixture into 2 liters of boiling water in which is dissolved 3 g. of potassium or sodium hydroxide. Two cc. of this solution are measured from a pipette or burette for each titration. Starch solution thus prepared will keep indefinitely and is not subject to the salting out of the colloidal starch which is the case when zinc chloride is added as a preservative.

To obtain uniform results a standard *modus operandi* must be adhered to. The volume of the HCl used to decompose the  $Cd_2S$ , the volume of the indicator, and the volume of the final solution must equal the volumes of the solutions used in standardizing the iodine or iodate solution.

A special titrating vessel is required, consisting of a white porcelain beaker, about 7 cm. in diameter and 16 cm. in depth. On the bottom of this beaker (inside) is cemented a thin, black disc of hard rubber or celluloid about 2 cm. in diameter. (A substitute for this vessel may be made by painting the black spot on the outside of a glass beaker, then covering the whole outside of the beaker with white enamel; the black spot should then appear sharply defined against the white of the beaker.)

The determination is carried out as usual until the titration is commenced, then the black spot is carefully observed, and as the solution darkens the iodine is added carefully with agitation. Finally a point will be reached when one drop of iodine will render the spot invisible on allowing the solution to come to rest. This is the end-point and the burette reading may now be taken. Owing to the milkiness of the solution when high sulfur iron or steel is being analyzed the black spot may not at first be apparent but will become plainly visible when the titration is about four-fifths completed and will remain so until the last drop of iodine renders it invisible. The end-point is sharp and the results in terms of per cent do not vary more than 0.001. An incandescent lamp may be placed at such a distance from the titrating vessel that the same results will be obtained with artificial light as with daylight. The light should not be situated directly over the beaker but to one side of it.

AMERICAN LOCOMOTIVE COMPANY  
SCHENECTADY, N. Y.

#### THE DETERMINATION OF BARIUM CARBONATE AND BARIUM SULFATE IN VULCANIZED RUBBER GOODS<sup>1</sup>

By JOHN B. TUTTLE

Received November 17, 1915

With the advent of buying rubber goods on specifications it became necessary to develop methods which would accurately determine the various constituents. One of the most important determinations is that of total sulfur. In a recent publication of this Bureau,<sup>2</sup> the sulfur-bearing constituents of vulcanized rubber

<sup>1</sup> Published by permission of the Director of the Bureau of Standards.

<sup>2</sup> Bureau of Standards, *Technologic Paper*, 45; *THIS JOURNAL*, 7 (1915), 658.

goods were mentioned, and a method was given for a quantitative determination of the sulfur which they contain. In this article, it was stated that sulfur may occur in various forms, including metallic sulfates, usually lead and barium. Many specifications now permit the use of barium sulfate (barytes) without having the sulfur which it contains count as part of the specified total sulfur. It is therefore necessary to be able to determine the percentage of this mineral. This was not at all difficult as long as the rubber compounds contained barium only in the form of the sulfate. When, however, manufacturers began using the carbonate as well as the sulfate, the problem became much more complex, since it became necessary to determine both salts of barium in the presence of each other, as well as in the presence of other sulfur-bearing minerals. It is with this phase of the problem that the present article deals.

The separation of barium carbonate from barium sulfate in the absence of other minerals is readily accomplished by solution of the carbonate in acids such as hydrochloric, acetic, etc. In rubber compounds, however, this method is not applicable, since lead sulfate may be present, in which case part of the lead sulfate will also be dissolved; the reaction between the lead sulfate in solution and the barium will cause the precipitation of barium sulfate, so that the results obtained will be low. Lead sulfate may be dissolved in ammonium acetate, and it was thought that this disturbing constituent could be eliminated by this procedure, which, however, was found to be too slow and unreliable to be an acceptable method. However, still another procedure is available, *viz.*, transforming the lead sulfate to the carbonate by boiling with alkaline carbonates, and filtering off the soluble sulfates. Sodium carbonate readily converts lead sulfate and barium sulfate<sup>1</sup> into their carbonates; ammonium carbonate reacts with lead sulfate, but tests made here show that it has only a slight effect on barium sulfate. By treatment with ammonium carbonate, we can therefore change the lead sulfate into the carbonate, and then filter the soluble sulfates from the lead carbonate, barium carbonate and barium sulfate. Calcium and zinc carbonates, which may be present, do not interfere with the desired separation.

**SAMPLES**—The four samples used in this investigation were of known composition (Table I), having been compounded and vulcanized at this Bureau. The barium carbonate used in Nos. 1 and 17 was

TABLE I—COMPOSITION OF SAMPLES

COMPOUND	No. 1	No. 13	No. 16	No. 17
Fine Para Rubber....	39.6	30.0	20.0	
Plantation Rubber....				40.0
Sulfur.....	2.5	3.0	2.0	4.0
Litharge.....	8.6	7.0	8.0	8.0
Zinc Oxide.....	8.7	20.0	20.0	15.0
Sublimed White Lead..	30.6			
Barium Carbonate.....	10.0			10.0
Barium Sulfate.....		20.0	30.0	20.0
Whiting.....		20.0	20.0	
Vaseline.....				3.0
Total Per cent.....	100.0	100.0	100.0	100.0

Merck's best quality, and was finely ground before compounding. The barium sulfate was tested and found to contain practically no soluble barium salts.

<sup>1</sup> Noyes and Bray, *J. Am. Chem. Soc.*, **29** (1907), 151, state that 80 per cent of barium sulfate is converted into barium carbonate when boiled with an excess of sodium carbonate.

It will be noted that No. 1 contained both barium carbonate and lead sulfate, No. 17 barium carbonate and barium sulfate, while Nos. 13 and 16 contained barium sulfate only.

**METHOD EMPLOYED**—Schaeffer<sup>1</sup> has shown that the organic matter in rubber can be removed by ignition in an atmosphere of carbon dioxide without change of sulfur to sulfide, or of either to sulfate. Slight reduction of barium sulfate to sulfide may occur during ignition of the rubber, but experience shows that the amount of sulfide formed is practically negligible. The apparatus used for the decomposition of the rubber was practically the same as that used by Schaeffer, the only change being that the sample was placed in a porcelain boat so as to facilitate the removal of the residue from the glass tube. One gram of the rubber was taken for each determination. After ignition and cooling in carbon dioxide, the boat was removed, the residue finely ground in an agate mortar, transferred to a 250 cc. beaker, and treated with 5 to 10 g. ammonium carbonate, 15 to 20 cc. of strong ammonia water and about 50 cc. of distilled water.

TABLE II—RESULTS OF BARIUM CARBONATE DETERMINATION  
(All results are expressed in percentages of the original sample.)

Sample	CONSTITUENTS	PRESENT	FOUND				
1	Barium Carbonate.....	10.0	9.72	9.67	9.98	10.02	
	Sulfur equivalent to BaCO <sub>3</sub> .....	1.63	1.58	1.57	1.62	1.63	
17	Barium Carbonate.....	10.0	10.28	9.76	10.73	10.71	
	Sulfur equivalent to BaCO <sub>3</sub> .....	1.63	1.67	1.59	1.74	1.74	
13	Barium Carbonate.....	0.0	0.17	0.08	0.17	0.25	
	Sulfur equivalent to BaCO <sub>3</sub> .....	0.0	0.03	0.01	0.03	0.03	
16	Barium Carbonate.....	0.0	0.29	0.19	0.31	0.09	
	Sulfur equivalent to BaCO <sub>3</sub> .....	0.0	0.05	0.03	0.05	0.02	

The mixture was boiled for 15 to 30 min., filtered, and the precipitate thoroughly washed to remove all soluble sulfates. The residue on the filter paper was washed back into the original beaker with distilled water; about 10 cc. of glacial acetic acid and sufficient water to make the total volume of the solution about 100 cc. were added. This was heated to boiling and then filtered through the same filter paper as before. By this procedure, lead, barium, calcium and zinc carbonates pass into solution while barium sulfate and lead sulfide are not attacked. Hydrogen sulfide was passed into the filtrate, the lead sulfide filtered off, the filtrate heated on the steam bath, and 10 cc. of 10 per cent sulfuric acid added. The solution was allowed to stand over night on the steam bath; the next day the precipitate was filtered off, ignited in a porcelain crucible, cooled and weighed.

#### DISCUSSION OF RESULTS

The barium sulfate (Table II) was calculated to barium carbonate, using the factor 0.845. The sulfur in the barium sulfate was also calculated, since it is desirable to know just what error will be introduced if the barium present in the form of the carbonate should be considered as being present as the sulfate. The results on Sample 1 show that in the presence of lead sulfate (in the sublimed white lead), barium carbonate can be determined with accuracy, the results, expressed in terms of sulfur, being within 0.06 per cent of the calculated amount. In Sample 17, we have present both the sulfate and carbonate of barium, and while the results are not as good as those

<sup>1</sup> THIS JOURNAL, **4** (1912), 837.



obtained on Sample 1, they are sufficiently accurate for all practical purposes, the maximum error on sulfur being only 0.11 per cent. Results slightly higher than those calculated must be expected, since Samples 13 and 16, which contain barium sulfate and no barium carbonate, yield small amounts of precipitate by this method, partly in consequence of slight reduction of barium sulfate to sulfide during the ignition of the rubber, and partly on account of the slight action of ammonium carbonate on barium sulfate. These amounts, in themselves, are negligible. It is apparent, therefore, that neither lead sulfate nor barium sulfate interfere appreciably with the determination of barium carbonate by this procedure.

**METHOD FINALLY ADOPTED**—The total barium in the rubber compound is determined as barium sulfate by the method for the determination of barytes in use at this Bureau.<sup>1</sup> This method was first suggested by C. E. Waters, and afterwards modified by W. H. Smith and the author. Barium carbonate is determined in a separate sample by the method just described, and an equivalent amount of barium sulfate is deducted from the total barium sulfate. The sulfur in the remaining portion of barium sulfate is calculated, and the total sulfur determination is corrected by this amount.

#### SUMMARY

A new method is given for the determination of barium carbonate in vulcanized rubber goods. It is shown that this method is sufficiently accurate in the presence of lead and barium sulfates.

The author wishes to acknowledge the assistance of Mr. H. A. Ehrman of this Bureau, who very kindly compounded and vulcanized the samples used in this investigation.

BUREAU OF STANDARDS, WASHINGTON

### A METHOD FOR THE DIRECT DETERMINATION OF THE RUBBER IN A COMPOUND

By ROBERT W. BELFIT

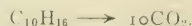
Received December 1, 1915

At present all published methods (with the exception of Wesson's "combustion method")<sup>2</sup> for determining the percentage of the rubber in a compound are inadequate. The most used method is the indirect one in which the sample is analyzed for fillers, total sulfur, and waxy hydrocarbons, and the "rubber" is considered as the difference between 100 and the sum of the three corrected percentages. As this method depends upon the accurate determinations of the fillers, total sulfur, and waxy hydrocarbons, it is unsatisfactory, for it is doubtful if exact methods exist for the determinations of the fillers and waxy hydrocarbons.

A number of direct methods have been proposed which depend upon the formation of known compounds, such as nitrosates, nitrosites, or bromides; but the exact formulas of these compounds are not constant or controllable. Therefore, these methods

are at present valueless for the estimation of the rubber in vulcanized goods.

Mr. L. G. Wesson in his method forms a nitrosite of the rubber, but only in order to obtain a product soluble in acetone. He then separates the fillers, takes an aliquot portion of the solution, evaporates off the solvent, and finally burns the nitrosite in a current of oxygen. From the carbon dioxide formed, he calculates the percentage of the rubber according to the equation



This method appears to give good results, but it is rather long and intricate, due to the necessity of forming a nitrosite and of handling the viscous rubber solutions.

The method presented in this paper is of the combustion type and is considered simple, quick, and accurate for high-grade compounds. In brief, a charge of the finely ground rubber is extracted with acetone, dried, treated with hydrochloric acid to decompose all carbonates, again dried, after which a portion is burned to carbon dioxide, from which the percentage of rubber is calculated.

#### PROCEDURE

The sample is ground so that it all passes through a 20 mesh sieve while but 20 per cent passes through a 40 mesh sieve. Then, 2 g. are extracted for 5 hrs. with acetone in an apparatus in which the solvent is continually at the boiling point. The residue is now placed in a weighed tube if not already in one. This tube containing the residue is inserted in an oven, kept at 100° C., and a current of dry carbon dioxide is passed through the tube in order to aid rapid drying and prevent oxidation. The dried sample is weighed, and the percentage loss in weight calculated. About one-half of this extracted sample is weighed out into a 250 cc. Erlenmeyer flask, where it is cautiously boiled for 30 min. with 150 cc. of HCl (1:5 by vol.). In this process all carbonates are driven off.

Now, the liquid is decanted through an alundum crucible on a suction, and the residue is washed three times by decantation with water at about 60° C. The rubber substance is then transferred to the crucible and washed ten more times with warm water. The residue is now placed in a tube<sup>1</sup> and dried in a stream of dry carbon dioxide at 100° C. for two to four hours. The tube is then removed and allowed to cool in a desiccator.

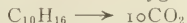
The resulting residue is now transferred to a weighing tube, from which 0.3-g. samples are weighed for the final process, that of combustion. The combustion is carried out in approximately the same manner as for any organic compound, except that no reduced copper spiral is used, as the water and nitrogen oxides are absorbed in a concentrated solution of potassium dichromate in sulfuric acid. A vessel of small volume is necessary for this solution, or otherwise it is almost impossible to displace all of the carbon dioxide after

<sup>1</sup> The author uses a tube about 2 in. long and 3/4 in. inside diameter with the lower third constricted to 1/4 in. inside diameter.

<sup>1</sup> Bur. of Standards, Circ. 38 (1915), 68, 3rd Ed.; *India Rubber World*, 81 (1914), 128.

<sup>2</sup> This Journal, 6 (1914), 459.

the sample has been completely burned. Beyond this tube is placed a U tube containing zinc dust to absorb all possible acid gases other than carbon dioxide. The potassium hydroxide absorption bulb is next and last in the train. The rubber substance is burned in a stream of oxygen, and the potash bulb is always weighed when full of oxygen.



This method on pure, fine para gum gave 96.19 and 96.57 per cent (av. 96.38).

The value of 0.96 was then used as the figure by which the weight of  $\text{C}_{10}\text{H}_{16}$  should be divided in order to obtain the weight of the rubber from which it came. This factor was used on the compounds made with other varieties of gums without determinations on those gums, as the factor would be valueless unless it applied to all high-grade rubber gums.

#### SAMPLE CALCULATION

Loss due to acetone extraction — 5.45 per cent  
Weight extracted with HCl — 0.9850 g.  
Weight after HCl extraction — 0.6483 g.  
Weight burned — 0.2824 g.  
Weight of  $\text{CO}_2$  absorbed — 0.4232 g.

$$\frac{136 \times 0.4232}{440} = \text{Wt. of } \text{C}_{10}\text{H}_{16} \text{ burned}$$

$$\frac{136 \times 0.4232}{440 \times 0.96} = \text{Wt. of rubber burned}$$

$$\frac{136 \times 0.4232 \times 0.6483}{440 \times 0.96 \times 0.2824} = R = \text{Wt. of rubber that would have been}$$

burned if all that extracted with HCl was burned

$$\frac{0.9850}{1.0000 - 0.0545} = \text{Wt. of unextracted sample which contained R grams of rubber}$$

$$\frac{136 \times 0.4232 \times 0.6483 \times 0.9455}{440 \times 0.96 \times 0.2824 \times 0.9850} = 30.01 \text{ per cent}$$

#### ANALYTICAL RESULTS

30 Per cent Fine Para Stock	30 Per cent Cameta Stock	31 Per cent Ceylon Stock (Red Oxide)	31 Per cent Ceylon Stock (Black)
30.31	30.01	30.50	30.18
30.12	30.38	30.87	30.80
...	29.60	...	...
Av., 30.22	30.00	30.69	30.49

#### CONCLUSIONS

This method is found applicable to *high-grade* compounds which do not contain lampblack, shoddy, or rubber substitutes. If the compound should contain lampblack, it is shown by the dark color of the gum when treated with dilute hydrochloric acid. Otherwise, the gum is grayish white. The presence of shoddies and rubber substitutes may be detected, respectively, by the dark color of the acetone extract or a high alcoholic potassium hydroxide (KOH) extract.

Should the described method be used alone for specification work, the percentage of rubber could be made to appear falsely high by adding ground leather, starch, egg albumen, or some other organic compounds which are insoluble in acetone, water, and dilute hydrochloric acid. But the addition of such substances would decrease the quality of the compound and probably their presence could be detected by qualitative chemical means or physical testing.

Therefore, even though this method is at present restricted to positively *high-grade* stocks, it is felt that its use may be made more general after further experimentation.

### THE REDUCTION OF $\text{As}^v$ TO $\text{As}^{iii}$ BY CUPROUS CHLORIDE AND THE DETERMINATION OF ARSENIC BY DISTILLATION AS ARSENIC TRICHLORIDE

By R. C. ROARK AND C. C. McDONNELL

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For the determination of arsenic in arsenical insecticides, the Association of Official Agricultural Chemists has adopted methods for Paris green, London purple, and lead arsenate only.<sup>1</sup> In recent years there have been placed on the market other arsenical insecticides, such as the arsenates and arsenites of calcium and zinc, and combinations of fungicides and insecticides which contain arsenic, such as Bordeaux-lead arsenate, Bordeaux-Paris green, Bordeaux-zinc arsenite, etc.

In attempting to find a method for the quick and accurate determination of arsenic in these products, recourse was had to the well-known distillation method, using ferrous sulfate as a reducing agent. This method was carried out as follows: An amount of the sample containing not over 0.5 g. arsenic calculated as  $\text{As}_2\text{O}_3$  and 10 g. of ferrous sulfate was transferred to a 500 cc. distilling flask, 100 cc. concentrated hydrochloric acid (sp. gr. 1.19) added, the solution heated to boiling and the vapors distilled through a well-cooled condenser into the arrangement of flasks shown in Fig. 1.

When the volume in the distilling flask was reduced to about 40 cc., an additional 50 cc. of concentrated hydrochloric acid was added by means of a dropping funnel. This process was continued until 200 cc. of acid had distilled over. The distillate was then made up to 1 liter in a graduated flask, an aliquot of 200 cc. taken, nearly neutralized with a concentrated solution of sodium hydroxide, sodium bicarbonate added in excess, and the arsenic trioxide titrated with an approximately  $N/20$  iodine solution, using starch paste as an indicator.

On analyzing a commercial dry lead arsenate in this way, only 26.3 per cent  $\text{As}_2\text{O}_3$  was found, whereas by the Official method<sup>2</sup> 31.9 per cent was obtained. This low result was somewhat surprising in view of the fact that distillation of samples of Bordeaux-lead arsenate with ferrous sulfate and hydrochloric acid had yielded the same amount of arsenic as other methods. In order to see if the copper salts present in the samples containing Bordeaux had any effect on the results, another distillation of this lead arsenate was made, with the addition of 5 g. crystallized copper sulfate to the 10 g. ferrous sulfate. Distilling as before, 31.8 per cent  $\text{As}_2\text{O}_3$  was found.

Cuprous chloride, as suggested by Olsen,<sup>3</sup> was then tried as the reducing agent, when, using the same procedure as before, 32.0 per cent  $\text{As}_2\text{O}_3$  was obtained.

In order to test this method further, a sample of pure lead hydrogen arsenate<sup>4</sup> ( $\text{PbHAsO}_4$ ) was analyzed

<sup>1</sup> Bur. of Chem., Bull. 107, Rev. (1908), 25-6, 28-9, 239; Bull. 132 (1910), 43-4; Jour. A. O. A. C., 1 (1915), 444-6.

<sup>2</sup> Bur. of Chem., Bull. 107, Rev. (1908), 239.

<sup>3</sup> "Quantitative Chemical Analysis," 1910, p. 139.

<sup>4</sup> Prepared by McDonnell and Smith, for use in another investigation, by precipitating potassium dihydrogen arsenate,  $\text{KH}_2\text{AsO}_4$ , with lead nitrate and recrystallizing from nitric acid.



by the distillation method, using cuprous chloride as the reducing agent, and 33.12 per cent  $As_2O_3$  was obtained, which is exactly the theoretical for  $PbHASO_4$ . By the present Official method, 33.11 per cent was found.

#### HISTORICAL

On looking up the literature on the distillation method for arsenic it was found that a number of modifications have been recommended.

Fyfe,<sup>1</sup> Penny and Wallace,<sup>2</sup> Schneider<sup>3</sup> and van Kerckhoff<sup>4</sup> determined arsenic by distillation as the trichloride, generating the hydrochloric acid in the distilling flask by the action of sulfuric acid upon sodium chloride, but in all cases the arsenic was present as  $As^{III}$  and not as  $As^V$ .

This method of distillation was also employed by Rieckher<sup>5</sup> to separate arsenious from arsenic acid in rosanilin.

Arsenic in copper was detected by the distillation method as early as 1863 by Odling.<sup>6</sup> The copper was dissolved in hydrochloric acid in the presence of ferric chloride, the mixture distilled and the arsenic detected in the distillate with hydrogen sulfide or by boiling with a piece of copper foil. This method has been used to determine arsenic quantitatively in copper by Thomas Gibb,<sup>7</sup> Clark,<sup>8</sup> Platten,<sup>9</sup> and Ulke.<sup>10</sup>

Emil Fischer<sup>11</sup> was the first to propose the use of a reducing agent so as to make the distillation method applicable to the determination of arsenic when present as an arsenate. He used ferrous chloride in the form of a saturated aqueous solution. His procedure was as follows: The solution containing arsenic was put in a distilling flask of about 600 cc. capacity; 10 to 20 cc. of a cold saturated solution of ferrous chloride, and sufficient 20 per cent hydrochloric acid to bring the volume to 150 cc. were added. The contents were then distilled through a well-cooled condenser into a large Erlenmeyer flask until the residue in the distilling flask amounted to 30–35 cc. According to Fischer, as much as 1.0 g. arsenic could be volatilized by distilling four times.

Hufschmidt,<sup>12</sup> on using Fischer's method, found traces of arsenic with hydrogen sulfide even in the tenth distillate. He modified the method by substituting 40 per cent for 20 per cent hydrochloric acid, and used a Woulfe flask containing either water or a solution of potassium hydroxide (sp. gr. 1.1 to 1.2) to catch the distillate. The contents in the distilling flask were first saturated with hydrochloric acid gas, and the distillation was carried out in a stream of the gas, which was generated by the action of sulfuric acid on sodium chloride in a separate flask.

Classen and Ludwig<sup>13</sup> substituted ferrous sulfate, or ferrous ammonium sulfate, for the ferrous chloride, using about 25 g. to not over 0.5 g. arsenic calculated as  $As_2O_3$ . They likewise carried out the distillation in a strong stream of hydrochloric acid gas.

The following writers record good results in distilling arsenic with the use of ferrous sulfate as a reducing agent: Ulke,<sup>14</sup> Heath,<sup>15</sup> Koch,<sup>16</sup> Kann,<sup>17</sup> and Bertiaux,<sup>18</sup> in the analysis of copper

or copper electrolytes; Heiduschka and Reuss<sup>1</sup> in the analysis of Paris green, and Brandt<sup>2</sup> in the analysis of iron. It should be noted that in all these cases one or more of the following conditions obtained: (1) metallic copper or a salt of copper was present, (2) the arsenic was present only in very small amount; (3) the arsenic was present largely (if not wholly) as metallic arsenic or as an arsenite and not as an arsenate. If the arsenic is present as an arsenite, no reducing agent is needed to effect its volatilization as arsenic trichloride, and, as we have shown, where large quantities of arsenic are present as arsenate, the presence of a copper salt greatly facilitates the reduction by means of a ferrous salt.

Kern and Wen,<sup>3</sup> using ferrous sulfate in the distillation of arsenic, obtained results which varied and were always low. They also state that the distillation was difficult to control on account of the violent bumping which occurred as the solution became concentrated.

Stead,<sup>4</sup> in determining arsenic in iron ores, steel and pig iron, used ferrous chloride in the distillation with hydrochloric acid, and considered it superior to any other method. On the other hand, Bishop,<sup>5</sup> in determining small quantities of arsenic in sulfuric acid, obtained unsatisfactory results by this method, and, owing to excessive bumping due to the precipitation of ferrous sulfate, its use was abandoned.

Hydrogen sulfide was proposed as a reducing agent by Piloty and Stock,<sup>6</sup> being passed through the solution, together with hydrochloric acid gas, during the distillation.

Friedheim and Michaelis<sup>7</sup> used methyl alcohol as a reducing agent, and Cantoni and Chautems<sup>8</sup> claimed to be able to remove all the arsenic from a hydrochloric acid solution of arsenic trioxide containing methyl alcohol by passing a stream of air through at ordinary temperature. Collins,<sup>9</sup> however, found the latter method to be of no value, and showed that if arsenic was present as arsenate the method of Friedheim and Michaelis did not work. He used ferrous chloride as a reducing agent, added the methyl alcohol in successive portions, and passed a stream of hydrochloric acid gas during the distillations. Collins substituted ethyl alcohol for methyl alcohol, but found it to be only about one-half as efficient as the latter. At about the same time, Moser and Perjatel<sup>10</sup> also showed that arsenic pentoxide is not reduced by methyl alcohol in hydrochloric acid solution. Using ferrous sulfate together with methyl alcohol for this purpose they obtained good results. Hilpert and Dieckmann<sup>11</sup> likewise failed to obtain good results with the Friedheim-Michaelis method.

Stannous chloride as a reducing agent was suggested by Guedras,<sup>12</sup> but Kern and Wen<sup>13</sup> found this to be objectionable in that it reduced the arsenic to the metallic state, in which condition it did not redissolve in the solution, and also some stannic chloride would pass over into the distillate.

Distillation with hypophosphorous acid was originated in 1901 by A. E. Knorr, according to Butler,<sup>14</sup> and has been used successfully by Walter C. Smith,<sup>15</sup> Heath,<sup>16</sup> and Kern and Wen,<sup>13</sup> who point out, however, that too much must not be used, otherwise it will reduce arsenic to the metallic state. In order to get

<sup>1</sup> *Philosophical Magazine*, [4] **2** (1851), 487.

<sup>2</sup> *Ibid.*, [4] **4** (1852), 361–5.

<sup>3</sup> Poggendorff's *Annalen der Physik und Chemie*, **85** (1852), 433–5.

<sup>4</sup> *Journal fuer praktische Chemie*, **56** (1852), 395–400.

<sup>5</sup> *Zeitschrift fuer analytische Chemie*, **9** (1870), 516–8.

<sup>6</sup> *Chem. News*, **8** (1863), 27–8.

<sup>7</sup> *Ibid.*, **45** (1882), 218.

<sup>8</sup> *J. Soc. Chem. Ind.*, **6** (1887), 352–5.

<sup>9</sup> *Ibid.*, **13** (1894), 324–6.

<sup>10</sup> *Eng. and Min. Jour.*, **68** (1899), 727–9.

<sup>11</sup> *Ber.*, **13** (1880), 1778–80; and Liebig's *Annalen der Chemie*, **208** (1881), 182–95.

<sup>12</sup> *Ber.*, **17** (1884), 2245–8.

<sup>13</sup> *Ibid.*, **18** (1885), 1112.

<sup>14</sup> *Loc. cit.*

<sup>15</sup> *J. Am. Chem. Soc.*, **29** (1907), 614.

<sup>16</sup> *Z. fuer anal. Chem.*, **46** (1907), 35.

<sup>17</sup> *Chem. Eng.*, **8** (1908), 159.

<sup>18</sup> *Annales de Chimie Analytique*, **18** (1913), 472; and **19** (1914), 49.

<sup>1</sup> *Zeitschrift fuer analytische Chemie*, **50** (1911), 269.

<sup>2</sup> *Chem.-Zeit.*, **33** (1909), 1114–5.

<sup>3</sup> *Met. and Chem. Eng.*, **9** (1911), 365–7.

<sup>4</sup> *Journal of the Iron and Steel Institute*, No. 1, **47** (1895), 110–5.

<sup>5</sup> *J. Am. Chem. Soc.*, **28** (1906), 178–85.

<sup>6</sup> *Ber.*, **30** (1897), 1649–55.

<sup>7</sup> *Ibid.*, **28** (1895), 1414–22.

<sup>8</sup> *Annales de Chimie Analytique*, **10** (1905), 213–4.

<sup>9</sup> *Analyst*, **37** (1912), 229–38.

<sup>10</sup> *Monats. fuer Chemie*, **33** (1912), 797–820.

<sup>11</sup> *Ber.*, **46** (1913), 152–5.

<sup>12</sup> *Rev. gén. Chim.*, **11** (1908), 251–2.

<sup>13</sup> *Loc. cit.*

<sup>14</sup> *Chem. Eng.*, **5** (1906), 66–7.

<sup>15</sup> *Eng. and Min. Jour.*, **88** (1909), 1062–3.

<sup>16</sup> *This Journal*, **3** (1911), 78–82.

rid of the excess, these authors fume with sulfuric acid for one-half hour before distilling with hydrochloric acid.

Sodium thiosulfate, with and without ferrous sulfate, was tried by Kern and Wen and found to be without value.

A stream of sulfur dioxide together with hydrochloric acid gas was successfully employed by Bishop in distilling arsenic from sulfuric acid.

Hydriodic acid was proposed by Gooch and Danner<sup>1</sup> as a reducing agent in the distillation of arsenic, but later Gooch and Phelps<sup>2</sup> found hydrobromic acid to be much better. Rohmer<sup>3</sup> used hydrobromic acid in combination with sulfur dioxide, passing the latter, together with hydrochloric acid gas, through the solution during the distillation. Schurmann and Böttcher<sup>4</sup> used Rohmer's method in analyzing pyrites.

Jannasch and Seidel<sup>5</sup> use hydrobromic acid together with a salt of hydrazine to effect the reduction, and the arsenic in the distillate is titrated with potassium bromate according to the method of Gyory.<sup>6</sup> This method has also been used by Billeter,<sup>7</sup> and Kleine.<sup>8</sup>

The earliest recorded suggestion of the use of cuprous chloride as a reducing agent is that of Dittmar,<sup>9</sup> as cited by Clark.<sup>10</sup>

Clark also recommended the use of cuprous chloride, which he obtained by dissolving metallic copper in a strong hydrochloric acid solution of cupric chloride. He also made use of a mixture of cuprous and ferrous chlorides, obtained by dissolving copper in ferric chloride. Both of these methods were suggested by Odling for getting copper into solution, but not for the purpose of reducing As<sup>v</sup> to As<sup>iii</sup>.

Platten made use of the copper-ferric chloride method, while Thomas Gibb modified the procedure by the addition of calcium chloride. This raised the boiling point and rendered the volatilization of the arsenic trichloride quicker. C. and J. J. Beringer<sup>11</sup> prepare a "ferric chloride mixture" by dissolving 600 g. of calcium chloride and 300 g. of ferric chloride in 600 cc. of hydrochloric acid and making up to 1 liter with water. Allan Gibb<sup>12</sup> used this method for determining arsenic, but substituted a saturated solution of zinc chloride for the calcium chloride when it was desired to determine antimony. The saturated solution of zinc chloride was mixed with an equal volume of hydrochloric acid containing 100 g. copper as cupric chloride per liter, and the mixture either concentrated or diluted in order that it should boil at 108° C. Unless the sample under examination was metallic copper, there was added to the contents of the distilling flask 0.25 g. of pure copper which acted as a reducing agent.

Skinner and Hawley<sup>13</sup> use a distilling mixture somewhat similar to that of Allan Gibb, except that the proportions are: 300 g. cupric chloride in 1 liter of hydrochloric acid (sp. gr. 1.20) plus an equal volume of a zinc chloride solution which boils at 180° C. In determining arsenic in a sample it is first reduced with ammonium bisulfite, precipitated with hydrogen sulfide, and the arsenic distilled from the sulfide. The authors state that in the distillation some uncombined sulfur comes over, but no sulfurous acid or hydrogen sulfide. Ferric chloride was not as satisfactory as cupric chloride as it allowed hydrogen sulfide to come over.

Heath determines arsenic in copper by distilling with a mixture of zinc and cupric chlorides. This mixture he prepares as follows: "Dissolve 150 g. C. P. zinc in 140 cc. of hydrochloric acid (sp. gr. 1.2) and 440 cc. of distilled water, and evaporate until the bulk is reduced to about 370 cc. Mix this solution with the solution of 100 g. of C. P. cupric chloride, dissolved in 330 cc. of concentrated hydrochloric acid."

Hilpert and Dieckmann<sup>1</sup> used cuprous chloride as a reducing agent in distilling arsenic from a mixture of arsenic and tungstic acids, and later<sup>2</sup> they record the use of cuprous bromide, or cuprous chloride in conjunction with potassium bromide, for the same purpose. Schurmann and Böttcher<sup>3</sup> have also used cuprous chloride.

# EXPERIMENTAL

In order to test the action of different substances in reducing As<sup>v</sup> to As<sup>iii</sup> they were added to a hydrochloric acid solution of pure lead hydrogen arsenate (As<sub>2</sub>O<sub>5</sub> = 33.12 per cent) and the solution distilled, using the apparatus previously described. About 1.5 g. of lead arsenate constituted a charge, and in each case 200 cc. of acid were distilled over. Some of the substances, e. g., the salts of manganese, nickel, cobalt and antimony, were tried to see if they would act as catalyzers. The results are shown in Table I.

TABLE I REDUCING ACTION OF VARIOUS SALTS ON LEAD HYDROGEN ARSENATE

REDUCING SUBSTANCE	Grams Used	% As <sub>2</sub> O <sub>5</sub> Found	REMARKS
Ferrous chloride....	5	12.70	Reduction not complete
	10	15.60	
	20	30.60	
	30	25.10	Reduction not complete
Ferrous sulfate....	5	18.50	
	20	22.60	
	30	23.00	Reduction not complete
Ferrous ammonium sulfate....	5	11.60	
	10	16.40	
	20	21.70	Reduces As <sup>v</sup> to metallic arsenic
Stannous chloride....	5	1.00	
Mercurous chloride....	5	None	
			{ Some HgCl <sub>2</sub> in the distillate
Manganous chloride.....	5	None	No reduction
Cobalt chloride....	5	None	No reduction
Nickel sulfate....	5	None	No reduction
Antimony trichloride.....	5	None	No reduction
Cuprous chloride....	5	33.12	{ A small amount of antimony came over
			{ Reduction complete
Ferric chloride....	10	14.90	{ Metallic arsenic precipitates on the copper foil
Copper foil.....	3.5		
Cuprous chloride....	5	33.10	{ Reduction complete
Antimony trichloride....	0.44		{ No antimony in distillate

In Table II are given the results obtained on various substances, using 5 g. cuprous chloride as the reducing agent, and also the results obtained by Official<sup>4</sup> or other standard methods.

As shown by the results in Tables I and II, cuprous chloride is very effective in reducing arsenates in the distillation method for arsenic. We have tried this method on a great number of commercial insecticides, including lead arsenates, Paris green, zinc arsenite, Bordeaux-lead arsenate, Bordeaux-Paris green, Bordeaux-zinc arsenite, etc., and in every case have obtained excellent results. (In case organic matter is present in the sample, as for example in London purple, it must be destroyed before distilling. This may be done by heating with nitric and sulfuric acids.)

The details of this method are as follows:<sup>5</sup>

<sup>1</sup> Ber., **46** (1913), 152-5.

<sup>2</sup> Ibid., **47** (1914), 2444-6.

<sup>3</sup> Chem.-Zeit., **37** (1913), 51.

<sup>4</sup> Bur. of Chem., Bull. **107**, Rev. (1908), 25-6; 239.

<sup>5</sup> These directions are essentially the same as those sent the chemists cooperating in the A. O. A. C. work on insecticides for 1915 by one of us (Roark), the present referee on insecticides for that association

<sup>1</sup> Am. Jour. Sci., **42** (1891), 308-12.

<sup>2</sup> Zeitschrift fuer anorganische Chemie, **7** (1894), 123-6.

<sup>3</sup> Ber., **34** (1901), 33-8.

<sup>4</sup> Chem.-Zeit., **37** (1913), 49-51.

<sup>5</sup> Ber., **43** (1910), 1218-23; J. fuer praktische Chemie, **91** (1915), 133-73.

<sup>6</sup> Zeitschrift fuer analytische Chemie, **32** (1893), 415-21.

<sup>7</sup> Mitteilungen aus dem Gebiete der Lebensmitteluntersuchung und Hygiene, **6** (1914), 280-7.

<sup>8</sup> Chem.-Zeit., **39** (1915), 43.

<sup>9</sup> "Exercises on Quantitative Analysis," p. 94.

<sup>10</sup> J. Soc. Chem. Ind., **6** (1887), 352-5.

<sup>11</sup> "Text Book of Assaying," 11th ed., 1908, pp. 384-5.

<sup>12</sup> J. Soc. Chem. Ind., **20** (1901), 185.

<sup>13</sup> Eng. and Min. Jour., **74** (1902), 148.



## SOLUTIONS USED

**STARCH SOLUTION**—Stir finely powdered potato starch in a small amount of cold distilled water until a uniform suspension results, then slowly add this, with constant stirring, to boiling distilled water. About 0.5 g. starch to each 100 cc. of the completed solution should be used. After the starch suspension is added to the boiling water the heating should be discontinued.

**STANDARD SOLUTION OF ARSENIC TRIOXIDE ( $As_2O_3$ )**—Chemically pure arsenic trioxide, which should satisfy all the requirements

200 cc., neutralize with sodium bicarbonate, adding 4 or 5 g. in excess, and add the standard iodine solution from a burette<sup>1</sup> (shaking the flask all the time) until the yellow color disappears slowly from the solution; then add 5 cc. of the starch solution<sup>2</sup> and continue adding the iodine solution drop by drop until a permanent blue color is obtained: from the number of cc. of iodine solution used calculate its value in terms of  $As_2O_3$  and  $As_2O_5$  (Factor:  $As_2O_3 \times 1.16168 = As_2O_5$ ).

**DETERMINATION**—Weigh carefully an amount of

TABLE II—ARSENIC DETERMINATION WITH CUPROUS CHLORIDE REDUCTION

LAB. NO.	SUBSTANCE	PER CENT ARSENIC FOUND		
		Distillation with $Cu_2Cl_2$	Official Method	Calc. as $As_2O_3$
11549	Lead hydrogen arsenate (crystals).....	33.12	35.73	$As_2O_3$
11550	Lead arsenate (commercial).....	28.65	28.32	$As_2O_3$
11552	Lead arsenate (commercial).....	30.50	30.59	$As_2O_3$
21165	Lead arsenate (commercial).....	31.65	31.55	$As_2O_3$
	Lead arsenate (1909 A. O. A. C.).....	30.85	30.85	$As_2O_3$
	Lead arsenate (1910 A. O. A. C.).....	31.80	31.79	$As_2O_3$
12312	Paris green (commercial).....	55.60	55.65	$As_2O_3$
12402	Paris green (commercial).....	56.70	56.81	$As_2O_3$
12404	Paris green (commercial).....	56.60	56.55	$As_2O_3$
12477	Paris green (commercial).....	57.20	56.95	$As_2O_3$
12480	Paris green (commercial).....	57.03	57.11	$As_2O_3$
12483	Paris green (commercial).....	56.90	57.17	$As_2O_3$
12488	Paris green (commercial).....	58.23	58.28	$As_2O_3$
12542	Paris green (commercial).....	57.20	56.83	$As_2O_3$
	Calcium arsenate.....	55.88	55.90(a)	$As_2O_3$
	Bordeaux & Paris green (1915 A. O. A. C.).....	31.93		$As_2O_3$
	Bordeaux & lead arsenate (1915 A. O. A. C.).....	14.20		$As_2O_3$
	Lead arsenate and lead arsenite.....	19.88	19.88	As
16151	Zinc arsenite (commercial).....	37.05	37.03(c)	$As_2O_3$
16452	Zinc arsenite (commercial).....	41.74	41.77(d)	$As_2O_3$
18985	Zinc arsenite (commercial).....	41.80	41.68(e)	$As_2O_3$
20,56(b)	Lead chlorarsenate— $Pb_2(AsO_4)_2 \cdot (AsO_4)_2 \cdot 2H_2O$ .....	23.20		$As_2O_3$

(a) Determined by a modification of Naylor's method (*Pharm. J. and Trans.*, [31] 10 (1879), 441-2).

(b) Value calculated from the arsenic content of the arsenical used. Dett. by "Official" Method

(c) Arsenic separated as the sulfide.

(d) Arsenic titrated in the presence of zinc (*Proc. A. O. A. C.*, 1915).

(e) Arsenic and zinc separated electrolytically (*THIS JOURNAL*, 7 (1915), 26-9).

(f) Prepared by McDonnell and Smith.

of the U. S. P. VIII as to strength and purity, should be used. Transfer (by washing) 2 g. of the arsenic trioxide to a 500 cc. graduated flask and dissolve by boiling in about 150-200 cc. water containing 10 cc. of concentrated sulfuric acid. When solution is complete, cool, and make up to volume.

**STANDARD IODINE SOLUTION**—Prepare an approximately N/20 solution of iodine as follows: Intimately mix powdered

the sample containing not over 0.5 g. arsenic calculated as  $As_2O_3$ , and wash into a distilling flask by means of 100 cc. of concentrated hydrochloric acid (sp. gr. 1.19). Add 5 g. of cuprous chloride ( $Cu_2Cl_2$ ) and distil through a well-cooled condenser into the arrangement of flasks as shown in Fig. I. When the volume in the distilling flask equals about 40 cc., add an additional 50 cc. concentrated hydrochloric acid by means of a dropping funnel and continue the distillation until 200 cc. of hydrochloric acid have been distilled; then wash down the condenser and all the connecting glass tubes carefully and transfer these washings, together with the contents of the three flasks that have received the distillate, to a 1-liter graduated flask, make to volume, mix thoroughly, pipette 200 cc. into an Erlenmeyer flask and nearly neutralize with a saturated solution of sodium or potassium hydroxide, using a few drops of phenolphthalein solution as indicator, being careful to keep the solution well cooled. If the neutral point is passed, add hydrochloric acid until acid again, then add sodium bicarbonate in excess and titrate with the standard iodine solution as directed under "Standardization." From the number of cc. of iodine used, calculate the per cent of arsenic (as  $As_2O_3$  or  $As_2O_5$ ) in the sample (if the result is desired in terms of metallic arsenic, calculate from the per cent of  $As_2O_3$  using the factor  $As_2O_3 \times 0.75748 = As$ ).

## CONCLUSIONS

I—It is shown that ferrous salts effect only in-

<sup>1</sup> The iodine solution may be added wholly from a burette, or the first 50 cc. may be added from a pipette.

<sup>2</sup> The starch solution should be added near the end of the reaction in order to produce a sharp end-point.

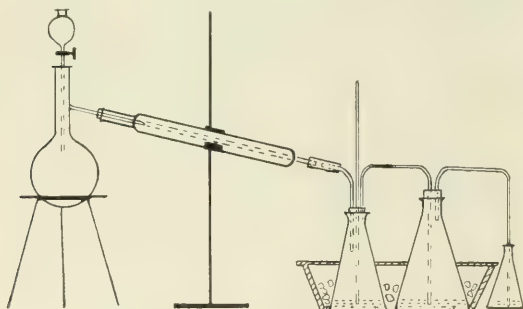


FIG. I—APPARATUS FOR THE DISTILLATION OF ARSENIC

The distilling flask is supported on a metal gauze which fits over a circular hole in a heavy sheet of asbestos board. The asbestos should extend out far enough to protect the sides of the flask from the direct flame of the burner. The first flask which receives the distillate is of 500 cc. capacity, the second of 1 liter capacity. The first flask should contain not over 40 cc. of water; otherwise a compound of arsenic will separate when the hot acid vapors strike the cold water which cannot readily be gotten into solution without danger of loss of arsenious chloride. Both of these flasks should be placed in a pan and kept surrounded with cracked ice and water. The third flask is added as a precaution; it is almost never found to contain any arsenic. The second flask should contain about 100 cc. of water, and the third flask sufficient to seal the end of the glass tube leading into it.

chemically pure iodine with twice its weight of powdered chemically pure potassium iodide, using 6.35 g. of the iodine for each liter of solution desired; dissolve in a small quantity of water and filter through a folded filter paper. Make filtrate up to volume and standardize as follows: pipette into an Erlenmeyer flask 50 cc. of the standard solution of arsenic trioxide, dilute to

complete reduction of  $As^v$  to  $As^{iii}$  in hydrochloric acid solution, and that in those cases in which satisfactory results have been obtained by the distillation method, using ferrous salts as reducers, one or more of the following conditions obtained: (a) metallic copper or a salt of copper was present, in which case some cuprous chloride would be formed; (b) the arsenic was present in very small amount; (c) the arsenic was present as metallic arsenic or as an arsenite and not as an arsenate.

II—Cuprous chloride effectively reduces  $As^v$  to  $As^{iii}$  in hydrochloric acid solution, and the arsenic trichloride is completely separated from antimony, lead, copper, zinc, iron and calcium by distillation.

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A SIMPLE AND RAPID ASSAY OF LEAD

By GREGORY TOROSSIAN  
Received November 13, 1915

The following simple and rapid method for the approximate quantitative determination of lead may be of value to metallurgists, mining engineers, prospectors and others who have occasion to estimate quickly and with reasonable accuracy the lead content of certain lead compounds and minerals.

The method is based upon the reduction of lead compounds by nascent hydrogen and is carried out

may be weighed directly on the plate in the cup) and moistened with a drop or two of dilute (1:3) hydrochloric acid. More acid is added, drop by drop, until the action of the acid on the aluminum is well started. The sample is subjected to this treatment for several seconds or until the original color of the sample almost disappears or is changed markedly. By this time the sample becomes spongy, may be turned over by a pointed glass rod or gently stirred and more acid is added drop by drop, if necessary. After a minute or two the contents of the cup are stirred with a pointed glass rod for about 5 min. or until all indications point to the completion of the reaction. In the case of PbS the fact that  $H_2S$  is no longer evolved is a good indication for the end of reaction. With colored lead compounds the disappearance of the color is indicative that the reduction is over. In the author's experiments the reductions took from 5 to 10 min.

When the reduction is over, a little pure water is added to the cup and after gentle stirring the liquor from the cup is decanted; this operation is repeated 4 or 5 times, or until the wash water shows no acid reaction (litmus test or "tongue touch"). Now the spongy metallic lead in the cup is pressed together with a glass rod so as to make it solid and compact, then a filter paper is pressed over the lead to dry it as completely as possible. Finally, one drop of water is placed near the cup on the plate which is now warmed above a small flame or a lighted match or any convenient small source of heat until the water is evaporated; this also dries the lead metal in the cup. The dried lead is now detached from the plate by a pocket knife and weighed, and the percentage of lead is calculated on the original sample.

This method is very simple and quick and sufficiently accurate to be of value in many instances of rapid estimation of lead in minerals and compounds.

The data in Table I show the degree of accuracy attained in this method. C. P. products were used for the experiments.

NATIONAL CARBON COMPANY, CLEVELAND

THE ANALYSIS OF MAPLE PRODUCTS, VII

The Electrical Conductivity Test for Purity of Maple Syrup

By J. F. SNELL  
Received August 20, 1915  
CORRECTIONS TO PAPER I<sup>1</sup>

In Paper I of this series, describing an electrical conductivity test for the purity of maple syrup, published in *THIS JOURNAL*, 5 (1913), 740, the following corrections should be noted:<sup>2</sup>

P. 745, Table VI, Column 8 (*i. e.*, fourth column from the right): The minimum value of "B/D" is 83 and the per cent deviation of the minimum from the mean is, therefore, 29.1 per cent instead of 21.4.

Column 10 (next to last): The heading should be "F/G" instead of "E/G."

Last column: The decimal point has been omitted from all but two of the ratios. Before each of these insert "0."

<sup>1</sup> Presented at the 51st Meeting of the American Chemical Society, Seattle, August 31 to September 2, 1915.

<sup>2</sup> In the edition of Paper I, published in *Trans. Roy. Soc. (Canada)*, [3] 7 (1913), 165-182, these errors were corrected

TABLE I

SAMPLE	Gram taken	Pb FOUND		Average Per cent	Theoretical Per cent
		Gram	Per cent		
PbO.....	0.1000	0.0925	92.50	92.62	92.83
	0.1000	0.0928	92.80		
	0.1290	0.1196	92.72		
	0.1858	0.1713	92.20		
	0.1308	0.1215	92.89		
	0.1355	0.1250	92.25		
PbSO <sub>4</sub> .....	0.1167	0.1085	92.97	69.32	68.31
	0.1890	0.1310	69.31		
	0.1435	0.1000	69.69		
	0.1190	0.0830	69.75		
	0.1774	0.1225	69.05		
	0.1875	0.1290	68.80		
Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> ·3H <sub>2</sub> O....	0.2010	0.1090	54.22	54.88	54.61
	0.1009	0.0552	54.71		
	0.1028	0.0568	55.26		
	0.1190	0.0657	55.20		
	0.1150	0.0635	55.22		
	0.1100	0.0596	54.19		
PbCO <sub>3</sub> .....	0.1056	0.0585	55.21	77.32	77.54
	0.1000	0.0552	55.20		
	0.1092	0.0597	54.67		
	0.1695	0.1305	76.99		
	0.1720	0.1325	77.04		
	0.1765	0.1370	77.80		
Red lead.....	0.1910	0.1480	77.48	...	...
	0.2090	0.1920	91.87		
	0.1915	0.1745	91.12		
Red lead.....	0.1740	0.1590	91.38	90.79	(Regular analysis, 90.17)
	.....	.....	90.79		

as follows: An aluminum plate 2 in. wide, 5 in. long and about 0.03 in. thick is used. About 1/4 in. from each end of the plate concave cups are formed by placing the plate over one of the thumb holes of a crucible tong or over a suitable ring and striking it with a pestle. The diameter of the cup need not be more than an inch and the depth about 3/16 in. Before using, the aluminum plate is rubbed with emery paper or sand so as to clean the surface from the aluminum oxide coating that hinders the action of acids. Each cup will serve for about fifteen determinations.

From 0.15 to 0.2 g. of the finely powdered sample is placed in the cup on the aluminum plate (it



P. 746, Table VII, Column 7 (next to last): The average value is 1.97, instead of "1.97."

Last column: Decimal points omitted, as in the corresponding column of Table VI. There should be two places of decimals in each of the ratios.

P. 746, in the paragraph at the head of the second column, the third sentence should read:

"On the 47 syrups examined by Jones the average value of this ratio is 0.98; on the 13 upon which Hortvet made these determinations it is 0.91; Bryan's general average for the 481 syrups is 0.81; although for the 100 syrups selected by him for ash analysis I find the average to be 0.87; and the average for the 12 syrups of Tables IV and VII of the present paper is 1.05."

P. 746, Table VIII, last column: Omit the decimal point in the first value, *i. e.*, read "251."

#### NEW FORM OF ELECTRODE

The form of electrode which the author now recommends<sup>1</sup> necessitates the use of 20 cc. of syrup instead of 15 cc.

#### RANGE OF VARIATION OF THE CONDUCTIVITY VALUE

Experience with the test subsequent to the publication of Paper I has shown that the range of variation of the conductivity value in genuine syrups is wider than it was then known to be. In Paper III,<sup>2</sup> a sample of genuine kettle-boiled syrup of normal water content was reported which showed the exceptionally high conductivity value of 230. Four other pan- and kettle-boiled syrups of the same season (1913), containing 37.90 to 44.88 per cent of water, likewise showed conductivity values over 200, *viz.*, 219, 205, 204 and 202. It is possible that these four might have come within the limits originally set had they been boiled down to correct density before the test. However, the exceptional instance of 230 would remain.

In 1914 samples were obtained from nine of the makers whose syrups we had analyzed in 1913. Among these were two from makers whose 1913 syrups had given conductivity values above 200 and two from makers whose syrups had shown the lowest values in 1913. The 1914 syrups from the former gave normal, and indeed comparatively low, conductivity values, *viz.*, 124 and 138, both makers having overconcentrated their syrups in 1914 but underconcentrated them in 1913. There were equally radical differences between the other analytical values of the 1913 and 1914 syrups from these makers—the total ash for instance being only about two-thirds as great in 1914 as in 1913. The 1914 syrups from the two makers whose 1913 product showed low conductivity values (112 and 113) both had conductivity values of 110 and their other analytical values were also very similar to those obtained in 1913. Our 1914 experience, accordingly, confirmed our conviction that conductivity values outside the limits 110 to 200 were very exceptional in genuine syrups.

Strikingly different results have been obtained in 1915, which was an exceptionally poor maple syrup year in Quebec, as regards both quantity and quality of product. Out of 61 syrups analyzed after reboiling and filtering through cotton wool (many of them

having undergone more or less fermentation) no fewer than 15 have given conductivity values below 110, four of them being actually below 100. The minimum is 96 and the maximum 189. We have carefully checked our results, recalibrating our cells with different potassium chloride solutions and redetermining the conductivity values of seven of the 1914 syrups with the new cell. In consequence we are compelled to admit that conductivity values below 110 may sometimes be encountered in pure maple syrups.

It may not be out of place to report that these 1915 syrups with very low conductivity values show also extraordinarily low percentages of total ash and of ash alkalinity. Three of them give percentages of total ash below the lowest previously recorded in genuine maple syrup. The minimum found was 0.56 per cent. An instance of alkalinity of soluble ash as low as 34 and one of alkalinity of insoluble ash as low as 35 occur among them.

#### COMPARISON OF RANGE WITH RANGES OF OTHER ANALYTICAL VALUES

In Table V of Paper III<sup>1</sup> a comparison was made of the ranges of variations of the various analytical values found in genuine syrups, as compiled from the investigations of Jones, Bryan, McGill and those made in this laboratory. Taking into consideration the results we have obtained with syrups of the seasons 1914 and 1915, we may substitute for the last column of that table the figures for conductivity value given below, adding also a column for the volumetric lead number (which, of course, may likewise require revision in the near future).

	Conductivity value	Volumetric lead number
No. of analyses.....	244	70
Average.....	142	5.64
Maximum.....	230	6.6
Minimum.....	96	4.8
Difference between maximum and minimum.....		
Range, expressed as per cent of average,	134	18
Range, expressed as per cent of minimum	140	38

By comparison with the other columns of Table V of Paper III it will be seen that the ranges of variation of both these newer values in genuine maple syrups are much narrower than those of any of the older analytical values.<sup>2</sup>

#### ADDITIONAL RESULTS WITH NON-MAPLE SYRUPS

We have recently prepared syrups boiling at 219° F. from 5 raw sugars and have made determinations of conductivity and other analytical values upon these syrups and also upon an additional sample of cane molasses.<sup>3</sup> The results, together with the corresponding figures from 5 of the 14 non-maple syrups whose conductivity values were reported in Paper I,<sup>4</sup> are given in the accompanying table. It should be noted that in making out the summaries given in the last column and at the foot of the table we have counted

<sup>1</sup> Snell and Scott, *THIS JOURNAL*, 6 (1914), 219.

<sup>2</sup> If the results of our ash determinations upon the 1915 syrups are taken into consideration the ranges of variation of the total ash and of the two alkalinities will be extended, becoming, respectively, in terms of the minima, 200, 259 and 494.

<sup>3</sup> These six samples were kindly donated by Dr. Chas. E. Bardorf, Superintendent of the St. Lawrence Sugar Refinery, Montreal.

<sup>4</sup> *Loc. cit.*, Table VIII.

<sup>1</sup> Van Zoeren, *J. Am. Chem. Soc.*, 38 (1916), 652.

<sup>2</sup> Snell and Scott, *THIS JOURNAL*, 6 (1913), 216.

every instance of a value outside the limits found in genuine maple syrups. In some of these instances the values found are so close to the limits that in actual control work the analyst would not venture to con-

- 5—Values above 200 have not been met with except in kettle-boiled and pan-boiled syrups.
- 6—Values below 110 have been found in the syrups of the year 1915, but not in those of the years 1911-14.

ANALYTICAL VALUES ON SOME NON-MAPLE SYRUPS AND SUGARS

ANALYTICAL VALUES ON SOME NON-MAPLE SYRUPS AND SUGARS														No. of the 10 tests con- demn- ing syrup
No.(a)	DESCRIPTION OF SYRUPS	Moisture	Ash Per Cent of Dry Matter				Alk. Sol. Ash	Alk. Insol.		Alk. Sol. Alk. Insol.	Can. Lead No.	Vol. Lead No.	Cond. Value 25° C.	
			Total	Sol.	Insol.	Insol.		Insol.	Ash					
5	Corn syrup, diluted.....	34.4	0.81	0.71	0.10	7.10	72	46	1.56	0.07	C(b)	209	4	
6	Golden syrup, diluted.....	34.4	2.09	1.89	0.20	9.45	132	53	2.49	2.69	—(c)	392	7(c)	
7	Golden syrup, diluted.....	36.0	1.99	1.85	0.14	13.21	109	28	3.90	1.92	C	403	7	
8	Molasses, diluted.....	34.4	6.35	4.28	2.07	2.07	49	403	0.12	17.25	R(d)	1121	8	
15	Molasses.....	30.23	4.53	3.50	1.03	3.39	320	248	1.29	9.88	R	817	8	
13	Syrup from light brown sugar.....	34.4	0.77	0.75	0.02	37.50	23	2	11.50	0.00	C	178	7	
RAW SUGARS(e)														
16	B. W. I. crystals, light.....	0.39	0.33	0.23	0.10	2.30	26	197	0.13	1.88	C	61	7	
17	B. W. I. crystals, dark.....	0.46	0.38	0.30	0.08	3.76	23	200	0.12	1.41	C	88	7	
18	Cuban crystals.....	0.50	0.36	0.28	0.08	3.50	30	194	0.15	1.71	C	71	8	
19	(Withheld).....	0.73	0.63	0.42	0.21	2.00	22	111	0.20	1.96	4.1	143	3	
20	Beet crystals.....	0.96	0.89	0.84	0.05	16.80	100	214	0.47	1.01	4.2	210	5	
LIMITS IN MAPLE SYRUPS:														
	Maximum.....		1.68	1.23	1.01	3.86	122	208	1.83	7.55	6.6	230		
	Minimum.....		0.56	0.30	0.12	0.53	34	35	0.21	1.74	4.8	96		
	Total samples, 11.....													
	No. distinguished from maple.....		7	6	8	5	7	5	8	7	All	7		

(a) The numbering corresponds to that of Table VIII, of Paper I.

(b) C represents a smooth curve plot.

(c) None of this sample was available for the volumetric lead subacetate test but we have assumed that the test would succeed here, as in the other instances.

(d) R, electrical resistance invariable.

(e) For determination of conductivity value the sugars were converted into syrups boiling at 219° F.

denn the sample on the strength of those values alone. Examination of this table shows that as a means of distinguishing these syrups from maple syrup the volumetric lead method surpasses all others, while the conductivity test is about as successful as any of the older tests, all of which involve the expenditure of more time.

REVISED DIRECTIONS FOR THE CONDUCTIVITY TESTS

Slightly amended to suit the new electrode the directions for this test are as follows:

From a (25 cc.) graduate, measure into a 100 cc. beaker a suitable quantity (20 cc.) of the syrup,<sup>1</sup> allowing thorough draining. Using the same graduate, add two successive portions of distilled water, each equal in volume to the syrup taken. Put in a dip electrode,<sup>2</sup> stir thoroughly, bring to exactly 25° C. and make the measurement. Divide the constant of the cell by the observed number of ohms and multiply the results by 100,000.

Genuine syrups have given values ranging from 96 to 230. In only one out of five years have results below 110 been obtained and results above 200 have not yet been obtained with patent evaporator syrups. Syrups giving normal conductivity values should be further examined by other tests.

SUMMARY

- 1- Errata in Paper I as published in THIS JOURNAL are corrected.
- 2- The test has now been applied to genuine syrups of five seasons—244 samples in all.
- 3- Conductivity values as low as 96 and as high as 230 have been met with in genuine syrups.
- 4- The limits of percentage variation of the conductivity value in genuine syrups are much narrower than those of any of the older analytical values but not as narrow as those of the volumetric lead number.

<sup>1</sup> In our 1915 work the syrups had been previously diluted with a little water, reboiled to 219° F. and filtered hot through cotton wool.

<sup>2</sup> Preferably of the Van Zoeren type (*Loc. cit.*), which is provided with a sensitive thermometer reading to tenths of a centigrade degree.

- 7—Some additional results on non-maple syrups are reported.
- 8—Revised directions for the test are given.

ACKNOWLEDGMENTS

The expenses of these investigations continue to be defrayed out of the money granted by the Dominion Government to the provincial governments for the encouragement of agriculture. During the last two years the appropriations from this grant have been supplemented by a donation from Mr. John H. Grimm, of Montreal. Thanks are due to the Hon. Martin Burrell, Dominion Minister of Agriculture, Hon. J. Ed. Caron, Quebec Minister of Agriculture, and Dr. F. C. Harrison, Principal of Macdonald College, for their approval of the appropriations, and to Mr. Grimm for his generous interest in the research. The author wishes also to express his appreciation of the hearty cooperation of his successive assistants, Messrs. J. M. Scott, N. C. MacFarlane and G. J. Van Zoeren.

MACDONALD COLLEGE, PROVINCE OF QUEBEC

THE OCCURRENCE OF SUCROSE IN GRAPES OF AMERICAN ORIGIN

By H. C. GORE  
Received August 13, 1915

The numerous analyses of the sugar content of European grapes that have accumulated during the last three-quarters of a century have led to the conclusion that invert sugar is the only recognizable saccharine constituent. In particular, sucrose has not been found in these grapes. Thus, for instance, von Babo and Mach<sup>1</sup> state "Sucrose has been found in many kinds of fruit, but not in grapes. \* \* \* Sucrose does not occur in grapes. \* \* \* Sucrose is widely distributed among plants, but does not occur in grapes." These statements evidently refer to European grapes. In 1909 the writer<sup>2</sup> reported the presence of sucrose

<sup>1</sup> "Kellerwirtschaft," 1910 edition, Vol. 2, pp. 4, 9, 10.

<sup>2</sup> THIS JOURNAL, 1 (1909), 436.



in two varieties of the American species *Vitis rotundifolia*, namely, Mish and Scuppernong, both of which are extensively cultivated southward from Virginia. The sample of Mish contained approximately 13 per cent of reducing sugar (invert sugar) and also there was found in it nearly 2 per cent of sucrose by both the copper reduction and the Clerget polarization method of analysis. An estimation of sucrose in a sample of Scuppernong by inversion with the enzyme invertase showed 0.69 per cent of that sugar. Two years later Alwood<sup>1</sup> reported the presence of sucrose in the Hayes, Worden, Illinois City, Pocklington and Nectar varieties of the American species *Vitis labrusca*, the percentages of sucrose ranging from 1.23 per cent to as high as 0.34 per cent. The sugar was estimated from copper reductions before and after acid hydrolysis. In Alwood's report a description is also given of a very interesting chance seedling grape of unknown origin which was found by Alwood and Eoff to contain unusually large amounts of sucrose, the percentage ranging in different samples from 3.44 per cent to 10.67 per cent. The presence of sucrose was inferred and the sugar estimated by the same methods of analysis that the writer used, namely, inversion by acid and by the enzyme invertase. Although sucrose has not been crystallized as yet from any varieties of grape, the results of Alwood and Eoff and of the writer indicate with a fair degree of certainty that it occurs in two of the American species, *rotundifolia* and *labrusca*.

During the past four seasons the selected samples of grapes which have been received at the Bureau of Chemistry from the Department's plantings at Vine-land, N. J., and from points in North Carolina, which furnished the *rotundifolia* varieties, have been examined for the presence of sucrose. The grapes were picked from the stems and pressed, in some cases without heating, in others after warming rapidly to 95° in a steam kettle. The juices were analyzed immediately after pressing and sucrose was tested for by the usual reduction and polarization methods. The analytical data were obtained by Messrs. F. T. Anderson, A. H. Bryan and S. F. Sherwood, of this Bureau. The varieties in the following list, 43 in number, showed no sucrose at any time. It is not believed that such heating causes any considerable inversion of sucrose in grape juice.

TABLE I VARIETIES IN WHICH SUCROSE WAS ABSENT

Agawam	Early Champion(a)	James (Rotund.)
Barry(a)	Eaton(a)	Jefferson
Berkmans	Elvira	Lampasas
Brighton	Eumelan(a)	Lindley
Brilliant	Flowers (Rotund.)	Martha
Canada(a)	Franklin(a)	Massasoit
Catawba	Gaertner	Merrimac
Centennial(a)	Goethe	Mo. Riesling
Clinton(a)	Hartford(a)	Montefiore(a)
Concord(a)	Herbmont	Niagara
Cynthiana(a)	Hybrid Seibel No. 1(a)	Noah
Delaware	Hybrid Seibel No. 2(a)	Nortons(a)
Diogenes(a)	Iona	Perkins
Dutchess	Ives(a)	Salem
		Ulster

(a) Heated to 95° before pressing; the others were pressed cold.

In Table II are recorded those varieties which at times showed small amounts of sucrose, and those in which the sugar was found always present.

<sup>1</sup> U. S. Dept. Agric., Bur. Chem., Bull. 140.

TABLE II VARIETIES IN WHICH SUCROSE WAS FOUND

VARIETIES	1911	1912	1913	1914
Campbell's Early(a)	Absent	0.36	0.61	Absent
Clematis(a)	1.40	Absent	Absent	Absent
Colerain	4.22	1.82	Absent	Absent
Diamond	Absent	Absent	Absent	0.30
Diana	Absent	Absent	Absent	0.52
Early Daisy(a)	Absent	Absent	0.65	Absent
Early Victor(a)	1.01	0.88	1.23	Absent
Eden (Rotundifolia)	0.61	0.59		
Herbert(a)	Absent	0.47	1.45	Absent
Isabella(a)	Absent	Absent	Absent	0.35
Lady	4.57	4.54	5.01	Absent
Lenora(a)	4.32	Absent	1.05	Absent
Moore's Early(a)	2.29	2.67	2.25	Absent
Nectar(a)	3.06	3.28	4.12	2.32
Pocklington	2.81	1.88	0.62	1.97
Rommel	Absent	Absent	Absent	0.33
Scuppernong (Rotund.)	0.91	1.18	1.14	Absent
Thomas (Rotund.)	2.97	2.91	3.36	2.39
Vergennes	Absent	Absent	Absent	0.34
Wildert(a)	1.22	Absent	Absent	
Winchell	0.44	Absent	Absent	Absent
Woodruff	Absent	1.00	0.95	0.34
Worden(a)	Absent	Absent	0.80	Absent

(a) Prepared by cooking the grapes and then pressing; the others were cold-pressed

In summary, an examination of these 66 varieties during four successive seasons shows that 43 of them contained no sucrose, 10 contained sucrose occasionally, and in 13 varieties it was frequently present. It is evident, therefore, that sucrose should be regarded as a normal constituent of many varieties of grapes of American origin.

#### FRUIT AND VEGETABLE UTILIZATION LABORATORY BUREAU OF CHEMISTRY, WASHINGTON

### THE OCCURRENCE OF SUCROSE IN RELATIVELY LARGE AMOUNTS IN A NEW SEEDLING GRAPE

By W. B. ALWOOD AND J. R. EOFF, JR.<sup>1</sup>

Received August 30, 1915

Although sucrose has never been found in European grapes, it has been shown by Gore<sup>2</sup> that many varieties of American origin, including representatives of both the *Vitis rotundifolia* and *labrusca* species, contain this sugar. The presence of sucrose in several varieties of the *labrusca* species was also reported by one of us.<sup>3</sup> In that bulletin there was described a seedling grape of unknown origin, the fruit of which had attracted the attention of one of us (Eoff) during a visit to the market in Sandusky, Ohio, in the fall of 1909. This grape was found to contain larger amounts of sucrose than had been reported previously from any American grapes. Although the origin of this seedling is uncertain, it appears to belong to the *labrusca* group. It was suggested in *Bulletin 140* that the seedling might be useful for cross-pollinating some of our strong-growing grapes, rich in acid and flavor, like the Catawba, because the flavor of the new grape is very mild—entirely without foxiness—and its acidity is very low. Seedlings from such crosses might result in improving the character of vintage grapes in the direction of milder flavor and lower acid content.

A further examination of this seedling was carried on for a period of 60 days during the season of 1911 so that the data might be very conclusive. This grape is characterized by fairly large bunches, well filled, berries large and beautiful, color darker when fully ripe than Delaware. The flavor is peculiar,

<sup>1</sup> The work described in this paper was performed while the authors were connected with the Enological Laboratory (now closed), Bureau of Chemistry, United States Department of Agriculture.

<sup>2</sup> THIS JOURNAL, 1 (1909), 436.

<sup>3</sup> Alwood, U. S. Dept. Agric., Bur. Chem., Bull. 140 (1911).

TABLE I—DATA ON THE OCCURRENCE OF SUCROSE IN A SEEDLING GRAPE I. R. EOFF AND S. F. SHERWOOD, ANALYSTS  
RESULTS IN GRAMS PER 100 G. OF JUICE

LAB. No.	Date analyzed	Specific gravity	Total solids	Sugar- solids	Invert sugar	Sucrose by inversion as invert	Total sugar as invert	Total acid as tartaric	CONDITION OF FRUIT
3054	Aug. 23	1.0648	16.80	2.24	7.90	6.66	14.91	0.56	Berries large, fine condition, not fully colored
3060	Aug. 27	1.0662	17.17	1.86	8.56	6.75	15.67	0.50	About same condition
3066	Aug. 30	1.0670	17.38	1.87	7.91	7.60	15.91	0.42	Maturing unevenly, some bunches appear fully ripe
3073	Sept. 3	1.0721	18.71	2.04	8.27	8.40	17.11	0.39	About same condition
3081	Sept. 6	1.0731	18.97	1.95	8.32	8.70	17.48	0.42	Continues to develop very unevenly
3103	Sept. 10	1.0746	19.31	2.00	7.97	9.34	17.80	0.47	Condition holds as for previous date
3112	Sept. 13	1.0817	21.23	1.96	8.91	10.36	19.82	0.30	Ripening unevenly
3132	Sept. 17	1.0824	21.41	2.36	9.15	9.90	19.57	0.34	Some bunches past best condition
3148	Sept. 20	1.0724	18.79	2.08	8.99	7.72	17.12	0.26	Condition holds, some bunches not fully colored
3179	Sept. 24	1.0827	21.49	2.02	9.52	9.95	19.99	0.30	Crop picked for market
3201	Sept. 27	1.0831	21.59	1.83	9.51	10.25	20.29	0.26	Flavor becoming peculiar, not vinous
3220	Oct. 1	1.0737	19.13	1.95	8.96	8.22	17.61	0.21	Fruit holding well on vines
3244	Oct. 4	1.0690	17.90	2.21	9.31	6.38	16.03	0.31	Fruit holding well on vines
3255	Oct. 8	1.0626	16.23	2.08	8.92	5.23	14.43	0.29	Fruit holding well on vines
3284	Oct. 15	1.0750	19.47	2.30	9.72	7.45	17.56	0.29	Fruit holding well on vines
3298	Oct. 18	1.0726	18.84	2.28	9.43	7.13	16.93	0.24	Fruit falling
3308	Oct. 22	1.0741	19.23	2.32	9.40	7.51	17.31	0.25	Fruit falling badly

mild, honey-sweet, not exactly grape-like in character, yet many persons have pronounced it as very pleasant and desirable for table use. It can be harvested for market over a long period by selecting the bunches.

Table I gives the chemical data in full, with notes on the character and condition of the fruit when analyzed. Our thanks are extended to Dr. B. G. Hartmann who has aided us in this investigation. The data herewith published complete three years' examination of this peculiar grape and quite fully cover the question of its composition. The further question of its practical value belongs to students of horticulture.

BUREAU OF CHEMISTRY, WASHINGTON

#### A COMPARISON OF METHODS FOR THE DETERMINATION OF CASEIN IN MILK

By C. B. HERSEY

Received October 20, 1915

As a part of a milk study<sup>1</sup> which was completed by the author during the past year at the University of California three methods for the determination of casein in milk were compared. The following résumé of the work is now submitted with results:

Ever since Dr. Babcock introduced his remarkably simple and accurate method for fat determination in milk, much effort has been spent on devising some equally simple and accurate determination for casein in milk by which the cheese maker could more carefully control his product and by which the dairyman could receive a more equitable return for his milk.

From among the several methods thus evolved the ones chosen for this comparison were the Van Slyke Volumetric,<sup>2</sup> the Hart Centrifugal<sup>3</sup> and the Official Nitrogen or Kjeldahl method.<sup>4</sup> A systematic comparison of the above methods had not been made, though Shutt<sup>5</sup> and Dean<sup>6</sup> each made a few tests comparing the Hart and the Nitrogen method. Literature com-

<sup>1</sup> "A Study of Milk from Individual Cows Showing Daily and Seasonal Variations in Composition and a Comparison of Methods for the Determination of Casein in Milk," being a thesis on which with other work the author was granted the M. S. degree in Food Chemistry, Univ. California Library, Berkeley.

<sup>2</sup> L. L. Van Slyke and A. W. Bosworth, "A Volumetric Method for Casein Determination in Milk," *N. Y. Exp. Sta. Tech. Bull.* **10**, 241-241.

<sup>3</sup> E. B. Hart, "A Simple Test for Casein in Milk and Its Relation to the Dairy Industry," *Wis. Exp. Sta., Bull.* **166**, 22.

<sup>4</sup> "Methods of Analysis of the Association of Official Agricultural Chemists," U. S. Dept. of Agr., Bur. of Chem., *Bull.* **107** (Revised), 117.

<sup>5</sup> F. T. Shutt, "Hart's Casein Test," *Canada Exp. Farm. Rpt.*, **1909**, p. 192.

<sup>6</sup> H. H. Dean, "Comparison of Hart's Method," *Ann. Rept. of Ont. Agri. Col. and Exp. Farms*, **34** (1908), 97-127.

paring the Van Slyke and Official or the Van Slyke and the Hart method seems to be lacking.

#### METHODS OF ANALYSIS

VAN SLYKE METHOD was performed exactly as given in the bulletin,<sup>1</sup> using the chemist's modification, that is, N/10 acid and base instead of acid of an arbitrary strength.

HART METHOD—The details of procedure were followed exactly as given in the bulletin with the exception that instead of using hand power the centrifuge was electrically driven with rheostat for speed control, which feature is greatly to be desired not only from a muscular point of view but because of the greater uniformity of speed attainable which is essential to the success of the test.

NITROGEN METHOD was carried out according to the Official Kjeldahl-Gunning method. In the latter part of the work 5 per cent of CuSO<sub>4</sub> was added to the K<sub>2</sub>SO<sub>4</sub> (Hibbard's mixture)<sup>2</sup> which expedited greatly the time required for the decomposition with the strong sulfuric acid with exactly the same result, as far as nitrogen is concerned.

Throughout the work all directions and precautions were carefully observed. Frequently full duplicate analyses were made.

#### RESULTS

Table I shows the average for each method of 143 samples of fresh milk each analyzed by the three methods, with a maximum and minimum for each method. The close check of the Hart and Official methods by the average and the corresponding doubtful check of the Van Slyke and Official are to be noted.

	Official	Hart	Van Slyke
Average.....	2.47%	2.52%	3.07%
Maximum.....	3.31	3.4	3.70
Minimum.....	1.71	1.81	1.05

Table II gives in detail the variation of the two methods from the Official method which is considered for the comparison to be the standard of accuracy. The variations are given in percentages of casein, showing the number and percentage of determinations which differed by various amounts both more and less or higher and lower for each method than by the Official method. Unless this "higher and lower" factor be determined it might be possible to arrive at a series of averages which would give an erroneous impression of the true condition; i. e., in any individual

<sup>1</sup> Loc. cit.

<sup>2</sup> P. L. Hibbard, "Notes on the Determination of Nitrogen by the Kjeldahl Method," *THIS JOURNAL*, **2** (1910), 463-6.



average half the data might be high and half low, with none near the mathematical average and great differences between. In Table II, however, this factor is taken care of and this table gives the complete data as to accuracy on each of the two methods as compared with the Official determination, all three analyses being made on the same milk sample, with the addition of a few odd pairs of determinations

Variations in Per cent Casein from Official Method		HART METHOD DETERMINATIONS		VAN SLYKE METHOD DETERMINATIONS	
		No. of	% of	No. of	% of
MORE	0.0 to 0.1	60	40.5	26	18.2
THAN	0.1 to 0.2	34	23.0	30	21.0
BY	0.2 to 0.3	2	1.4	16	11.2
OFFICIAL	0.3 to 0.5	2	1.4	17	11.9
METHOD	0.5 to 1.0	1	0.7	10	7.0
	Over 1.0	0	0.0	11	7.7
EQUAL TO	OFFICIAL METHOD	9	6.1	2	1.4
LESS	0.0 to 0.1	25	16.9	16	11.2
THAN	0.1 to 0.2	—	—	9	6.3
BY	0.2 to 0.3	1	0.7	1	0.7
OFFICIAL	0.3 to 0.5	3	1.5	2	1.5
METHOD	0.5 to 1.0	0	0.0	2	1.5
	Over 1.0	0	0.0	1	0.7
TOTAL		148		143	

(where a third analysis was lost) but which in no way affects the accuracy of the results. Thus from Table II it would seem that as to accuracy the Hart method far exceeds the Van Slyke method both in smaller total average variation from the Official and in the number of determinations with much variation. It is also seen that while approximately 75 per cent of the Hart determinations check the Official method to within 0.1 per cent, only 36 per cent of the Van Slyke determinations check within the same limits. It was also found that where there was

TOTAL TIME TO COMPLETE METHOD			PERSONAL ATTENTION REQUIRED		
VARIATION	AVERAGE		VARIATION	AVERAGE	
Official	3 6 Hrs.	(a) 3 1/2 Hrs.,	20-60 Min.	40 Min.	
Hart	15-20 Min.	(b) 5 Hrs.	5-15 Min.	(c) 5 Min.,	(d) 15 Min.
Van Slyke	15-90 Min.	45 Min.	20-60 Min.	30 Min.	
(a) With Hibbard mixture			(b) Without Hibbard mixture		
(c) With electric centrifuge			(d) Without electric centrifuge		

a maximum variation between the Hart and Official methods of 0.54 per cent casein, there were 12 determinations by the Van Slyke method which varied over 1 per cent from the Official, with one maximum variation of 1.88 per cent.

Table III shows the comparative rapidity of the three methods based both on consideration of the total time required from beginning to completion of the test, and on the actual time which the analyst would have to give the test in undivided personal attention. This table gives the approximate figures showing the time required to make the determinations after all standard solutions are made and the analyst has acquired a fair degree of proficiency in the methods.

Table III shows in a rough way that not only is the Hart method greatly superior to the other methods as to rapidity but that there is little choice in the actual time of personal attention required between the Kjeldahl-Gunning and the Van Slyke methods. Especially is this so when the Hibbard mixture is used with the former. It must be borne in mind, however, that in total time required the nitrogen method is much longer than either of the other methods. Furthermore, the Hart method required not only the

least total time but also the least personal attention, *i. e.*, barely five minutes with electric centrifuge.

#### CONCLUSION

**ACCURACY**—Though the Official Nitrogen method is the standard of accuracy for the determination of casein in milk, the above results show that for all ordinary work the Hart method with electric centrifuge is dependable, checking very closely the Official method, and is far superior to the Volumetric method.

**RAPIDITY**—As to the time required by the three methods, the Official is longest in total time, with about the same time required in personal attention as the Van Slyke method. The Hart method requires, however, but a small fraction of the time of the other methods and has the added advantage of requiring neither exactly standard solutions nor final calculation of results.

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#### SOME CHEMICAL CHANGES IN THE RESWEATING OF SEEDLEAF TOBACCO

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Received November 4, 1915

Since Nessler<sup>1</sup> stated that the process of sweating tobacco was a fermentation, much investigational work has been done upon the study of the agents which induce the process. Numerous conflicting theories have arisen. There are those who maintain that bacteria are the foremost agents in producing the fermentation, others uphold the enzyme theory and still others attribute it to inorganic catalytic agents.

Although much work has been done to study the agents which cause the fermentation, little has been done to study in detail the chemical changes which occur. Now it seems that a more thorough knowledge of the chemical changes which occur should throw some light upon the nature of the agents which produce these changes.

#### AGENTS PRODUCING THE FERMENTATION IN THE RESWEATING PROCESS

**I. MICROORGANISMS**—Suchsland<sup>2</sup> believed that there existed a ferment, the action of which was similar to that of lactic, acetic and butyric acid ferments. Having isolated numerous bacteria from fermenting tobacco, he attributed the fermentation mainly to bacteria, and thought that if pure cultures could be obtained from Havana tobacco, it would be possible to produce, in home-grown tobaccos, aromas similar to those of Havana tobacco. This plan, however, was not a commercial success. Behrens<sup>3</sup> isolated a number of organisms from fermenting tobacco, among which were *Aspergillus fumigatus* and *Bacillus subtilis*. He concludes that microorganisms play an important part in fermentation. König<sup>4</sup> isolated *Diplococcus tabaci* and *Bacillus tabaci*, which he thought played an important part in fermentation.

<sup>1</sup> J. Nessler, "Gährung des Tabaks," *Der Tabak*, 1867, p. 122, Mannheim.

<sup>2</sup> Emil Suchslands, "Über Tabakfermentation," *Ber. d. Bot. Ges.*, 9 (1891), 79.

<sup>3</sup> J. Behrens, *Centr. fuer Bakt. und Par.*, 2, Abt. II, 1896.

<sup>4</sup> C. J. König, *Ibid.*, 2, Abt. VI, 1909, pp. 344-355.

Schlösing<sup>1</sup> worked upon snuff tobaccos and concludes that microorganisms were not necessary for the production of that type of tobacco.

2. ENZYMES—Loew<sup>2</sup> combats the theory that microorganisms are responsible for the fermentation of tobacco, advanced by Behrens and numerous workers. He attributes the fermentation to numerous enzymes which he finds in tobacco leaves, among which are the oxidases and catalases. In a later publication Loew<sup>3</sup> shows the presence of oxidase, peroxidase and catalase in tobacco leaves. Jensen<sup>4</sup> excluded the action of bacteria by means of antiseptics and concludes that bacteria may play some part in the fermentation, but that the process can be carried out without the aid of bacteria.

3. CHEMICAL—Boekhout and De Vries<sup>5</sup> maintain that the fermentation is purely a chemical process. They claim that the changes are brought about by the oxygen of the air and that the metals in the plant such as manganese and iron act as catalytic agents.

#### LOSSES IN WEIGHT

Frear<sup>6</sup> found the loss in weight during fermentation greater in tobacco fertilized with barnyard manure than in tobacco grown with commercial fertilizers. Tobacco fertilized with double carbonate showed greater losses than that fertilized with sulfate of potash. Jenkins<sup>7</sup> found the average loss of weight of the crop to be 13.8 and<sup>8</sup> 14.0 per cent. Behrens<sup>9</sup> found a loss in organic matter of 5.6 per cent.

#### CHANGES IN COLOR

One of the most apparent changes in the tobacco during the fermentation is the disappearance of the greenish color of the cured leaf. Nessler<sup>10</sup> attributes this to the destruction of chlorophyll.

#### CHEMICAL CHANGES

Nessler<sup>11</sup> studied the effect of air, pressure and heat upon the fermentation of tobacco, concluding that chlorophyll is destroyed, and that ammonia is formed but only under certain conditions when subjected to pressure so that the free access of air is prevented. Furthermore, he finds the nicotine content diminished. Fesca and Imai<sup>12</sup> found a loss of nitric acid, an increase in amides and a loss in nicotine.

Behrens<sup>9</sup> analyzed samples of tobacco before and after the fermentation from which he concludes: (a) In the fermentation there is a loss of material, followed by a formation of carbon dioxide: reckoned on the basis of ash content the loss was 5.6 per cent.

(b) The losses occur especially in the soluble carbohydrates and the non-volatile acids. (c) Thirty per cent of the original content of nicotine was destroyed: this loss of nicotine must be attributed to the action of bacteria which use it as a foodstuff, rather than to volatilization. (d) Nitric acid disappears entirely during the fermentation. (e) The protein and amide content were not altered during the fermentation. (f) The ether extract showed a marked loss. (g) In the fermentation, acids are formed which are volatile in steam. Finally he compares the process to that of making brown hay.

Johnson<sup>1</sup> analyzed some samples of Connecticut tobacco before and after the fermentation. He found that the nitric acid, ammonia, fiber and starch content were affected very little by the process and that the main loss of dry matter occurred in the nicotine, nitrogen-free extract and ether extract.

Garner<sup>2</sup> studied the effect of fermentation upon the different "forms" of nicotine. He found the total amount of nicotine lost during fermentation to be about equal to the amount soluble in petroleum ether lost during the fermentation. From this he concludes that for the most part the nicotine is lost by volatilization.

#### PROCESSES OF RESWEATING

In order that we may understand the position of the resweat in the preparation of cigar tobaccos, a statement of the customary processes may not be amiss. When the leaves of the tobacco plant have become well ripened the farmer cuts the crop and places it in large barns equipped with ventilators to regulate the moisture conditions, during the curing<sup>3</sup> process, which usually requires from 6 to 10 weeks. After being cured, the leaves are stripped from the stalk, graded, sized and tied into hands (about 15 to 20 leaves each) which are then pressed into bales of from 75 to 100 lbs. The tobacco is now ready to leave the farmer and is usually bought by men who are known as packers.

After the packer receives the tobacco from the farmer, which is usually during the winter or early spring months, he puts the raw tobacco, as it is now termed, through the first sweating process, for which there are two methods now in common use: (1) bulk sweating and (2) case sweating.

In "bulk sweating," the bales of tobacco previously mentioned are torn apart and a large bulk is built up by keeping the butt ends of the hands towards the outside of the bulk. If the tobacco is not in good "case," it is dipped in water. By means of a pipe placed horizontally at about the center of the bulk, a thermometer is inserted and the temperature of the bulk is watched carefully as it begins to heat. If it goes too high, the bulk is torn down and rebuilt so that the hands which were formerly on the outside of the bulk are placed near the center of the new bulk.

<sup>1</sup> Th. Schlösing, "Sur la fermentation en masses du tabac pour poudre," *Mémoires des manufactures de l'état*, Tome I, H 4, 1888, pp. 514-552.

<sup>2</sup> Oscar Loew, *Centr. fuer Bakt. und Par.*, 1900, pp. 590, 108.

<sup>3</sup> Oscar Loew, *Report 68*, U. S. Department of Agriculture

<sup>4</sup> Hjalmar Jensen, *Centr. fuer Bakt. und Par.*, 21, *Abt. II*, 1908, p. 469.

<sup>5</sup> Boekhout and De Vries, "Ueber Tabakfermentation," *Centr. fuer Bakt. und Par.*, 24, *Abt. II*, 1909, p. 496.

<sup>6</sup> Wm. Frear, Pennsylvania State College Agr. Exp. Sta., *Bull.* 30.

<sup>7</sup> Jenkins, Conn. State Agr. Exp. Station, 1893.

<sup>8</sup> *Ibid.*, 1894.

<sup>9</sup> J. Behrens, "Weitere Beiträge zur Kenntniss der Tabakpflanze, VII, Die Fermentation," *Landw. Vers. Sta.*, 43 (1894), 293.

<sup>10</sup> J. Nessler, "Gährung des Tabaks," *Der Tabak*, 1867, p. 122, Manheim.

<sup>11</sup> *Ibid.*

<sup>12</sup> Fesca and Imai, *Landw. Jahrb.*, 17 (1888), 327.

<sup>1</sup> S. W. Johnson, Conn. State Agr. Exp. Station, *Ann. Rep.*, 1892.

<sup>2</sup> W. W. Garner, "The Relation of Nicotine to the Quality of Tobacco," *Bull.* 141, Part I, B. P. I., U. S. Dept. Agric.

<sup>3</sup> Garner ("Research Studies on the Curing of Leaf Tobacco," *Bull.* 79, U. S. Dept. Agric. has studied very thoroughly the chemical changes occurring during this curing process.



Usually the more up-to-date packers are able to control the temperature and moisture conditions of the sweating room by means of steam pipes. It is impossible for an expert packer to give explicit directions for controlling and handling the bulk, but the temperature and moisture conditions must be controlled carefully by the operator. The temperature of the bulk is allowed to rise gradually until about 125° F. to 140° F. is reached. Sometimes it is necessary to turn the bulk a great number of times while in other cases two or three times may be sufficient.

The "case sweating" is done in wooden cases built very strongly and holding from 300 to 400 lbs. each. These cases are not tight but have spaces of 1 in. between the boards in order to allow the moisture to escape. In some instances the crops lose from 10 to 14 per cent and it is necessary to give this moisture some means of escape.<sup>1</sup>

In packing the case the butt ends of the hands are placed towards the outside and the case is packed moderately by means of a press. After this the case is covered with a lid. The tobacco is cased during the winter and is then stored in rows three or four cases high and allowed to go through a sweat. The store-room may be heated artificially or the tobacco may be allowed to sweat under the influence of the natural heat of the summer. After the sweat is completed, the cases are sampled and the tobacco is again placed in the cases. This completes the "case sweating."

#### SAMPLES USED IN INVESTIGATION

The samples used in this work were of the Pennsylvania Seedleaf variety grown in Lancaster County, and hence a cigar-filler type. All samples were taken from the same crop, grown and cured under as nearly the same conditions as it was possible to obtain them.

A 2-lb. sample which represented the crop as nearly as it was possible to judge was selected before the re-sweating process, and after the process another 2-lb. sample was selected. The midveins were stripped from the leaves of each sample and after being allowed to dry the samples were carefully pulverized in a grinder.

The samples were of the 1911 crop, obtained from a very extensive and successful cigar manufacturer of Lancaster, Pa., who purchased the tobacco in a raw state directly from the grower. The manufacturer here had direct supervision over the first sweat which was a case sweat. The tobacco, having been case sweated in 1912, was stored until 1913, at which time it was put through the resweating process.

**RESWEATING PROCESS**—The cases of tobacco were opened and the hands of tobacco were dipped in water and again replaced in the case. The cases were then placed in large sweating rooms until, in the opinion of the operator, they had reached the proper stage. The temperature and moisture conditions of the sweating room were very well controlled. Since this operation was performed by a commercial company, it is not possible to give a record of the temperature and moisture conditions of the sweating room.

#### METHODS OF ANALYSIS

**MOISTURE** was determined by drying over sulfuric acid in a vacuum desiccator.

**ASH** according to the Optional method, *Bulletin 107*, Bureau of Chemistry, U. S. Department of Agriculture, page 238.

**TOTAL NITROGEN** by the Kjeldahl method modified so as to include nitrates.

**NITRIC NITROGEN** by difference between the results of the Ulsch method modified by Street and the Magnesium Oxide method for ammonia as given in *Bulletin 107*, Bureau of Chemistry, U. S. Department of Agriculture, page 5. Ammonia by the Folin method.

**PROTEIN** according to Sherman's "Organic Analysis," page 317.

**AMIDES** by difference.

**NICOTINE** by a combination of the Kissling method and the new method as given in *Bulletin 102*, Part VII, Bureau of Plant Industry, U. S. Department of Agriculture.

**CRUDE FIBER** by the Official method, *Bulletin 107*, Bureau of Chemistry, U. S. Department of Agriculture.

**ETHER EXTRACT** by extracting with ether and drying at 100° C. to constant weight.

All of the determinations were made in duplicate with the results given in Table I.

TABLE I—PERCENTAGE ANALYSES BEFORE AND AFTER THE RESWEAT (g)

	LEAF ANALYSES		MIDVEIN ANALYSES	
	Before	After	Before	After
Total nitrogen.....	3.76	3.55	2.66	2.61
Protein (factor 6.25).....	11.24	10.39	7.32	6.85
Ammonia.....	0.59	0.53	0.36	0.16
Nitric acid (N <sub>2</sub> O <sub>5</sub> ).....	1.01	0.37	0.45	0.19
Nicotine.....	4.21	2.18	1.48	1.21
Amides (factor 4.7).....	1.67	4.40	3.53	5.15
Ash.....	22.44	25.17	23.72	24.36
Crude fiber.....	9.11	9.27	..	..
Ether extract.....	5.08	4.63	1.94	1.54
Nitrogen-free extract.....	44.63	38.80	..	..
Reducing substances.....	2.77	4.10	..	..
Organic matter.....	77.56	74.83	76.28	75.64
Moisture.....	5.00	5.07	7.05	7.03

(a) All results computed to a dry basis except moisture.

#### DISCUSSION

The fermented samples show an increase in ash of 2.73 per cent. This can not be considered as a true gain in ash constituents but must be due to the fact that the sample lost considerable organic matter during the fermentation. Assuming that the ash remains constant we find that the leaves lost 11.11 per cent and the midveins 2.32 per cent organic matter. Table II shows the results calculated to one base.

TABLE II—RESULTS OF TABLE I RECALCULATED TO BASIS OF CONSTANT ASH CONTENT

	LEAF ANALYSES		MIDVEIN ANALYSES	
	Before	After	Before	After
Total nitrogen.....	3.76	3.15	2.66	2.55
Protein (N × 6.25).....	11.24	9.22	7.32	6.69
Ammonia.....	0.59	0.47	0.36	0.15
Nitric acid (N <sub>2</sub> O <sub>5</sub> ).....	1.01	0.32	0.45	0.18
Nicotine.....	4.21	1.93	1.48	1.17
Amides (N × 4.7).....	1.67	3.90	3.53	5.03
Ash.....	22.44	22.44	23.72	23.72
Crude fiber.....	9.11	8.21	..	..
Ether extract.....	5.08	4.10	1.94	1.50
Nitrogen-free extract.....	44.63	34.45	..	..
Reducing substances.....	2.77	3.64	..	..
Organic matter.....	77.56	66.45	76.28	73.96

Behrens<sup>1</sup> and Johnson<sup>2</sup> analyzed samples of tobacco before and after the fermentation. Table III gives a comparison of the changes which they found and the changes found in this work upon the resweat: these results have all been recalculated as in Table II. In

<sup>1</sup> J. Behrens, "Weitere Beiträge zur Kenntnis der Tabakpflanze, VII. Die Fermentation," *Landw. Vers. Sta.*, **43** (1894), 293.

<sup>2</sup> S. W. Johnson, Conn. State Agric. Exp. Station, *Ann. Rep.*, **1892**.

<sup>1</sup> Report 60, U. S. Dept. Agric.

comparing these results, it should be remembered that the work of both Behrens and Johnson was upon the first sweat and that the work presented in this paper was done upon the resweat.

TABLE III—COMPARISON OF (PERCENTAGES) CHANGES IN THE FIRST SWEAT AND THE RESWEAT

	FIRST SWEAT CHANGES			
	RESWEAT CHANGES (Author)	(Johnson)		(Beh- rens)
		Leaves	Midveins	
Total nitrogen.....	-0.61	-0.11	.....	-0.19
Protein (factor 6.25).....	-2.02	-0.63	.....	-0.02
Ammonia.....	-0.12	-0.21	+0.02	-0.03
Nitric acid (NaO <sub>3</sub> ).....	-0.69	-0.27	+0.04	+0.22
Nicotine.....	-2.28	-0.31	-0.99	-0.44
Amides (factor 4.7).....	+1.23	+1.50	.....	.....
Ash.....	0	0	0	0
Crude fiber.....	-0.90	.....	+0.87	+0.29
Ether extract.....	-0.98	-0.44	-0.70	-0.28
Nitrogen-free extract.....	-10.18	.....	-2.53	-0.85
Reducing substances.....	+0.87	.....	.....	.....
Organic matter.....	-11.81	-2.32	.....	.....
Other nitrogenous matter.....	.....	.....	+1.03	0.73
Starch.....	.....	.....	+0.09	+0.14
Acids (reckoned as lactic acid).....	.....	.....	.....	-0.02
Organic non-volatile acids (reckoned as malic acid).....	.....	.....	.....	-3.18
Acids volatile in steam (reckoned as butyric acid).....	.....	.....	.....	+0.16
Sulfuric acid (as SO <sub>3</sub> ).....	.....	.....	.....	0.07

# SUMMARY

1—The greatest loss of dry matter during the re-sweating process occurs in the proteins, nicotine, ether extract and nitrogen-free extract. The total nitrogen, ammonia, nitric acid, and crude fiber show slight losses.

2—The amides and reducing substances show an increase.

3—The changes during the resweat are quite similar to those of the first sweating process. It seems, therefore, that the resweat is a continuation of the first sweating process. The changes during the resweat seem to be greater than during the first sweat, but this is what we should expect because the re-sweating process is more severe.

4—The loss in protein nitrogen minus the gain in amide nitrogen is 0.06 per cent and this plus the loss in ammonia (0.09 per cent) and nitric acid nitrogen (0.18 per cent) equals 0.33 per cent. The total loss in nitrogen is 0.61 per cent. The difference between the total loss of nitrogen and the loss of nitrogen as nitric acid, ammonia, and amides (loss of protein nitrogen minus amide gain in nitrogen) is 0.28 per cent. It appears from this that the most of the nicotine which is lost, is lost by volatilization. This is in accord with the results of Garner.<sup>1</sup>

5—It is evident that a breaking down of proteins into amides occurs. From this we can readily see that there is probably an enzyme present which is capable of breaking down the proteins.

6—Since the increase in amide nitrogen is not so great as the loss in protein nitrogen it suggests that there may be present a ferment which breaks up the amino acids, although no definite conclusions can be drawn.

7—The total loss of organic matter in the leaf samples was 11.11 per cent and in the midveins 2.32 per cent. Behrens<sup>2</sup> reports a loss of 5.6 per cent.

<sup>1</sup> W. W. Garner, "The Relation of Nicotine to the Quality of Tobacco," *Bull.* **141**, Part I, B. P. I., U. S. Dept. of Agric

<sup>2</sup> J. Behrens, "Weitere Beiträge zur Kenntniss der Tabakpflanze, VII, Die Fermentation," *Landw. Vers. Sta.*, **43** (1904), 293.

8—The changes in the midveins are similar to the changes in the leaf but are not nearly so great.

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## NEW METHODS FOR THE ANALYSIS OF LIME-SULFUR SOLUTIONS. II—THE ESTIMATION OF "POLY-SULFUR"

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Whatever may be the actual atomic grouping of sulfur in the various calcium polysulfides which constitute the important ingredient of lime-sulfur solutions, it is convenient to discuss the combinations of the element as if it occurred therein in two distinct forms, namely, "mono-sulfur" and "poly-sulfur." The general formula for these calcium polysulfides may then be expressed as Ca(*m*-S) (*p*-S)<sub>*y*</sub>. A previous paper<sup>2</sup> on the analysis of lime-sulfur solutions has described among other things the estimation of mono-sulfur. In continuation of the work a volumetric method now has been developed for the estimation of poly-sulfur with, apparently, a desirable degree of both accuracy and convenience.

### DESCRIPTION OF THE METHOD

That the reaction  $S + Na_2SO_3 = Na_2S_2O_3$  applies to the poly-sulfur of soluble polysulfides has long been known. The reaction  $Ca(m-S) (p-S)_y + yNa_2SO_3 = CaS + yNa_2S_2O_3$  is the basis of the new method. Mono-sulfur is removed as zinc sulfide and excess of sulfite as insoluble strontium sulfite, after which thiosulfate is determined by titration with iodine. From the total thiosulfate thus obtained must naturally be subtracted the thiosulfate originally present in the lime-sulfur solution. The detailed execution of the method is as follows:

Into a mixture of 10 cc. of a recently prepared 10 per cent solution of C. P. anhydrous sodium sulfite and 20 cc. of *N*/5 ammoniacal zinc chloride, contained in a 200 cc. Erlenmeyer flask, pipette 10 cc. of a dilution of the sample containing 1.5 to 2.0 per cent "sulfide sulfur." Mix, wash down with about 25 cc. water and place on the steam bath at full heat. At intervals of 10 min. mix the contents of the flask and rinse down with a little hot water from a wash-bottle. After heating for 45 min. with four intermediate mixings, remove from the heat, add 20 cc. of a 10 per cent solution of crystallized strontium chloride, and mix well. Let settle for five minutes, then filter into a 250 cc. volumetric flask and wash with hot water. Cool in water to room temperature, add 0.5 to 1.0 cc. of a 10 per cent solution of crystallized disodium phosphate, make to the mark, shake well and filter through a dry paper into a dry flask, first using about 20 cc. to wet the paper, the runnings being discarded. To 200 cc. of the clear filtrate add

<sup>1</sup> Published with the permission of the Secretary of Agriculture.

<sup>2</sup> This JOURNAL, **8** (1916), 151.



methyl red indicator, then, slowly, and with thorough mixing, a 10 per cent solution of tartaric acid to a permanent slight acid reaction. Add starch and titrate with *N*/10 iodine. The whole process should be executed without intermediate delays. From the observed iodine titration subtract a blank of 0.10 cc., multiply the remainder by 1.25 to convert to the basis of 10 cc. lime-sulfur solution, and from this figure subtract the "thiosulfate figure" previously obtained. The resultant figure is the "poly-sulfur figure" of the lime-sulfur solution as diluted for analysis, that is, it represents cubic centimeters of *N*/10 iodine equivalent to the poly sulfur in 10 cc. of diluted lime-sulfur in the ratio of 1 atom of iodine to 1 of sulfur.

From the titration "figures" mentioned in this and the previous paper are naturally calculable the percentages of the various forms of sulfur existing in the diluted lime-sulfur solution, according to the following formulas:

Sulfide-acid figure  $\times 0.0016035 \times 10 =$  per cent mono-sulfur

Poly-sulfur figure  $\times 0.003207 \times 10 =$  per cent poly-sulfur

Thiosulfate figure  $\times 0.006414 \times 10 =$  per cent thiosulfate sulfur.

#### HELPFUL NOTES ON THE EXECUTION OF THE METHOD

1—The zinc solution is best prepared by dissolving about 6.537 g. of C. P. metal in some excess of hydrochloric acid, diluting to about 900 cc., adding sufficient concentrated ammonia to obtain a clear solution, and then diluting to 1000 cc. The zinc solution is to be used in 50 to 100 per cent excess of the amount called for by the previously described "sulfide-acid figure," for the precipitated zinc hydroxide is relied upon to render filterable the finely divided strontium sulfite.

2—In order to be certain that sufficient sodium sulfite is present it is well to measure in slightly different amounts in duplicate determinations, in which case the duplicates cannot check if sufficient sulfite has not been added.

3—The volume of sodium phosphate solution is varied between 0.5 and 1.0 cc., depending on the amount of strontium sulfite which appears to have passed the first filter. Even if no precipitate is visible, this step must not be omitted. The non-appearance of a considerable precipitate of strontium phosphate would of course indicate an insufficient addition of strontium chloride. In the final filtration from the strontium phosphate a plated filter may be used with considerable saving of time if the filtrate is repressed until perfectly clear.

4—Tartaric acid is known to promote liberation and decomposition of thiosulfuric acid far less rapidly than do mineral acids in equivalent excess, and is therefore much preferable.

5—The necessity for subtraction of the blank from the observed iodine titration will be discussed in the experimental section of this paper.

6—Both mono-sulfur and poly-sulfur are calculated from titrations which must be corrected for the amount of thiosulfate originally present in the lime-sulfur solution. The accurate determination of thiosulfate therefore becomes a matter of much importance. In the experience of the writer, methods which involve aliquot filtration from precipitated mono-sulfur and poly-sulfur are prone to yield somewhat low and irregular results, apparently owing to adsorption of thiosulfate by precipitated sulfur and sulfides.<sup>1</sup> The following method is therefore

advised for the determination of thiosulfate: Into 20 cc. of *N*/5 ammoniacal zinc chloride contained in a 150 cc. beaker, pipette 10 cc. of the diluted lime-sulfur solution. Mix, dilute to about 75 cc., heat on the steam bath 30 min. with occasional stirring, then filter and wash with hot water. Cool the filtrate, add about 1 g. C. P. potassium iodide, methyl red indicator, and cautiously render slightly acid with 10 per cent tartaric acid, finally titrating with iodine.

#### EXPERIMENTAL

The scheme at first investigated was to pipette the sample into a freshly boiled and hot solution of sodium sulfite and ammonia, boil a sufficient length of time, and then to add both ammoniacal zinc chloride and strontium chloride after which the determination was completed as in the regular method. This procedure is more rapid and by the speed of decolorization indicates to the eye whether sufficient sulfite has been employed. Two obvious objections are that excess lime may react with some poly-sulfur, producing low results, and that some mono-sulfur may become oxidized, producing high results. With the object of testing these sources of error the regular method previously outlined was tried, without, it must be confessed, much hope that the sodium sulfite would successfully perform its function upon precipitated poly-sulfur. When such was found to be the case the first conceived method was abandoned, at least for the present, for in the regular method described the solution is alkaline with ammonia only, and all mono-sulfur is in the form of non-oxidizable zinc sulfide.

EXPERIMENT 1, following the regular method except in the matter of heating, indicates the speed of the reaction between sulfite and poly-sulfur.

TEST	TIME HEATED MINUTES	NO. OF MIXINGS	IODINE TITRATION
a.....	15	3	39.49
b.....	23	2	39.56
c.....	60	3	39.50
d.....	120	-3	39.45

The results indicate that the prescribed conditions make ample provision for solution of all poly-sulfur, provided the full heat of the steam bath is used. They further indicate that properly executed duplicates will yield figures in satisfactory agreement.

Since strontium sulfite could not be assumed to be absolutely insoluble, it was necessary to determine a blank for sulfite reaching the stage of iodine titration.

EXPERIMENT 2—Blanks run with 5 cc. of sodium sulfite solution gave 0.12 and 0.11 cc. *N*/10 iodine. A blank run with 10 cc. sodium sulfite, using 30 cc. strontium chloride, gave 0.11 cc. iodine. In each case about 2 g. C. P. potassium iodide were added to the filtrate before titration.

Since the size of the blank was not affected by the quantity of sodium sulfite used the blank titration must be attributed solely to the solubility of strontium sulfite and not to the presence of sodium thiosulfate as an impurity in the sample of sodium sulfite employed. Remembering that in the execution of the method in practice no correction for the end point with starch is called for, since that is automatically provided through the necessity of subtracting the thiosulfate figure, it is fair to set for the solubility of strontium

<sup>1</sup> THIS JOURNAL, 8 (1916), 151.

<sup>2</sup> Compare Thompson and Whittier, Delaware College Agric. Exp. Sta., Bull. 105, p. 7.

sulfite a correction of 0.10 cc.  $N/10$  iodine per 200 cc. filtrate.)

Incidentally it may be noted that we have here the basis for a good practical method for estimating thio-sulfate in the presence of sulfite.

If, as the writer believes, the combined determination of mono-sulfur and poly-sulfur as described constitutes a method for the estimation of sulfide sulfur which is more accurate in practice than any other previous method, it is obviously impossible to check the accuracy of the new method by comparing its results with those afforded by other methods. But such a comparison is of importance for practical reasons and has been undertaken.

**EXPERIMENT 3**—Taking the standard method<sup>1</sup> of the A. O. A. C. as a basis, procedure was modified in accordance with facts regarding the estimation of sulfuric acid as barium sulfate brought out by Allen and Johnston,<sup>2</sup> and by Walter Allen and Bishop.<sup>3</sup> Using 10 cc. of the diluted sample, sulfide sulfur was separated by ammoniacal zinc in the usual way. Next followed digestion with 10 cc.  $N \times 10$  caustic potash, adding water as needed, oxidation with hydrogen peroxide and strong acidification with 25 cc. concentrated hydrochloric acid. To remove chlorates<sup>4</sup> and silica—which must necessarily be present from the action of alkali on glass—the solution was evaporated to dryness and the residue was heated several hours at 105 to 110° C. It was then taken up with hot water and 5 cc. concentrated hydrochloric acid, and the filtered solution, after cooling and diluting to about 700 cc., was precipitated cold with a 5 per cent solution of barium chloride through a capillary tube according to the procedure of Walter Allen and Bishop. The next day the precipitate was filtered on paper, cautiously washed in a platinum crucible and ignited for 30 min. in the covered crucible over a No. 3 Méker burner.

To determine the value of the factor  $S/BaSO_4$  under these conditions, 25 cc. of  $N/2$  sulfuric acid were precipitated after the addition of hydrochloric acid only, and after the addition of 10 cc. of  $N \times 10$  caustic potash, acidification, evaporation, etc., as in the method of analysis, and this factor was used in calculating the results. The trace of sulfur derived from the reagents was determined and allowed for in all the work. All operations were performed in duplicate.

The samples were made after different formulas in connection with another investigation. They were diluted and analyzed, using the gravimetric method for sulfide sulfur, 1 to 3 days after preparation. For the determination of the poly-sulfur figure the dilutions unfortunately were not made until between 8 to 10 weeks later, the concentrates being preserved meanwhile in well-filled and well-sealed bottles. It is not desired to discuss at the present time changes which may occur in lime-sulfur solutions during storage, but it is necessary to give here the results for thio-sulfate sulfur also.

The results obtained appear in Table I, expressed as percentages of the diluted samples.

TABLE I. RESULTS IN PERCENTAGES

Sample	FIRST DILUTION			SECOND DILUTION		
	Thiosul-fate S	Sulfide S	Sum	Thiosul-fate S	Sulfide S	Sum
A.....	0.387	1.622	2.009	0.378	1.644	2.022
B.....	0.458	1.674	2.132	0.445	1.744	2.189
C.....	0.453	1.755	2.208	0.443	1.815	2.258
D.....	0.418	1.801	2.219	0.408	1.839	2.247
E.....	0.444	1.790	2.234	0.440	1.819	2.259

The volumetric method for sulfide sulfur gave distinctly higher results in all cases, the actual differences varying from 0.022 per cent to 0.070 per cent. But it is evident that the thiosulfate sulfur decreased slightly during storage in all cases. If it is permissible to assume that some thiosulfate sulfur had become changed to sulfide sulfur, and comparison is made between the sums of the two forms of sulfur, the volumetric method still gives the higher results in all cases, the actual differences varying from 0.011 per cent to 0.057 per cent. The parallelism indicates a greater fault in the factors employed for calculating the results than in the rationale of either method, and since the factor  $S/BaSO_4$  is purely empirical under the conditions of the gravimetric method the probability of error rests there.

No experiments have been performed upon the applicability of the method to use dipping baths contaminated with filth from animals.

#### CONCLUSIONS

Methods are now available for estimating iodometrically the three important forms of sulfur in lime-sulfur solutions; thiosulfate sulfur, mono-sulfur and poly-sulfur, thiosulfate being the substance directly titrated in each case. The methods appear theoretically sound and practically applicable. The use of a single standard solution which can be so easily and accurately prepared and used as  $N/10$  iodine means a possibility of increased accuracy, as well as a saving of time, over the gravimetric estimation of sulfur as barium sulfate under conditions which demand the employment of an empirical factor.

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#### A NEW APPARATUS FOR THE DETERMINATION OF SOIL CARBONATES AND NEW METHODS FOR THE DETERMINATION OF SOIL ACIDITY<sup>1</sup>

By E. TRUOG

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In recent years a number of methods and forms of apparatus have been devised for the determination of soil carbonates and acidity. The present paper makes no attempt to discuss in detail the methods and apparatus which have been devised and advocated. The apparatus here described is the result of an attempt to devise a form which embodies simplicity, ease of operation and accuracy of results. In these respects it is believed to have certain marked advantages.

<sup>1</sup> Published with the permission of the Director of the Wisconsin Experiment Station. The writer is greatly indebted to G. P. Wolf, T. L. O'Hara and A. H. Neumann for assistance in trying out the apparatus and methods.

<sup>1</sup> Bur. of Chem., Bull. 152, p. 70.

<sup>2</sup> J. Am. Chem. Soc., 32 (1910), 588.

<sup>3</sup> Proc. 8th Intern. Congr. Appl. Chem., 1 (1912), p. 33.

<sup>4</sup> Compare Ramsay, J. Agr. Sci., 6 (1914), 194.



## SOIL CARBONATE DETERMINATION

The old method of heating with strong acid at boiling temperature to decompose the carbonates has been largely abandoned in recent years, due to the action of the boiling acid on organic matter with consequent liberation of  $\text{CO}_2$ , causing high results. To overcome this, Marr<sup>1</sup> used weak  $\text{HCl}$  and boiled at  $50^\circ \text{C}$ . with reduced pressure, under which conditions he found that the  $\text{CO}_2$  obtained is practically all derived from carbonates. Gaither<sup>2</sup> confirmed Marr's results, and also devised an ingenious apparatus<sup>3</sup> for carrying out the determination. MacIntire<sup>4</sup> and Willis<sup>5</sup> devised a method in which the carbonates are decomposed by  $1/15 \text{ H}_3\text{PO}_4$ , at room temperature. Lately,<sup>6</sup> in order to be assured of complete carbonate decomposition, they have replaced the  $1/15 \text{ H}_3\text{PO}_4$  with  $1/10 \text{ HCl}$  and in the case of soils high in carbonates recommend  $1/5 \text{ HCl}$ . They state that the action of  $1/10 \text{ HCl}$  on soil organic matter at room temperature is negligible on ordinary charges of average soil. Due to its simplicity this method has certain advantages

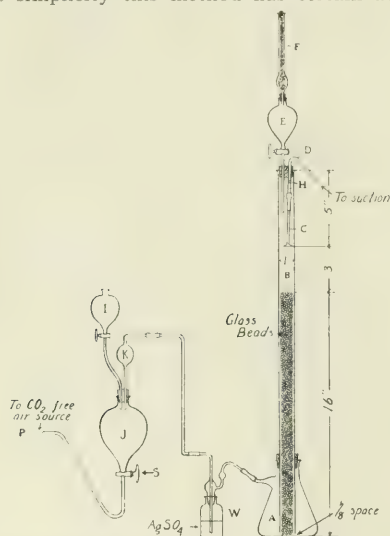


FIG. 1.—A NEW FORM OF APPARATUS FOR THE DETERMINATION OF SOIL CARBONATES AND SOIL ACIDITY

over the Marr method. A disadvantage in the method as operated by MacIntire and Willis is that the soil-containing vessel has to be agitated either by hand or motor. In order to overcome this difficulty and also make the titration of the evolved  $\text{CO}_2$  simpler and more accurate, the writer has devised the new form of apparatus shown in Fig. 1.

## THE NEW APPARATUS

**DESCRIPTION**—The apparatus shown in Fig. 1 consists of an evolution bulb, *J*, a wash bottle, *W*, and an absorption tower, *A*. The evolution bulb *J* consists of a 300 cc. dropping funnel with the stem bent as shown. The finely ground soil or other material is placed in this bulb with the acid solution. On

aspirating, the air enters through *P* and rises from the narrow neck of the bulb, effecting an efficient agitation of the soil and solution, thus eliminating the necessity of shaking, as is the case with the apparatus of MacIntire and Willis. A rather wide-mouthed dropping funnel should be selected in order to take at least a No. 3 stopper. The sides of the funnel should slope uniformly to the outlet in the stopper and should not leave a considerable shoulder around the outlet of the stopper on which soil may rest. The wash bottle *W* containing  $\text{AgSO}_4$  is inserted to remove  $\text{HCl}$  when this acid is used to decompose the carbonates. The absorption tower is similar to the one previously described in detail by the writer.<sup>1</sup> Its advantages have been fully stated. It makes possible the use of  $\text{Ba}(\text{OH})_2$  as well as alkali hydroxides as an absorbing medium for both slow and rapid aspirations of low and high amounts of  $\text{CO}_2$ . Contamination from the air is eliminated and washing is reduced to a minimum.

**METHOD OF OPERATION**—A finely ground sample of 1 g. to 25 g. of soil, depending on the amount of carbonates present, is placed in the evolution bulb with 50 cc. of water. Fifty cc. of  $1/5 \text{ HCl}$  are poured into the funnel *I*. Forty cc. of  $0.4 \text{ N Ba}(\text{OH})_2$  are run into the dropping funnel *E*. The soda lime tube is quickly replaced and the funnel is attached to the tower. After making the proper connections the whole apparatus is freed of  $\text{CO}_2$  by aspirating. In starting the aspiration the suction should always be turned on before stop-cock *S* is opened in order to prevent soil passing through the stop-cock. With continual aspiration and stop-cock *S* only slightly opened, the  $\text{Ba}(\text{OH})_2$  is allowed to run out of the funnel *E* into the tower and then the stop-cock of *E* is closed. The soda lime tube is removed and 40 to 50 cc. of  $\text{CO}_2$ -free water are quickly poured into the funnel and the soda lime tube is replaced. This water is now allowed to run into the tower, thus washing the funnel practically free of  $\text{Ba}(\text{OH})_2$  when the stop-cock of *E* is again closed. The suction draws the absorbing solution up into the tower. The  $\text{HCl}$  is allowed to run out of *I* into *J*, to decompose the soil carbonates. After aspirating 30 min., slowly for the first 10 min. followed by more rapid passage, the  $\text{CO}_2$  is usually completely liberated and absorbed in the tower.

When the decomposition and absorption are complete, the suction is closed off with a pinch-cock or stop-cock, and the stop-cock of *E* is gradually opened, allowing  $\text{CO}_2$ -free air to enter, when the absorbing solution settles into the flask. The flask is next disconnected from the  $\text{CO}_2$  source, and then after the solution has fully settled into the flask, the stop-cock of *E* is closed. The tower is washed out as directed<sup>2</sup> in a previous article and the excess of  $\text{Ba}(\text{OH})_2$  is immediately titrated with  $0.4 \text{ N HCl}$ . The amount of  $\text{CO}_2$  is obtained by difference.

**PRECAUTIONS**—If soil is allowed to set in the evolution bulb for sometime without aspiration, it will

<sup>1</sup> Jour. Agr. Sci., 3 (1908), 155.

<sup>2</sup> THIS JOURNAL, 5 (1913), 138.

<sup>3</sup> Ibid., 4 (1912), 611.

<sup>4</sup> Tenn. Agric. Expt. Sta., Bull. 100.

<sup>5</sup> THIS JOURNAL, 7 (1915), 227.

<sup>1</sup> THIS JOURNAL, 7 (1915), 1045

<sup>2</sup> Regarding further details in the preparation of reagents, use of various kinds of beads and operation of tower, see previous article in THIS JOURNAL, 7 (1915), 1045.

stick to the sides and it is then necessary to shake the bulb until it becomes loosened. The stop-cock *S* should be adjusted so as to secure a slight vacuum in the bulb *J*, in which case the air expands on entering, resulting in a violent agitation of the soil and a more rapid liberation and removal of  $\text{CO}_2$ . With proper manipulation, a moderately rapid current of air suffices to keep all the soil, if finely powdered, in rapid motion. With proper adjustment of stop-cocks, there is no trouble in soil passing through stop-cock *S*.

According to the preceding directions, the soil is treated with 1/10 strength  $\text{HCl}$ . Stronger  $\text{HCl}$  up to 1/5 strength has been used with little apparent objection. A further study is being made of the strength of  $\text{HCl}$  which suffices to decompose the carbonates and minimizes the liberation of  $\text{CO}_2$  from organic matter.

#### SOIL ACIDITY DETERMINATION

A great many methods have been proposed for the determination of soil acidity. In several of these methods the soil is treated with a neutral salt solution and the resulting acid extract is titrated. Since the reaction of salt solution and soil acids is one of equilibrium (competition between acid of salt used and soil acids) the titration does not indicate the total acidity and necessitates the use of a factor. In advocating the same factor for all soils, the bold assumption has to be made that the acids in all soils are of the same strength. That this is not true will be shown later. Since soil acids are quite insoluble, methods depending on the liberation of  $\text{CO}_2$  from solid  $\text{CaCO}_3$  cannot be expected to prove satisfactory since this requires a reaction between two rather insoluble materials which, necessarily, is slow. Methods which depend on boiling the soil with an excess of  $\text{Ba(OH)}_2$  and an ammonium salt are open to serious objection because practically all solutions of ammonium salts when boiled give an alkaline distillate and an acid residue. The method of Veitch,<sup>1</sup> in which is determined the amount of  $\text{Ca(OH)}_2$  that must be added to the soil to make the boiled water extract alkaline to phenolphthalein, also has certain objections as follows: The method is long and tedious. The end-point varies according to the period of contact and amount of shaking, due to hydrolysis of neutralized substances. The method never determines the total acidity, but simply indicates a certain point of equilibrium of an hydrolysis reaction between the water applied and the various salts in the soil. All of the methods just described have been of value in that the results indicate in a comparative way the degree of acidity. None of them, however, indicate the absolute amount of acidity as has sometimes been assumed. Lately, Hutchinson and MacLennan<sup>2</sup> and also MacIntire<sup>3</sup> have described methods in which a solution of  $\text{CaCO}_3$  in carbonated water is used. The former claim the results correspond closely to cultural practice. The insoluble nature of the soil acids must be clearly recognized in any attempt to devise satisfactory

methods for detecting and determining them. If soil acids were comparatively soluble in water, soil acidity would never be a serious problem in soils having good drainage, since the acids would be carried away in the drainage water. Because of their insolubility, it is necessary to use soluble reagents in their detection and determination. This feature has been recognized in a new test<sup>1</sup> devised by the writer for the detection and determination of the degree of active soil acidity. This test is designed for practical work and it indicates more satisfactorily the urgency of the need of lime and amount to be used under field conditions than an absolute quantitative method. However, for research regarding the nature of soil acidity and related problems, an absolute quantitative method is of great value. For this reason the following methods have been devised:

#### PROPOSED METHOD FOR ACTIVE SOIL ACIDITY<sup>2</sup>

**PRINCIPLE**—The principle of the method is as follows: The soil is treated with an excess of  $\text{Ba(OH)}_2$ ; a current of  $\text{CO}_2$  is passed in, changing the excess to carbonate, and after evaporation, a carbonate determination gives the excess, from which the amount required to neutralize the acidity is calculated.

**METHOD OF OPERATION**—The soil is prepared by passing the sandy ones through a 20 mesh and the others through a 100 mesh sieve. Samples are taken as follows: of sands and sandy loams, 25 g.; of silts, clays, and loams, 20 g.; and of peats and mucks, 2 1/2 g. The soil is placed in a casserole, 35 cc. of water are added and the soil is stirred till thoroughly moistened. Gentle heating aids greatly in moistening peats. Fifteen cc. of 0.4 *N*  $\text{Ba(OH)}_2$  are added and allowed to act with constant stirring for just one minute, and then a moderately rapid current of  $\text{CO}_2$  is immediately passed in for about two minutes with continued stirring, changing the excess of  $\text{Ba(OH)}_2$  to the carbonate. A little phenolphthalein may be added to indicate the point of complete carbonation, which is best observed by the disappearance of the color around the edges. After evaporating immediately to complete dryness on a steam or water bath, never with a free flame, the soil is transferred to the evolution bulb of the soil carbonate apparatus and the  $\text{CO}_2$  determined, from which the  $\text{Ba(OH)}_2$  required to neutralize the acidity is calculated. For carbonate decomposition 1/15  $\text{H}_3\text{PO}_4$  is used in place of the  $\text{HCl}$  used for soil carbonates. In the case of coarse, sandy soils, the evolution bulb should be shaken occasionally to get all the material in motion. With the most strongly acid soils, the amount of  $\text{Ba(OH)}_2$  applied to the soil should be increased to about 20 cc. to neutralize the acidity. The use of  $\text{Ba(OH)}_2$  is preferred to other hydrates because it is easily prepared  $\text{CO}_2$  free and the same stock solution also serves for use in the absorbing tower. For titration 0.4 *N*  $\text{HCl}$  is used. By using the weights of soil samples and strength of  $\text{Ba(OH)}_2$  indicated, and assuming that the weight of an acre, 8 in. layer of sandy soil, is 2,500,000 lbs. (clays, silts and loams 2,000,000

<sup>1</sup> *J. Am. Chem. Soc.*, **24** (1902), 1120.

<sup>2</sup> *Chem. News*, **1914**, p. 2854.

<sup>3</sup> *This Journal*, **7** (1915), 864.

<sup>1</sup> *Wis. Agric. Expt. Sta., Bull.* **249**.

<sup>2</sup> *Science*, **42** (1915), 505.



lbs., and peats 500,000 lbs.), the calculation of the acidity in terms of  $\text{CaCO}_3$  is greatly simplified. Under

TABLE I. ACTIVE SOIL ACIDITY IN C.C. OF 0.4 N SOLUTION PER SAMPLE (OR TONS  $\text{CaCO}_3$  PER ACRE), ON USING HYDRATES INDICATED(a)

KIND OF SOIL	No.	$\text{Ba(OH)}_2$	$\text{NaOH}$	$\text{Ca(OH)}_2$
Sand	1	3.8	3.5	3.7
Sandy loam	2	6.2	7.9	6.5
Silt loam	3	6.3	6.4	5.7
Silt loam	4	8.5	9.1	7.7
Peat	5	11.5	11.5	11.3
Peat	6	5.6	5.6	5.3

(a) Results for peat calculated to 5 g. sample

these conditions the number of cc. of  $\text{Ba(OH)}_2$  used to neutralize the acidity of the sample also represents the tons of  $\text{CaCO}_3$  required per acre except with peats where the result is in half tons. If other weights are assumed then the samples should be chosen accordingly. Correction for moisture is made by using per cent dry weight as divisor. Duplicates should check within 0.2 cc.

DISCUSSION OF RESULTS—In Table I are given a few of the results secured by this method and also results when the  $\text{Ba(OH)}_2$  applied to the soil is replaced by equivalent amounts of  $\text{Ca(OH)}_2$  and  $\text{NaOH}$ . The results are several times as great as are obtained with the Veitch method. The close concordance of results when different hydrates are used indicates clearly that the method proposed measures a rather definite part of the acidity in soils. This acidity may be called the *active acidity*, since it combines instantly with bases that are brought in contact. If the period of contact of hydrate and soil is prolonged considerably over one minute, the results show a slow but gradual rise up to a certain limit beyond which no more base is taken up. By heating and evaporating before carbonating this reaction is hastened. This part of the acidity which reacts only after continued contact may be called the *inactive* or *latent acidity*. The total amount of latent acidity is usually several times that of the active. The existence of active and latent acidity may be shown in another way by treating an acid soil for varying periods with a neutral salt solution preferably an acetate, and titrating the acid extract. Extracts secured after a contact of one minute show a certain acidity which is very large in comparison with the additional acidity indicated after a contact of many hours and even days. After one minute contact, the rise is slow, but gradual, indicating the coming into play of the latent acidity.

In Fig. II are given the results obtained by shaking 20 g. samples of acid silt loam soil with 150 cc. of *N* sodium acetate solution (neutral) for the periods indicated. The solutions were quickly filtered with a Buchner funnel and titrated with *N/25*  $\text{NaOH}$ . The existence of active and latent soil acidity is clearly indicated. From other data, although inconclusive, it appears that in upland soils, the active acidity is due largely to acid silicates, and the latent acidity to a peculiar condition of kaolinite and allied compounds.

#### PROPOSED METHOD FOR LATENT SOIL ACIDITY (PROVISIONAL)

METHOD—A 5 g. sample (in case of peats  $2\frac{1}{2}$  g.) is placed in a casserole or other suitable vessel, moistened with water, 10 to 20 cc. of 0.4 *N*  $\text{Ba(OH)}_2$  according

to acidity are added and then water, making the final volume 150 cc. The mixture is boiled for 30 min., evaporated to dryness on a steam bath and heated for  $2\frac{1}{2}$  hrs. at  $110^\circ \text{C}$ . in an oven. About 50 cc. of water are added, and  $\text{CO}_2$  is run in to carbonate the excess of  $\text{Ba(OH)}_2$ . After evaporation carbonates are determined as before, from which the total acidity is calculated. The total acidity minus the active gives the latent acidity.

DISCUSSION—The latent acidity is usually two to three times the active. By repeating the boiling and evaporation of  $\text{Ba(OH)}_2$  with the soil, the result is usually increased slightly. On the soils studied, the results have been nearly the same whether  $\text{NaOH}$  or  $\text{Ba(OH)}_2$  was used. The method for latent acidity is being further studied and the procedure given is not final. Latent soil acidity is undoubtedly much less injurious than active. The strength or avidity of the active acids is a very important matter and the

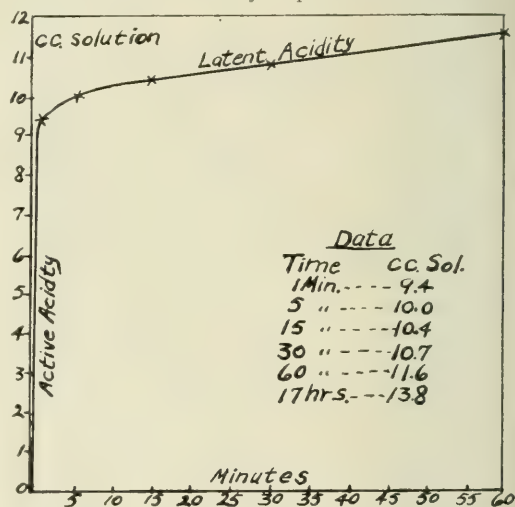


FIG. II—ACTIVE AND LATENT SOIL ACIDITY AS INDICATED BY ACIDITY OF EXTRACT IN C.C. *N/25* SOLUTION AFTER VARIOUS PERIODS OF CONTACT BETWEEN ACETATE SOLUTION AND SOIL

method for active acidity also makes possible a method for avidity of the active acids.

#### PROPOSED METHOD FOR AVIDITY OF ACTIVE SOIL ACIDS

By avidity of an acid is meant its competing power for a base in comparison with another acid taken as a standard. In order to determine avidity, it is then only necessary to determine the distribution between equivalent amounts of the unknown and standard acids, of a quantity of base just sufficient to neutralize one of the acids. It is comparatively easy to determine the relative avidity of the active acids in different soils, if the amount of active acidity is known.

METHOD—To a sample of soil which is  $2\frac{1}{2}$  times the weight of the one used for active acidity determination, is added a 150 cc. solution of potassium acetate which contains an amount of  $\text{KC}_2\text{H}_3\text{O}_2$  equivalent to the active acids in the soil sample. This solution is conveniently made by taking the same number of cc. of neutral *N*  $\text{KC}_2\text{H}_3\text{O}_2$  as there was used of 0.4 *N*

Ba(OH)<sub>2</sub> to neutralize the active acidity, and diluting it to 150 cc. with CO<sub>2</sub>-free water. The soil and acetate solution are vigorously shaken together in a 300 cc. flask for two minutes and then quickly filtered on a Buchner funnel and titrated with *N*/25 NaOH using phenolphthalein. Calculations are made as follows:

Let *a* = avidity of acetic acid (conveniently taken as 1000)

*b* = cc. *N*/25 NaOH required by titration

*c* = cc. *N* KC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> used

*x* = relative avidity of active soil acids (average of all)

Then:

$x = ab/25c - b$ , and by substitution of known values, *x* is solved for. Since soil acids are quite insoluble compared to acetic acid, the relation between the figure obtained for avidity of soil acids and that taken for acetic acid (1000) does not represent the strength of the active soil acids compared to acetic acid. However, since the acids in different soils are practically all insoluble, the avidity figures for different soils are comparable.

**GENERAL DISCUSSION**—In Table II are given a few values of avidity secured by this method together with the active acidity in tons per acre of CaCO<sub>3</sub> as measured by the method described in this article, and also the degree of active crop-injurious acidity as measured by the new test previously described. It is clearly evident that the avidity of the active soil acids in different soils varies greatly, from which it must be concluded that the seriousness of a soil's acidity and the urgency of the need of lime are not indicated by the total active acidity alone. It is necessary to also consider the avidity of the active acids. Soil 7, for example, is much higher in total active acids than No. 6, yet in cultural practice No. 6 responds decidedly to liming and No. 7 does not. What is the explanation? It is clearly a matter of avidity, since the avidity figure for No. 6 is nearly 8 times that of No. 7. From this it is evident that any practical method for the determination of the ur-

TABLE II—AMOUNT OF ACTIVE SOIL ACIDS, AVIDITY OF ACTIVE SOIL ACIDS, AND DEGREE OF CROP-INJURIOUS ACIDITY IN SEVERAL SOILS

KIND OF SOIL	No.	Active Acidity in tons CaCO <sub>3</sub> per acre	Avidity of Active Acids	Degree of Crop-Injurious Acidity by New Test
Silt loam.....	1	4.9	72	Slight to Medium
Silt loam.....	2	3.1	42	Very Slight
Silt loam.....	3	9.3	96	Medium to Strong
Clay.....	4	6.6	152	Very Strong
Sand.....	5	1.2	26	Very Slight
Sand.....	6	3.4	113	Strong
Peat.....	7	5.6	15	Very Slight

gency as to the need of lime must take into account both the quantity and the quality (strength) of the soil acids. That the new simple test for acidity actually does this is evident from Table II. The degree of acidity indicated by this test is the resultant of two factors, *viz.*, quantity and strength of active soil acids which may conveniently be called the degree of crop-injurious acidity. Because of this feature, it is superior to an absolute quantitative method in indicating the seriousness of the acidity and the advisability of using a light, medium or heavy application of lime. Because of the varying needs of different crops, the enormous yearly loss of lime through

leaching, and the great complexity of soil acidity and related phenomena, it is ridiculous to advocate methods for practical purposes which are said to indicate down to hundreds of pounds per acre the amount of lime which a farmer should use. An approximation in tons or perhaps half tons is the best that can be expected and all that is necessary. However, an absolute quantitative method is of the greatest value as an aid in many lines of research on soils.

Since nearly equivalent amounts of different hydrates are required, as shown by Table I, the intervention of a true chemical reaction is indicated, and it may safely be accepted that soil acidity is due to true acids and not selective ion adsorption by colloids and other adsorbing substances, as often stated. The reason that NaOH sometimes gives a slightly higher result and Ca(OH)<sub>2</sub> a slightly lower result than Ba(OH)<sub>2</sub> is undoubtedly due to side reactions, such as action on inorganic matter, latent acidity, etc., which clearly would be different for the different hydrates. For a further discussion regarding nature of soil acidity see previous publication.<sup>1</sup>

The enormous supply of latent acid substances in many soils of the humid region as indicated by these methods is of the greatest importance in preventing excessive losses of bases by leaching. It also offers a further explanation why MacIntire,<sup>2</sup> Hardy and Willis were able to secure large decompositions of MgCO<sub>3</sub> when this material was left in contact with soil that supposedly had been completely neutralized. A more detailed paper regarding the nature of soil acidity is in preparation.

#### SUMMARY

I—A new form of apparatus for the determination of soil carbonates is described. It has certain marked advantages.

II—Evidence is given indicating the existence of two kinds of soil acidity, which are conveniently called *active* and *latent* soil acidity.

III—Methods are proposed for the determination of active and latent soil acidity, and also the average avidity of the active soil acids.

IV—Data are given indicating as follows: Soil acidity is due to true acids and not selective ion adsorption by colloids; the avidity of the active acids in different soils varies greatly, which is of prime importance; and the new test for soil acidity previously described gives a more reliable indication as to the seriousness of the acidity than an absolute quantitative method.

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#### THE COMPARISON AND IDENTIFICATION OF VARIOUS TYPES OF SMOKING OPIUM<sup>3</sup>

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#### DESCRIPTIVE

Smoking opium may be classified, according to the method of preparation, as the product obtained by:

<sup>1</sup> *Science* 42 (1915), 505.

<sup>2</sup> *Tenn. Agric. Expt. Sta., Bull.* 107.

<sup>3</sup> Published by permission of the Secretary of the Treasury and the U. S. Appraisers of Merchandise, Baltimore, Md.



I—Simple aqueous extraction of the crude gum opium, filtration or straining of the mass, and evaporation of the filtrate to a thick sirup containing 15 to 20 per cent water.<sup>1</sup>

II—Careful heating, kneading and partial roasting of the crude opium before extraction, filtration and evaporation<sup>2</sup> as in I.

III—Addition to either of the above products of an appreciable amount of yen shee (pipe scrapings).

IV—Mixing materials foreign to opium with any of the above, or substituting factitious substances for the whole body.

The first method of manufacture is essentially the same as that described in the old U. S. Pharmacopoeia for the preparation of the extract of opium. It is to be noted that in the eighth revision of that work the aqueous extract is directed to be evaporated, instead of to "proper consistence," to "constant weight," when, after powdering, etc., it becomes the official extract. Further, too, the larger manufacturing drug houses in this country have now, and for several years past, discontinued the preparation and sale of the moist extract. Whether this elimination was due wholly to its omission in the present Pharmacopoeia or in part to apprehension that their product might be used for smoking purposes, thereby making them liable to controversy with the government as traffickers in smoking opium, is uncertain. In this connection a definition of smoking opium by the judge, presiding in a somewhat recent criminal prosecution for the illegal manufacture of that material, is of interest.<sup>3</sup> Holding that Wyeth's Aqueous Extract of Opium was not an illegal manufacture and was not suitable for smoking, he said in comparing it with an extract similarly prepared but intended for smoking:

"But in the process of boiling instead of stopping at the point where the substance becomes merely sticky they (Wyeth Co.) carry it further and they boil it down until it gets to a greater consistency than the ordinary smoking opium. This opium they sell for medicinal use \* \* \* \* \* that is not opium manufactured for smoking purposes."

It is well known, however, that the ordinary pharmaceutical extract can be and has been used for smoking.

The second method yields a product much favored by certain smokers—notably the Chinese—who desire the elimination of those disagreeable volatile substances said to be present in the raw opium and to be destroyed in the process of roasting. This particular type of smoking opium is variously designated tschandu, tschandoo, tjandoo, chandu, etc., and its method of preparation is briefly as follows: Two or three balls of opium, after removing the leaf covering, are cut up and macerated with water. After standing one day the opium and the extract are transferred to a shallow copper pan and carefully evaporated over a free fire, with constant rotating and skimming of impurities, until the mass contains 5 or 6 per cent of water. This is then kneaded for a few minutes with a copper spatula and afterwards spread over

the whole dish in a layer 15–20 mm. thick. The mass is now covered with a thin layer of wood ashes and the pan turned so that the contents face the fire. In a few minutes the temperature of the opium rises to 200–210°, and the surface layer 3–4 mm. thick, losing water and becoming blistered and brittle, is taken off, heated on both sides, and transferred to a larger copper pan. This operation is repeated until 12–14 layers are taken, when the united mass thus obtained is rubbed with water and allowed to stand until the next day; then it is strained and filtered, first through bamboo and then through coarse filter paper. After completely exhausting the residue with hot water, the extract is carefully evaporated to a thick sirup, and then stirred for one hour (where there is a constant circulation of air) with a broad, wooden spatula. It is now transferred to a loosely covered earthenware vessel where it is allowed to ferment for several months, during which period bacteria—especially *Mucor* and *Aspergillus* (*A. niger*) develop, whereby it is claimed the taste of the opium is improved. Thus prepared for smoking, the yield of the material ready for use should be about 60 per cent. During the roasting there is lost through volatilization and carbonization from 15 to 20 per cent of the original opium. The insoluble residue, representing about 60 per cent of the roasted cake and remaining after the extraction of the tschandu, should be practically free (except some insoluble narcotine) of the characteristic opium alkaloids; it is, however, further extracted, and this extract, known as ching ko, mixed with pipe scrapings, is sold as "refuse opium." The better grades of smoking opium formerly imported, but now, by reason of the prohibition, sporadically smuggled, into this country, are said to have been prepared substantially as described above. Analyses, made in this laboratory of representative samples of a seizure at the port of Baltimore of a large number of cans of smoking opium, showed the material to be practically identical with tschandu.

The use of the product of the third method, *viz.*, the addition of yen shee (tinko, dross, pipe scrapings, etc.), or its evaporated aqueous extract, to the extract of opium or to tschandu, may be attributed to one or more of the following reasons:

- 1—Economy of the smoker.
- 2—Reduction of the cost to the manufacturer—yen shee being sold for about \$12 a pound.
- 3—Taste to the smoker. The claim is made that this addition, or adulteration, imparts an agreeable aromatic flavor to the drug—more especially to the unroasted opium, the acrid, harsh taste of which it is supposed to soften. This would seem to be borne out by the fact that a new (unsmoked) pipe is not fancied by the smoker, and becomes desirable only after extended use or when a substantial coating of incompletely burned opium has formed in the bowl and stem. It also may be stated that, by the addition of yen shee, the temperature in the pipe during smoking is considerably raised, thus promoting the decomposition or volatilization of the alkaloids, which may or may not be of advantage to the smoker.

The fourth class of smoking opium comprises simply sophisticated or factitious products which may even, in some cases, contain no trace of opium ex-

<sup>1</sup> Adams and Dorman, *This Journal*, 4 (1912), 429; also Thorpe's *Dict. Appl. Chem.*, Vol. III, p. 72.

<sup>2</sup> Browne, *Apoth. Zeit.*, 1910, p. 489.

<sup>3</sup> *Herman Seidler v. U. S. A.*, Court of Appeals, 2nd Circuit N. Y. Original Indict., Jan. 28, 1914.

tract. Usually, however, there is present a considerable proportion of that body, and often of the crude gum itself.

# EXPERIMENTAL

An examination of samples of each of the foregoing types of smoking opium was made in an attempt to classify them correctly.

To distinguish between Types I and II seemed to offer quite a problem. Organoleptic tests give, at the best, but the slightest clue—the odor of tschandu being perhaps more peculiarly sweet and suffocating than that of the extract of the unroasted gum. Comparison of the diluted aqueous extracts of the two samples showed the latter to be of a brighter amber color than the former, the appearance of which was a somewhat dirty brown. In searching for a possible chemical change, resultant from the roasting process, wherein the opium attains momentarily a temperature of 200–210°, the melting points of the principal alkaloids were compared. These melting points are given as follows:

ALKALOID	°C.	ALKALOID	°C.
Papaverine.....	147	Codamine.....	120–126
Codeine.....	155	Laudanine.....	166
Narceine.....	170	Tritopine.....	182
Thebaine.....	193	Lanthopine.....	200
Narcotine.....	176	Protropine.....	202
Hydrocotarnine.....	50	Xanthaline.....	206
Meconidine.....	58	Cryptopine.....	213–218
Laudanosine.....	89	Gnoscopine.....	228–233
Oxynarcotine.....	140–150 (carbonizes)	Rhoeadine.....	232
Pseudomorphine..	Not fusible(a)	Morphine.....	254 (about)

(a) Above 120° it decomposes without melting

From the above list of 20 alkaloids it is seen that 12 of them melt at or under 200°, 2 decompose below that temperature, and 2 melt between 200–210°, thus leaving but 4 which do not melt under the temperature reached in the production of tschandu. It seemed, therefore, highly probable that some appreciable volatilization or decomposition of part of them might have ensued when the opium was roasted. In fact, it has been stated that the exact melting point of narceine cannot be determined as the alkaloid begins to decompose before that temperature has been reached, and also that narcotinè at about 200° is decomposed into meconin and cotarnine. Further, thebaine has been said by some to sublime at 135°, but this is denied by both Dott and Hesse. The content of morphine, as would be expected from the melting point, was found to be unchanged after the roasting process. With this fact established, attempt was made to show a variation in the ratio of the morphine to the total alkaloidal content in the tschandu from the average normal ratio existing in the extract of the uncooked gum, and possibly also, to prove a diminished amount, or even entire absence, of one or more of the more important by-alkaloids. The normal alkaloidal content of good raw opium, compiled from figures published by a number of different analysts, shows a percentage composition approximately as follows:

	Average	Range
Morphine.....	10.0	8.0–12.0
Narcotine.....	6.0	4.0–8.0
Codeine.....	1.0	0.5–1.5
Thebaine.....	1.0	0.8–1.2
Narceine.....	0.5	0.3–0.7
Papaverine.....	1.0	0.8–1.2
Other alkaloids.....	0.5	0.4–0.6

Thus a ratio of morphine to the total alkaloids is indicated as about 1 : 2.0.

While working with this end in view, *i. e.*, to show a decided variation from the normal alkaloidal composition, my attention was called by Dr. H. Engelhardt, of Baltimore, to an article written by C. Hartwich and N. Simon,<sup>1</sup> wherein the authors seemed to have anticipated to some extent this investigation. After a very comprehensive study of smoking opium and the active bodies present in its smoke, they were able to state among other things that

“kneaded opium still shows the same composition as the crude material \* \* \* \* however, when extract of opium is roasted decomposition of the alkaloids takes place. While the percentage of morphine is only slightly altered, some of the narcotine is decomposed. The presence of codeine, papaverine, narceine can hardly be proven after roasting, and thebaine is present only in traces. After treating the roasted cake with water the decomposition products and the free narcotine remain undissolved; of the alkaloids only the morphine and a part of the narcotine go into solution. The proportion of morphine to the total alkaloids is therefore relatively high in tschandu, since the other alkaloids are chiefly decomposed or remain undissolved.”

In a series of four experiments they obtained for raw opium and for tschandu, prepared by them from duplicate samples, an average morphine percentage of 6.883 and 11.650 and a total alkaloidal percentage of 13.287 and 13.770, respectively. This gives a morphine total-alkaloids ratio of 1 : 2.220 for raw opium, and 1 : 1.182 for tschandu; or, to express it differently, 45.03 per cent of the total alkaloids in raw opium is morphine, while in tschandu, the same relative percentage is 84.60. In the above samples the usual opium by-alkaloids, narcotine, codeine, papaverine, narceine and thebaine, were identified in the raw material, while only narcotine and thebaine were found in the resultant tschandu. Five samples of opium, prepared for smoking and purchased in China, etc., showed an average morphine total-alkaloids ratio of 1 : 1.26, which closely approximated that found for the tschandu prepared by them.

The experimental work conducted in this laboratory comprised an examination of the following described samples:

1—Two samples of raw Smyrna opium imported through the port of Baltimore: partly air-dried when experimented with.

2—Aqueous extracts of duplicate samples of the above: made in conformance to the directions given for the former U. S. P. Extract of Opium (moist).

3—Insoluble residues left after making the above extracts.

4—Tschandu (not fermented) prepared in this laboratory from duplicate samples of the raw opium (No. 1) above and as nearly as possible in accordance with the method already described.

5—Exhausted residues (from which ching ko is extracted) obtained in the preparation of the tschandu (No. 4) above.

6—Two samples of smuggled opium, representative of a seizure made by U. S. Customs officers at Baltimore, of a number of cans of smoking opium. The cans, weighing about 5 taels (6<sup>2</sup>/<sub>3</sub> ozs.) each,

<sup>1</sup> *Apoth. Zeit.*, 58 and 59 (1903), 505–514.—Abstr.



bore labels inscribed with Chinese characters, and may or may not have been manufactured in China.

7—One sample of yen shee: the residue and extract examined separately.

8—One sample of moist extract of opium prepared by a manufacturing chemical company for medicinal use: dried somewhat.

9—Average of four samples of regularly imported Smyrna opium. Table I gives the results obtained on analysis.

It will be seen that the results obtained for the morphine total-alkaloids proportions for the extracts of raw and roasted opium, respectively, closely agree with the figures reported by Hartwich and Simon (see above), and further, that the same deductions—*viz.*, the occurrence of a partial decomposition and perhaps a slight volatilization of some of the principal by-alkaloids during the roasting process—as were expressed by them, may be made. The most noteworthy change, however, taking place in the opium as a result of the roasting, is the practical elimination of codeine, papaverine and narceine, and the reduction in the amount of thebaine from an ordinarily significant percentage to a mere trace. This change from the normal composition of opium is both characteristic and conclusive evidence for the recognition

opium (presumably crude) that *Aspergillus niger* (see fermentation of tschandu above) does not affect morphine but attacks both narcotine and codeine. Also, Allen says of moist opium that fungoid growths which soon appear gradually diminish and destroy the aroma, and materially reduce the alkaloidal value.

The identification of a sample as belonging to the third type, *i. e.*, tschandu or ordinary extract of opium to which yen shee or its aqueous extract has been added, must, of necessity, be largely dependent upon the amount of that material used. A very high ash percentage, an unusual alkaloidal composition, or, in cases where yen shee without previous aqueous extraction was used, a considerable water-insoluble residue might indicate the presence of yen shee. The ash content of tschandu (smuggled and laboratory products) and of the aqueous extract of opium (U. S. P. product of manufacturing chemists, and other extracts prepared from regularly imported Smyrna gum) are approximately the same, and in the various samples examined it has been found to average in the dry material about 6.22 with a maximum of 7.09 per cent. Adams and Dorman obtained for 5 samples of smuggled smoking opium an average ash percentage of 5.53 and for 13 samples of regularly imported smoking opium an average of 5.98. They

TABLE I

DETERMINATION (percentages)	No. 1		No. 2		No. 3		No. 4		No. 5		No. 6		No. 7		No. 8		No. 9
	A	B	A	B	A	B	A	B	A	B	A	B	Extract	Residue	A	B	
Moisture.....	8.06	8.97									15.90	14.52		5.41	7.81		18.97
Ash, dry sample.....	5.20	5.06	6.15	5.93	3.90	3.70	7.09	6.80	4.73	4.53	6.04	6.04	17.68	1.53	5.46		5.97
Insoluble in water, dry sample.....	40.00	37.80									3.03	2.71		33.38	2.18		38.50
Morphine, dry sample.....	13.02	13.54	21.63	21.75	0.0	0.0	20.18	20.95	0.0	0.0	8.10	8.32	1.49	0.0	20.04		13.09
Total alkaloids, dry sample.....	27.46	27.98	40.78	40.64	6.01	6.98	24.13	24.89	12.76	12.75	9.60	10.01	1.62	0.38	38.28		27.88
Morphine in total alkaloids.....	47.41	48.39	53.04	53.52			83.63	84.17			84.38	83.12	92.00		52.35		46.95
Morphine total-alkaloids ratio.....	1:2.109	1:2.066	1:1.885	1:1.868			1:1.196	1:1.188			1:1.185	1:1.203	1:1.087		1:1.910		1:2.130
Narcotine (a).....	+	+	+	+	+	+	—	+	+	+	+	+	—	?	+	+	+
Codeine.....	+	+	+	+	—	—	—	—	—	—	—	—	—	—	—	—	—
Papaverine.....	+	+	+	+	—	—	—	—	—	—	—	—	—	—	—	—	—
Narceine.....	+	+	+	+	—	—	—	—	—	—	—	—	—	—	—	—	—
Thebaine.....	+	+	+	+	—	—	?	+	—	—	?	+	—	—	+	+	+

(a) Positive test indicated by + sign. Negative test indicated by — sign.

of the material. It is also of interest to the smoker, since it is said that thebaine is the most poisonous (Allen, p. 361) and narceine the most strongly narcotic<sup>1</sup> of all the opium alkaloids. Attention should be called to the very considerable amount of alkaloidal reacting bodies (exclusive of some free narcotine which is also present) remaining in the water-insoluble roasted cake left after the preparation of the tschandu. These unnamed alkaloids or decomposition products were identified as such by their behavior towards solvents and towards the general alkaloidal precipitants, Mayer's reagent, etc., and also by their forming salts by direct union of the base with an acid. In this connection a statement made by Browne (reference above), that ching ko "contains no opium" (supposedly meaning usual opium alkaloids), is to be noted as strengthening the conclusion that the alkaloidal bodies found in the exhausted roasted cake exist in a physical state which renders them entirely insoluble in water. No attempt was made to study the possible changes that might occur during fermentation of tschandu. Hartwich and Simon found no apparent alteration in the alkaloidal constituents, but that there may be a change is indicated by the investigation of C. v. Friederichs,<sup>2</sup> who found of

mention also two samples manufactured in the United States which contain very high percentages, *viz.*, 9.43 and 10.48, respectively, but do not state whether or not the addition of yen shee was suspected. In another sample, manufactured also in the United States, they found the per cent ash to be but 4.61. The ash content of the very few samples of yen shee examined by the author varied from 12 to 15 per cent for the whole dry material, and from 17 to 22 per cent for its dry aqueous extract. The high degree of solubility in water of the opium ash, which is composed mainly of the sulfates and phosphates of lime and magnesium, may serve to distinguish it from many of the mineral adulterants commonly used for sophistication. The alkaloidal composition of yen shee, naturally, is somewhat similar to that of tschandu; it should vary, however, from the ordinary extract even more markedly than the latter, because of the higher temperature to which it has been subjected. Moissan<sup>1</sup> states that the temperature of pure tschandu in the pipe at the moment fumes are given off is about 250°. This temperature, however, lasting as it does but a few seconds, neither decomposes nor volatilizes all of the morphine, but does decompose most of the principal by-alkaloids. Volatilization of morphine in the pipe has been both affirmed and denied; however, the

<sup>1</sup> Von Schröder, *Arch. f. Exp. Pathol.*, 1883, p. 132

<sup>2</sup> *Z. physiol. Chem.*, 93 (1914), 276.

<sup>1</sup> *Compt. rend.*, 1892, p. 988.

majority of investigators incline to the belief that no undecomposed morphine passes off in the opium smoke. Should the whole pipe scrapings, instead of its aqueous extract, be used for adulteration, a large amount of water-insoluble residue (consisting chiefly of carbon, and yielding but little ash), found in conjunction with the indications above, would point to the addition of that material to the smoking opium. Lack of opportunity and material prevented the writer from determining by experiment the possibility of detecting significant amounts of *yen shee in tschandu* or in the ordinary extract, and also from obtaining sufficient data to be able to give entirely satisfactory constants for it. The foregoing facts, therefore, can serve only as suggestions to those who may have occasion to investigate the matter.

No especial study of samples of the fourth type was made. An indication of foreign adulteration is ordinarily shown by an abnormal ash or an unusual water-insoluble residue of the material under examination. Among the adulterants said to have been used may be mentioned starch, glucose, gums, extract of poppy plants, Chinese lily buds, chalk, gypsum, litharge, ashes, etc.

#### METHODS OF ANALYSIS

I—20 g. of the dry pulverized sample are mixed with sand and exhausted with 1 per cent tartaric acid solution. The mixture is filtered and washed with water until the washings no longer give a test with Mayer's reagent. Evaporate filtrate and washings on steam bath to dryness; take up the alkaloidal salts with alcohol, make alkaline, and again evaporate to dryness. From this residue extract the now free alkaloids with isobutyl alcohol, and evaporate the solvent *in vacuo* on a sand bath; or, if no vacuum evaporating apparatus be at hand, extract the free alkaloids with successive exhaustions by ether, acetic ether, and a mixture of 10 per cent alcohol in chloroform, and evaporate these combined solvents to dryness in the ordinary way. Treat the residue with 1 per cent hydrochloric acid which dissolves the alkaloids as salts; filter, if necessary, and wash the residue with water. Concentrate the solution of the alkaloidal salts (or the combined filtrate and washings as the case may be) to a small volume, and add an excess of a 10 per cent caustic soda solution. This precipitates (A) the narcotine, papaverine, thebaine, laudanose, protopine, hydrocotarnine and some of the cryptopine, etc., while in solution (B) remain the morphine, codeine, narceine, lanthopine, laudanine, codamine, meconidine, a part of the cryptopine, etc. Filter and wash the precipitate with a small amount of water, and treat as follows:

(A)—Digest the precipitate in dilute alcohol, render faintly acid (to litmus) with acetic acid, and add 3 volumes of boiling water. This precipitates the narcotine and papaverine, which are filtered out, washed with a little water and dissolved in a minimum of dilute hydrochloric acid. Dilute the liquid until it contains not more than  $\frac{1}{400}$  of narcotine, when potassium ferricyanide is added which, precipi-

tates the whole of the papaverine. Filter after standing 24 hrs., and either weigh the precipitate as papaverine ferricyanide, or wash it with a little water, decompose with dilute caustic soda, and dissolve the liberated alkaloid in dilute hydrochloric acid, and reprecipitate with ammonia. The narcotine is determined in the filtrate from the precipitate produced by ferricyanide, by precipitation with ammonia; or, by making the filtrate alkaline with caustic soda, shaking out with ether and crystallizing the extracted narcotine from a definite amount of 90 per cent alcohol, and weighing. The filtrate obtained from the acetic acid and water precipitate is concentrated to a small volume, made exactly neutral and then mixed with a 20 per cent solution of sodium salicylate. After 24 hrs. the separated crystalline precipitate of thebaine salicylate is collected on a tared filter, washed with a little water, dried at 100° and weighed. To obtain the pure thebaine, treat the precipitate on the filter with dilute caustic soda until the washings, after evaporation, no longer give a test with ferric chloride for salicylic acid. The mother liquor, from which papaverine, narcotine and thebaine have been separated, is acidified with hydrochloric acid which precipitates most of the salicylic acid. This is filtered off, and the filtrate shaken with chloroform to remove the last traces of the salicylic acid. The acid filtrate (1), now free from salicylic acid, is set aside to be mixed with solution (2).

(B)—The original alkaline filtrate containing morphine, codeine, narceine, etc., is acidulated with dilute hydrochloric acid, concentrated on the steam bath, and then mixed with a slight excess of 2 per cent ammonia water. This precipitates the larger amount of morphine which, after standing several hours in the cold, is filtered and washed with cold water. The filtrate and washings are, after concentrating, acidulated with hydrochloric acid, and again supersaturated with ammonia water. If some additional morphine should separate, the process is repeated in the same manner, and the morphine collected on the same filter. The total morphine may then be determined by titration, using methyl red as indicator. The filtrate is made acid with hydrochloric acid, evaporated until it measures 75 cc., made alkaline with 2 per cent ammonia water, and shaken out with benzol, which takes up the codeine only. The benzol is separated and evaporated, and the residue (codeine) estimated either gravimetrically or volumetrically—if the latter, use cochineal as indicator. The alkaline liquid from the benzol extraction is acidulated with hydrochloric acid, and shaken out with chloroform. The chloroform is separated and evaporated, and the residue (narceine) determined by titration, using methyl red as indicator. The acid solution (2), still containing rare alkaloids of the original alkaline filtrate (B), is mixed with the acid solution (1), which contains the rare alkaloids of the original caustic soda precipitate (A), and, after adding a good excess of magnesium oxide, the combined liquids are evaporated to dryness on the steam bath. The total free alkaloids thus formed are dissolved in a suitable solvent or sol-



vents, the solvent evaporated to dryness, and the residue dissolved in an excess of *N*/100 hydrochloric acid, and titrated with *N*/100 alkali, using methyl red as indicator—1 cc. *N*/100 acid equals 0.00355 g. alkaloids (estimated factor).

The above process, which may be open to some criticism for lack of exact accuracy in the final determination of some individual alkaloid (due to its imperfect purification), has given very satisfactory results in this laboratory, and, considering the difficulties obtaining in the quantitative separation of the principal alkaloids in a single sample of opium, is to be recommended for its comparative accuracy and ease of manipulation. In the process are embodied parts of the schemes employed for the estimation of single alkaloids by a number of investigators.<sup>1</sup> The manipulations, however, are somewhat modified, and the whole is so arranged as to be fairly well adapted to the estimation of the principal alkaloids in a single sample.

II—As a corroborative method for the determination of the morphine total-alkaloids proportions, in which, however, only the morphine is individually separated (the by-alkaloids being estimated as a whole), advantage was taken of the very accurate and rapid process devised by the U. S. Bureau of Chemistry (Dept. of Agriculture) and modified by Dohme and Englehardt, for the determination of morphine in opium. The procedure, with directions for the collection and estimation of the by-alkaloids as used in this laboratory, is as follows:

One gram of the sample is extracted and the alkaloids are obtained in solution as hydrochlorides in just the same manner as in the preceding process. Then add to the concentrated solution caustic potash solution until a distinct alkaline reaction is obtained. The entire volume should not exceed 40–45 cc. Shake out with various portions of ether to remove by-alkaloids; separate, and evaporate the ethereal liquid to dryness. Dissolve the residue in dilute hydrochloric acid, and set aside.

The alkaline aqueous liquid is slightly acidified with hydrochloric acid, and in the mixture about 13 to 14 g. of powdered sodium chloride are dissolved. The mixture is then made slightly, but distinctly, alkaline with ammonia, and the morphine is shaken out with a mixture of 8 to 10 cc. of alcohol and 30 cc. of chloroform. The shaking should be continued for 2 min. The chloroform is drawn off and filtered through 3 or 4 in. of cotton, evenly packed in the stem of a funnel and wetted with chloroform. The shaking out of the aqueous liquid is then continued with 5 more portions of 25, 20, 20, 20, 20 cc. of chloroform containing 5 to 7 cc. of alcohol. The chloroform solutions are filtered through the same funnel, the chloroform is evaporated and the residue taken up in an excess of standardized acid, and the excess titra-

ted back with standard alkali, using methyl red as the indicator.

The alkaline (ammonia) liquid left is now made slightly acid with hydrochloric acid, and then mixed with the acid solution of the ether residue set aside before. The combined solutions are treated with a good excess of magnesium oxide and evaporated on the steam bath to dryness. The free alkaloids are extracted from the residue and estimated by titration in the usual manner. In this case, however, assume 1 cc. *N*/10 acid equal to 0.0393 g. by-alkaloids.

#### QUALITATIVE TESTS

The following color tests for the principal alkaloids are to be recommended as giving very characteristic and delicate reactions:

**MORPHINE**—Oliver's test (*Chem. and Drug*, **85** (1914), 249). Add a few cc. of hydrogen peroxide and a small amount of strong ammonia water to a solution of morphine or its salts. Stir with a copper wire: gas is evolved and a deep port wine color is produced. Any blue color, due to the copper, may be destroyed with a few drops of potassium cyanide.

**NARCEINE**—Treat solution of alkaloid in hydrochloric acid with bromine: a yellow precipitate forms which dissolves on heating. On adding gradually bromine water and boiling, a rose color is produced which is destroyed by an excess of bromine. (Allen, p. 402.)

**CODEINE**—Lafon's reagent (1 g. ammonium selenite in 20 cc. strong sulfuric acid) gives a fine green color with even traces of codeine.

**PAPAVERINE**—Warren's recently published test (*J. Am. Chem. Soc.*, **37** (1915), 2402). Treat papaverine ferricyanide with Marquis' reagent (sulfuric acid containing a small amount of formaldehyde): a blue color is produced which changes to violet, to green, and finally to a dirty brown.

**NARCEINE**—Plugge's test (*J. Chem. Soc.*, **52** (1888), 870). Evaporate the solution of the alkaloid with dilute sulfuric acid at 100°. When the acid is sufficiently concentrated a violet-red color is produced, changing to cherry-red by continued heating. After cooling, the addition of a trace of nitric acid causes bluish violet streaks to appear in the red liquid.

**THEBAINE**—The alkaloid when heated with dilute sulfuric acid gives a red color, changing to yellow and finally to violet. (Hartwich and Simon, reference above.)

#### SUMMARY

To determine whether samples of Type I were manufactured for medicinal use or prepared solely for smoking purposes, dependence must be placed upon the water content, which, while its line of demarcation between the two classes is very faint, still can afford the basis for comparatively reliable judgment. In the case of "moonshine" extract of opium, however, a decided variation of the morphine content from the 20 per cent requirement of the Pharmacopoeia should be valuable circumstantial evidence in support of an opinion.

Samples of Type II are partly demonstrated by the proportion of morphine found in the total alkaloids, and may be conclusively identified by the practical absence of codeine, papaverine and narceine and the diminished amount of thebaine in the smoking opium under examination. The morphine total-alkaloids ratio for tschandu should lie between 1 : 1.11

<sup>1</sup> Hartwich and Simon, reference above. D. B. Dott, Allen's "Com. Org. Anal.," 4th Ed., **6** (1912), 372. Hesse, *Ibid.*, Plugge, *Analyst*, **12** (1887), 197. Andrews, *Ibid.*, **36** (1911), 489. Caspari, *Pharm. Review*, **1904**, p. 348. Van der Wielen, *Bull. Sci. Pharm.*, **17** (1910), 59; *Pharm. Zeit.*, **10** (1903), 267.

and 1 : 1.50, and the amount of morphine should never be less than two-thirds of the entire alkaloidal content. For the extract of the unroasted opium the ratio should vary between 1 : 1.50 and 1 : 2+, and the proportion of morphine should naturally be the reverse of that for tschandu.

Samples of Type III will show an abnormal alkaloidal composition similar to that of tschandu; this, however, may be moderated or exaggerated, depending on whether yen shee was added to the ordi-

nary extract or to tschandu. Suspicion will also be directed towards a sample when its ash percentage exceeds 8.0, or its water-insoluble residue (consisting largely of carbon) exceeds 5.0 in the dry material. The peculiar and characteristic odor of yen shee may also furnish a clue if noticed in the smoking opium.

Samples of Type IV may be identified by the usual physical, chemical and microscopical tests.

U. S. CUSTOMS LABORATORY  
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## LABORATORY AND PLANT

### THE MANUFACTURE OF GASOLINE AND BENZENE-TOLUENE FROM PETROLEUM AND OTHER HYDROCARBONS

By W. F. RITTMAN, C. B. DUTTON AND E. W. DEAN

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The U. S. Bureau of Mines has just published *Bulletin 114*, bearing the above title. In view of the wide-spread interest in the processes described in this publication, the authors have, upon request, prepared the following abstract, including supplementary information acquired since the completion of the original manuscript.—[EDITOR.]

The bulletin deals with the cracking of petroleum and other hydrocarbons and the productions thereby of gasoline or of benzene and toluene. The first part is devoted to a discussion of the principles involved. The second deals with the large-scale development of both processes. The latter section is of primary interest to readers of *THIS JOURNAL*, as the matters discussed in the forepart of the bulletin have been covered generally by articles previously published.<sup>1</sup>

#### PURPOSE OF EXPERIMENTS

In connection with the description of and comment on the large-scale development of the benzene-toluene process which follows, it should be kept in mind that the object in view was to demonstrate the commercial feasibility of the process. Certain refinements in mechanical equipment were out of the question at the outset since such devices were not suited to minute study of each step in the process, but could be installed at any time after the commercial possibilities of the process had been demonstrated; *e. g.*, such obvious improvements as feeding the oil by a single pump through a common header, or the use of one large condenser for all the tubes in place of individual condensers for each tube, were set aside in favor of less desirable mechanical arrangements by which each tube could be kept as a separate unit and its products analyzed apart from those of the remaining tubes.

It will be recognized readily that it was first necessary to prove that the process would work as well on a commercial basis as in the laboratory. This could be done only at the sacrifice of a very considerable percentage of the product formed. Elimination of

this loss was regarded as a mere matter of course, to be taken up at will. These losses continued, however, throughout the period covered by the data published.

#### LARGE-SCALE DEVELOPMENT OF BENZENE-TOLUENE PROCESS

Under the terms of the agreement with the Aetna Explosives Co., the work incident to the development of the benzene-toluene process on a scale of commercial magnitude was begun at Pittsburgh, Pa. A plant was acquired and the experimentation was begun which was to result in the successful working out of the process on a commercial scale.

#### EXPERIMENTS WITH VARIOUS SIZES OF TUBES

The original apparatus used in the laboratory experiments consisted of a tube 1½ in. in diameter by 3 ft. in length. When the development work was undertaken, a small number of experiments with a tube of the same internal diameter, but 4½ ft. in length, sufficed to show that the longer tube gave the same general results. A second tube 2½ in. in diameter and 4 ft. long gave equally satisfactory results, and was, therefore, promptly abandoned in favor of a tube 4½ in. in diameter and 6 ft. long which was found to give results comparable with those obtained with the original small tube. Some half dozen or more runs were made at varying temperatures and rates of feed, at a pressure of 250 lbs. per sq. in. At a temperature of 600° C. and a rate of feed of 8 gal. per hour an oil of 0.94 specific gravity was recovered, which on distillation in the laboratory gave a benzene yield of 12 per cent and a toluene yield of 8 per cent, on the basis of recovered oil. Thus sufficiently favorable results were obtained with this apparatus to justify its abandonment in favor of one of still larger size.

In the next series of experiments the length of the tube was increased from 6 to 10 ft., the diameter remaining the same. It was found that operations at comparable temperatures and pressures with those used in the shorter tubes gave the same relative yields of aromatic hydrocarbons. The increased length, however, which exposed the gases for a longer period of time to the influence of temperature and pressure, made it possible to increase the rate of feed from 8 to 10 gal. per hour. This change illustrates one of the important means of controlling the time element in a gaseous hydrocarbon reaction.

The results obtained with the single 4½-in. tube were of such a character as to justify experiments to determine whether or not satisfactory yields could be obtained by encasing 10 tubes in a single combustion chamber. Accordingly, a furnace containing a battery of 10 tubes, 4½ in. in diameter by 10 ft. in length, was constructed.

Experience with this installation proved that the 4½-in. tube was of too small diameter to give efficient results. It

<sup>1</sup> *THIS JOURNAL*, 6 (1914), 383, 472; 7 (1915), 945, 1014, 1019; 8 (1916), 20; *Met. and Chem. Eng.*, 13 (1915), 682.



was demonstrated by later experiments that to obtain maximum efficiency a tube at least double or treble this diameter should be used. Tubes of  $10\frac{3}{4}$  in. internal diameter are now being efficiently employed.

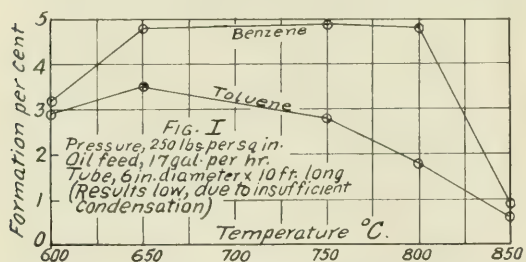
#### EXPERIMENTS WITH 6-IN. $\times$ 9-FT. TUBE

With a tube 6 in. in diameter and 9 ft. long it was found that the feed could be increased to 14 gal. per hour, an increase in capacity of 4 gal. per hr. over the  $4\frac{1}{2}$ -in. tube. An average of 5 runs, which were made at a temperature of  $600^{\circ}\text{C}$ . and 250 lbs. pressure, and a rate of flow of 15 gal. per hr., gave 8.3 per cent toluene and 13.5 per cent benzene, on the basis of recovered oil. Approximately 40 runs were made at temperatures ranging from  $500^{\circ}\text{C}$ . to  $725^{\circ}\text{C}$ . and at a constant pressure of 250 lbs., but with varying rates<sup>1</sup> of oil feed. With Oklahoma crude oil the optimum conditions were approximately  $600^{\circ}\text{C}$ ., a feed of 14 gal., and a pressure of 250 lbs. per sq. in.

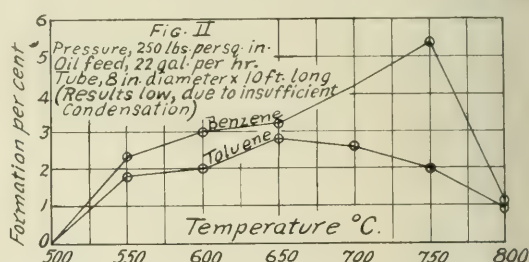
This tube was abandoned in favor of one of the same diameter, but 1 ft. longer, since it had previously been demonstrated in experiments with the smaller tubes that an increase in length

This is confirmed by the data obtained in this series of experiments. It will be seen from Fig. I that the amount of benzene formed increases progressively with increase of temperature up to  $750^{\circ}\text{C}$ ., and shows a slight decrease from this point up to  $800^{\circ}\text{C}$ . As the temperature is increased beyond  $800^{\circ}\text{C}$ . the percentage of benzene formed sharply drops until at  $850^{\circ}\text{C}$ . it is practically negligible. Toluene formation, on the other hand, shows a consistent and steady decrease above a temperature of  $650^{\circ}\text{C}$ . This result again is in accord with the evidence obtained from the experiments in the small electrically heated furnace.

It will be noted that the total yields of benzene and toluene shown in Table I are considerably below the total percentage of aromatic hydrocarbons, formed in the small laboratory apparatus.<sup>1</sup> This is due to two causes: (1) the xylene formed is left out of consideration; (2) the condensation was wholly inadequate to permit a full recovery of the aromatic hydrocarbons formed. The gases, after passing through the condenser, issued from the end of the pipe in the form of a white cloud, whereas the gases could not have been noted if none but fixed gases



FIGS. I AND II—EFFECT OF VARYING TEMPERATURES ON FORMATION OF BENZENE AND TOLUENE WHEN AN OKLAHOMA CRUDE OIL IS CRACKED AT CONSTANT PRESSURE AND RATE OF OIL-FEED IN TUBES OF DIFFERENT DIAMETERS



permitted more oil to be fed in during a given period of time, owing to the increase in heating surface.

#### EXPERIMENTS WITH 6-IN. $\times$ 10-FT. TUBE

With the installation of a 6-in.  $\times$  10-ft. tube a force-feed pump was employed, with the object of obtaining a more constant flow than could be obtained by gravity feed, where the pressure exerted by the column of oil was relied on to overcome the pressure of the gases and force the oil into the tube. It was found possible to obtain a better adjustment of temperature and pressure conditions with relation to the amount of oil supplied.

Oklahoma crude oil was used in most of these experiments, the results of which appear in Table I. Little uniformity is shown in the tabulated results unless the data be compared for the same rate of feed at different temperatures and pressures. At a constant temperature and rate of feed, but with varying pressures, the percentage of benzene and toluene formed increased with increase of pressure; e. g., at a temperature of  $600^{\circ}\text{C}$ . and a rate of feed of 12 gal. per hr., 4.3 per cent of benzene was formed at a pressure of 100 lbs.; at 150 lbs., 4.9 per cent, and at 225 lbs., 6.7 per cent. Similar variations were obtained when the pressure was increased at higher temperatures; e. g., at  $750^{\circ}\text{C}$ . and a feed of 14 gal. per hr., 4.4 per cent of benzene-toluene was formed at a pressure of 175 lbs., and 5.2 per cent at 225 lbs.

The higher temperatures, as has been stated,<sup>2</sup> are favorable for benzene formation, but prejudicial to toluene formation.

<sup>1</sup> A smaller number of runs were made at temperatures between  $600^{\circ}$  and  $725^{\circ}\text{C}$ . and 125 lbs. pressure, but the yields were considerably decreased, this result being due as much to failure to obtain the proper rate of oil feed as to the unsuitability of the pressure for converting oil to aromatic hydrocarbons. The necessity of obtaining concrete results with a minimum loss of time made it necessary to suspend experiments with varying rates of pressure for the time being.

<sup>2</sup> W. F. Rittman, THIS JOURNAL, 7 (1915), 945.

escaped: a large proportion of the volatile liquids formed were thus carried away by the gases, the quantity of which could

TABLE I—BENZENE AND TOLUENE FORMED FROM CRACKING OKLAHOMA CRUDE OIL IN A SINGLE-TUBE FURNACE (TUBE 6 IN. IN DIAMETER AND 10 FT. LONG), AT VARYING TEMPERATURES, PRESSURES, AND RATES OF OIL FEED(a)

Distillation of Oklahoma Crude Oil Used for Cracking		No.							PER CENT IN OIL RECOVERED			Per cent on Basis of Original Oil		
Temp. of Cut.	Temp. of Cr.	1	2	3	4	5	6	7	Benz.	Tol.	Total	Benz.	Tol.	Total
Volume %	Sp. Gr.	1.5	3.5	7.0	11.0	14.0	8.0	15.5						
Sp. Gr.		0.720	0.722	0.735	0.752	0.782	0.786	0.836						
Pressure		Lbs. per sq. in.							PER CENT IN OIL RECOVERED			Per cent on Basis of Original Oil		
No. of Runs	Temp. (°C.)	100	125	150	175	200	225	250	Benz.	Tol.	Total	Benz.	Tol.	Total
1	600	100	12	25	...	...	...	...	7.2	10.0	17.2	1.8	2.5	4.3
1	650	100	12	21	...	...	...	...	16.7	12.0	28.7	3.5	2.5	6.0
1	700	100	18	...	...	...	...	...	...	...	...	0.9	1.3	2.2
1	700	100	5	17	...	...	...	...	19.4	11.8	31.2	3.3	2.0	5.3
1	600	150	12	25	...	...	...	...	9.6	10.0	19.6	2.4	2.5	4.9
1	650	175	9	42	...	...	...	...	7.6	7.6	15.2	3.2	3.2	6.4
1	700	175	18	22	...	...	...	...	12.3	10.5	22.8	2.7	2.3	5.0
1	750	175	14	21	...	...	...	...	10.5	10.5	21.0	2.2	2.2	4.4
1	650	200	15	22	...	...	...	...	21.0	11.0	32.0	4.6	2.4	7.0
1	675	200	27	54	...	...	...	...	3.0	5.2	8.2	1.6	2.8	4.4
1	700	200	12	20	...	...	...	...	12.5	9.5	22.0	2.5	1.9	4.4
1	600	225	12	18	...	...	...	...	23.3	13.9	37.2	4.2	2.5	6.7
1	650	225	18	22	...	...	...	...	20.4	13.7	34.1	4.5	3.0	7.5
1	700	225	18	22	...	...	...	...	13.2	12.3	25.5	2.9	2.7	5.6
1	750	225	14	20	...	...	...	...	16.5	9.5	26.0	3.3	1.9	5.2
1	650	250	19	17	...	...	...	...	21.8	12.4	34.2	3.7	2.1	5.8
4	650	250	18	35	...	...	...	...	10.6	9.7	20.3	3.7	3.4	7.1
1	650	250	19	44	...	...	...	...	5.5	9.1	14.6	2.4	4.0	6.4
1	675	250	16	22	...	...	...	...	10.9	10.9	21.8	2.4	2.4	4.8
3	700	250	17	24	...	...	...	...	14.2	11.2	25.4	3.4	2.7	6.1
1	750	250	17	17	...	...	...	...	20.0	12.9	32.9	3.4	2.2	5.6
2	600	150	17	40	0.89	...	...	...	5.0	3.0	8.0	2.0	1.2	3.2
2	650	150	17	34	0.91	...	...	...	7.0	4.0	11.0	2.4	1.4	3.8
5	600	200	17	33	0.92	...	...	...	8.0	6.0	14.0	2.6	2.0	4.6
5	600	250	17	32	0.93	...	...	...	10.0	9.0	19.0	3.2	2.9	6.1
4	650	250	17	30	0.96	...	...	...	16.0	11.5	27.5	4.8	3.5	8.3
4	750	250	17	27	0.99	...	...	...	18.0	10.5	28.5	4.9	2.8	7.7
2	800	250	17	18	1.01	...	...	...	26.0	10.0	36.0	4.8	1.8	6.6
2	850	250	17	15	1.03	...	...	...	6.0	4.0	10.0	0.9	0.6	1.5

(a) Average results low, due to insufficient condensation.

(b) Temperatures measured by pyrometer attached to wall of tube

not be determined with the facilities at hand. The percentage of loss was not of so much moment in these experiments as was

<sup>1</sup> W. F. Rittman, THIS JOURNAL, 7 (1915), 945.



FIG. III—GENERAL VIEW OF THE IRVINE PLANT, AETNA CHEMICAL COMPANY, PITTSBURGH

the question whether the conversion could be properly carried out in the larger tubes. It was readily recognized that efficient condensation would make a great improvement in the results.

In the series of runs made at a constant rate of flow of 17 gal. per hr., the total percentage of aromatic hydrocarbons formed, including the higher aromatic compounds, is shown to increase progressively with increase in temperature. The results obtained at temperatures of 750° to 850° C. are unfavorable, as the recovered oil was of higher specific gravity than has been found desirable for maximum yields of benzene and toluene.

The general results obtained with the 6-in.  $\times$  10-ft. tube were satisfactory and in harmony with those obtained with other tubes. It was proved that the reaction could be carried on as successfully in a tube of this size as in the much smaller tubes which were first used, but it was also evident that the maximum size of furnace body had not yet been found.

#### EXPERIMENTS WITH 8-IN. $\times$ 10-FT. TUBE

With a tube 8 in. in diameter and 10 ft. long, it was found possible to increase the rate of feed 5 gal. per hr. over that for the 6-in. tube.

OKLAHOMA CRUDE OIL (see Table II) was used. It will be observed that a uniform series of runs at fixed temperatures, pressures and rates of feed was not attempted, but that each one of these variables was changed in relation to the others so that a number of combinations could be studied.

The characteristic effect of high temperatures on the relative amounts of benzene and toluene formed, is observable in the results of these tests. The percentage of benzene tends to increase progressively as the temperature is raised, whereas the relative percentage of toluene drops.

It will be noted further that at a given temperature and pressure, *e. g.*, 700° C. and 250 lbs. per sq. in., the yields of benzene and toluene decrease as the rate of feed is increased. Experi-

ments (not recorded here) in which the oil was fed at rates varying from 36 to 50 gal. per hr., at temperatures ranging from 575° to 650° C., gave little or no conversion into aromatic hydrocarbons, indicating that sufficient time was not allowed for the molecular rearrangement incident to the formation of such hydrocarbons.

TABLE II—BENZENE AND TOLUENE FORMED FROM CRACKING OKLAHOMA CRUDE OIL IN A SINGLE-TUBE FURNACE (TUBE 8 IN. IN DIAMETER AND 10 FT. LONG) AT A CONSTANT PRESSURE OF 250 LBS. PER SQ. IN. WITH VARYING TEMPERATURES AND RATES OF OIL FEED(a)

(For distillation analysis of Oklahoma crude oil used, see Table I)

No. OF RUNS	Temp. °C.	Gal. OIL RECOVERED		PER CENT IN BEN- zene	PER CENT IN Tol- uene	PER CENT IN TOTAL B.+T.	Per cent on Basis of Original Oil		
		per hr.	Sp. Gr.				Ben- zene	Tol- uene	TOTAL B.+T.
1	650	18	27	8.5	8.9	17.4	2.3	2.4	4.7
1	650	28	25	13.6	12.4	26.0	3.4	3.1	6.5
1	675	11	23	21.0	13.5	34.5	4.8	3.1	7.9
1	675	14	25	24.0	13.6	37.6	6.0	3.4	9.4
2	675	36	75	1.8	3.6	5.4	1.3	2.7	4.0
1	700	11	21	18.7	13.8	32.5	3.9	2.9	6.8
1	700	14	25	23.2	12.0	35.2	5.8	3.0	8.8
1	700	18	22	20.0	12.7	32.7	4.4	2.8	7.2
1	700	24	25	10.8	10.0	20.8	2.7	2.5	5.2
2	700	27	29	...	...	...	1.5	2.2	3.7
2	750	17	35	9.2	10.3	19.5	3.2	3.6	6.8
2	850	22	50	0.88	4.6	5.4	2.3	1.8	4.1
1	600	22	35	0.92	8.6	5.7	3.0	2.0	5.0
2	650	22	31	0.93	10.3	9.0	19.3	3.2	2.8
2	700	22	26	0.98	16.1	10.0	26.1	4.2	2.6
2	750	22	21	1.00	25.7	9.5	35.2	5.4	2.0
1	800	22	17	1.03	6.5	5.3	11.8	1.1	0.9

(a) Average results low, due to insufficient condensation.

The results of a series of runs with Oklahoma crude oil, at a constant rate of feed of 22 gal. per hr. and at a constant pressure of 250 lbs. per sq. in., but varying temperatures, are presented in Table II. There is a constantly increasing yield of both benzene and toluene up to approximately 650° C., the ratio of increase being nearly uniform. At higher temperatures the percentage of toluene steadily diminishes, whereas the percentage of benzene sharply increases with temperature rise up to about 750° C. Here again, however, the percentage of in-



crease in benzene is greater at the higher temperatures than the diminution in toluene. Only small percentages of benzene and toluene were recovered at 800° C., indicating that at this and higher temperatures there is too much formation of polycyclic aromatic compounds and too much decomposition into the ultimate end products—hydrogen and carbon. This assumption is borne out by the rapid decrease in yield of oil. These facts are shown by Fig. 11.

A DISTILLATE OIL was used in the series of experiments reported in Table III. Possibly the most striking feature of these results is the indicated ability to change the yields of either benzene or toluene by varying the temperature and pressure.

TABLE III—BENZENE AND TOLUENE FORMED FROM CRACKING A DISTILLATE OIL IN A SINGLE-TUBE FURNACE (TUBE 8 IN. IN DIAMETER AND 10 FT. LONG) AT VARYING PRESSURES, TEMPERATURES, AND RATES OF OIL FEED(a)

Distillation Analysis of Oil Used												
First drop at 170° C.; specific gravity, 0.817												
Temperature of Cut		DISTILLATION PRODUCTS				Remarks						
°C.		Vol. '.	Sp. Gr.									
200° C.		2.0			Stuck at 290° to 296° C.							
250		7.3	0.792									
300		57.0	0.818									
350		28.0	0.827									
Residue		5.3										
No. of RUNS		Temp. °C.	Pressure Lbs. Gal. per sq. in. per hr.	OIL RECOVERED Per cent Sp. Gr.		PER CENT IN OIL RECOVERED Benzene Toluene B.+T.		Per cent on Basis of Original Oil Benzene Toluene B.+T.				
1	1	600	150	14	36.3	0.890	7.0	10.8	17.7	2.5	3.9	6.4
1	1	625	175	14	30.0	0.936	14.3	13.9	28.2	4.3	4.2	8.5
1	1	700	200	14	20.0	1.000	23.6	13.0	36.6	4.7	2.6	7.3
2	1	650	200	15	24.0	0.981	20.4	16.4	36.8	4.9	3.0	8.8
1	1	625	200	14	30.0	0.938	14.7	15.3	30.0	4.4	4.6	9.0
1	1	600	200	14	30.0	0.873	8.0	11.4	19.4	2.4	3.4	5.8
1	1	550	200	14	55.0	0.837	0.0	4.2	4.2	0.0	2.2	2.2
2	1	700	250	15	22.5	0.998	22.4	12.9	35.3	5.0	3.9	8.9
2	1	650	250	15	23.5	0.972	20.2	15.7	35.9	4.8	3.7	8.5
1	1	600	250	15	31.2	0.900	9.1	12.8	21.9	2.8	4.0	6.8

(a) Average results low, due to insufficient condensation.

The lower pressures for a given rate of feed and constant temperature are shown to be more favorable for toluene production than the higher pressures of benzene.

It is characteristic of this oil, as well as all the other distillates used, that the percentage formation of toluene is greater than that of benzene. On the basis of yields it is evident that this oil is more favorable for cracking to form benzene and toluene than is the Oklahoma crude oil.

Experiments were also made with two other distillates, but

TABLE IV—BENZENE AND TOLUENE FORMED FROM CRACKING OKLAHOMA CRUDE OIL IN A SINGLE-TUBE FURNACE (TUBE 8 IN. IN DIAMETER AND 14 FT. LONG) AT A CONSTANT PRESSURE OF 250 LBS. PER SQ. IN., WITH VARYING TEMPERATURES AND RATES OF OIL FEED(a)

PER CENT IN OIL RECOVERED									
Per cent on Basis of Original Oil									
No. of Runs		Temp. °C.	Pressure lbs. sq. in.	Oil recovered per cent	Sp. Gr.	Benzene	Toluene	Total	Per cent on Basis of Original Oil
1		625	32	25	20.23	12.57	32.80	5.10	3.10
1		650	24	14	31.17	15.51	46.68	4.30	2.20
2		650	27	22	26.40	12.70	39.10	5.70	2.80
1		650	28	25	24.10	12.00	36.10	6.00	3.00
1		650	29	29	12.42	13.26	25.68	3.60	3.90
2		650	31	23.2	18.45	13.17	31.62	4.30	3.00
2		650	32	29	10.64	9.97	20.61	3.00	2.90
1		675	29	16	27.47	12.88	40.35	4.50	2.10
1		775	35	23	4.84	6.37	11.21	1.90	2.50
2		800	30	16.5	18.30	21.95	40.25	3.00	3.60
1		800	33	27	8.80	9.04	17.89	2.37	2.46
4		800	35	25.5	13.44	10.10	23.54	3.43	2.57
1		825	23	17	26.00	10.10	36.10	4.43	1.72
1		825	35	33	7.60	8.60	16.20	2.51	2.82
2		825	38	28.5	11.60	8.00	19.60	3.30	2.28
1		850	21	18	20.20	8.04	28.24	1.62	6.43
1		850	33	23	10.70	10.30	21.00	2.46	2.37
1		850	36	20	16.20	10.30	26.50	3.24	2.06
1		875	33	25	10.90	10.40	21.30	2.73	2.61

(a) Results low, due to insufficient condensation.

(b) Temperature readings approximate only, judged by color of tube and by pyrometer in checkerwork of furnace.

the results were of the same general character as with the distillate referred to, and need not be discussed in detail.

#### EXPERIMENTS WITH 8-IN. × 14-FT. TUBE

With a view to obtaining increased capacity, the 8-in. × 10-ft. tube used in the previous experiments was replaced by

one 14 ft. long. The increased heating surface afforded by the gain in length made it necessary to determine experimentally the most favorable conditions for carrying out the reaction in this tube. A large number of experiments, covering the entire range of possible temperatures and pressures, and with rates of oil feed varying from 10 to 50 gal. per hour showed that the rate of feed could be increased from 22 to 30 gal. per hr. with a satisfactory amount of conversion. The chemical reaction could be obtained with the same facility as in the other tubes, but the added length of heating zone caused an increase in mechanical difficulties for the time being.

OKLAHOMA CRUDE OIL, used for some thirty-odd experiments at a uniform pressure of 250 lbs. furnished the data given in Table IV. As was the case with the distillate oil the average results are less favorable than in the 10-ft. tube of the same diameter. The longer exposure to heat permitted by the 4-ft. increase in length evidently condensed the low-boiling aromatics into hydrocarbons of greater molecular weight, as well as increasing the formation of end-product gases and carbon. The results show an improvement, however, over those obtained with the same oil in the 6-in. × 10-ft. tube, where the mean production of benzene and toluene was 5.7 per cent as against 6.4 in the new furnace.

#### EXPERIMENTS WITH 8-IN. × 7-FT. TUBE

The fact that in the experiments just described the optimum length of tube had been exceeded led to experiments with an 8-in. × 7-ft. tube. A number of tests at a constant pressure of 250 lbs., temperatures varying between 500° and 750° C., and rates of feed between 12 and 25 gal. per hr. brought out the interesting fact that the percentage recovery of oil is higher for the same temperatures, pressures, and rates of feed than with either the 8-in. × 10-ft. or the 8-in. × 14-ft. tubes. This indicates clearly that a lesser degree of conversion took place, an assumption which is borne out by the decreased yields of benzene and toluene for the given conditions of operation. The results were mostly of a negative character.

The greatly decreased capacity of the tube as compared with those of greater length made it apparent that the 7-ft. tube was too short for commercial purposes, although the reaction was proved to take place readily therein.

#### GENERAL CONCLUSIONS REGARDING DIMENSIONS OF TUBES

The experiments show that conversion into low-boiling aromatic hydrocarbons will take place in tubes of any size from 1½ in. × 3 ft. to 8 in. × 14 ft., reactions occurring as readily in one size of tube as another. The variation in extent of heating surface, however, makes it necessary properly to adjust conditions of temperature, pressure, and rate of feed in order to obtain maximum conversion and minimum waste in the form of ultimate decomposition products. The desirable combination of conditions must be experimentally determined for each oil used as original material. It was found that, for an 8-in. diameter, 14 ft. exceeded the optimum length which could be used, because of mechanical rather than chemical disadvantages, and that a 7-ft. tube was too short on account of the commercial factor of greatly decreased capacity. The most efficient length for tubes 8 in. in diameter was determined to be 10 ft. (for the heated zone).

Each progressive increase in the diameter of the reaction tubes has given improved results. In the latest benzene-toluene plant, tubes of 10¾ in. internal diameter

are being most efficiently employed. The flow capacity per hour has been more than trebled as compared with the 8-in. tubes. Rates of feed exceeding 60 gal. per tube per hour are now being attained without difficulty as contrasted with a feed of 15 gal. per hr. in the Aetna Company installation. The conversion results have been equally as satisfactory. There is no reason for assuming that tubes of even larger diameter cannot be employed. In fact, experiments with an 18-in. tube will shortly be undertaken.

#### EXPERIMENTS WITH BATTERIES OF 10 TUBES 8 IN. IN DIAMETER AND 14 FT. LONG

As soon as a sufficient number of runs had been made with the single 8-in. tubes to demonstrate the feasibility of carrying out the reaction in a tube of this diameter, a decision was reached on the part of the Aetna Company to install six furnaces containing batteries of 10 tubes each. The individual tubes were to be 8 in. in external diameter and 14 ft. in over-all length, as the construction of the furnace necessarily reduced the effective length and it was considered that this length would bring the parts of the tubes in which the reaction was substantially accomplished relatively near the favorable limits found by experimentation.

The construction of furnaces on such a large scale before a single furnace was carefully tried out has been justified by the results obtained.

The furnaces have been operating efficiently over a period of 8 months. They have been in practically continuous operation, day and night, and have convincingly demonstrated the ability of the process as well as the mechanical installation designed to carry out such process, to turn out any desired quantity of benzol and toluol consistent with the rated capacity of the tubes. The operation has become as well standardized as any other industrial pro-

cess. As an indication of the success attained by the plant it may be said that it has attained efficiencies as high as 118 per cent. In other words, the plant has, from time to time, done 18 per cent better than what was considered the maximum efficiency by the Aetna Company. These results have been obtained since the plant has been on a settled operating basis, and after the mechanical problems incidental to the first operation of a new mechanical development had been overcome. It must at all times be kept in mind that the data reported in the bulletin were gathered during the period of minimum operating efficiency.

The above explanation must be kept constantly in mind in passing on the results recorded, as otherwise entirely erroneous impressions will be formed concerning the availability of the process for general use under normal conditions.

#### CARBON DEPOSITION

Throughout the operations for which results are recorded in Table V, an Oklahoma crude oil was used. The semiasphaltic character of this oil caused a very large percentage of carbon formation, and its use was discontinued in favor of a distillate, from Pennsylvania crude, with a boiling range between 250° and 400° C. This does not imply that Oklahoma oils are unsuitable for use in the process, but means that it is

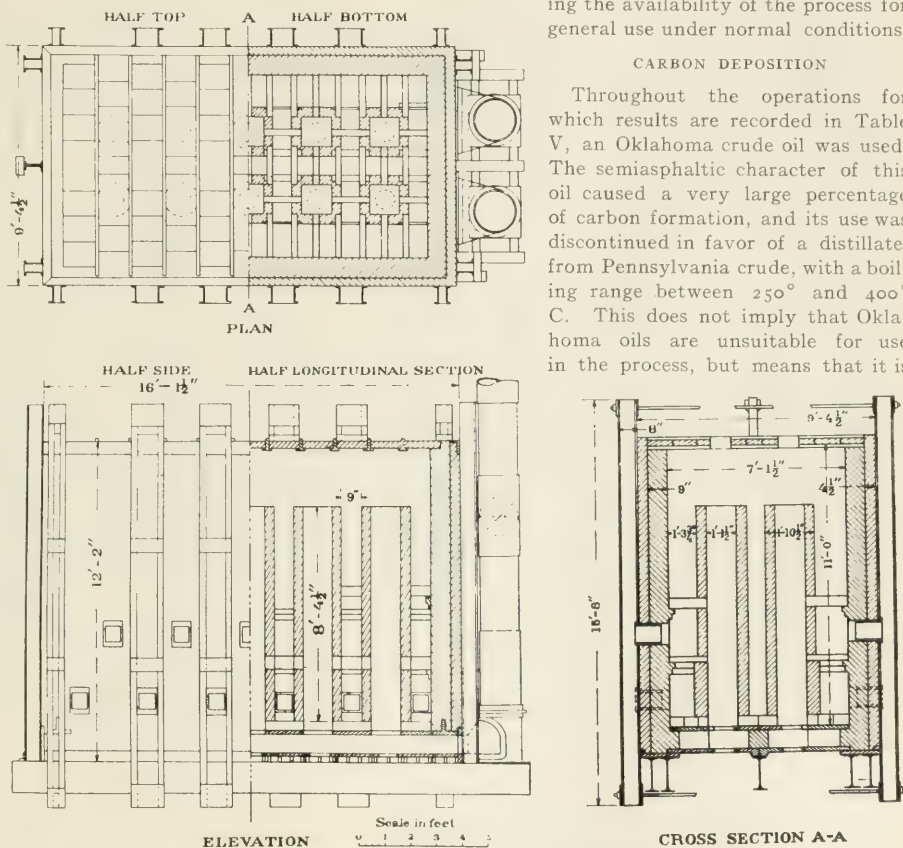


FIG. IV. PLAN, ELEVATION AND CROSS-SECTION OF FURNACE AT DEVELOPMENT PLANT

desirable first to remove the gasoline fraction and the heavy residuum. Laboratory tests have shown clearly that if this were done an Oklahoma oil would probably give more satisfactory results than the Pennsylvania distillate which has since been used, because the asphaltic properties of some of its constituents favor splitting into benzene and its homologues.

The total amount of carbon formed, on the basis of oil used, has been rather roughly determined by



scraping the carbon from the carbon receptacles into wheelbarrows and weighing it. It was found to average between 1 and  $1\frac{1}{2}$  lbs. per gal. of oil used. This means that for every 1,000 gal. of oil the process made and cared for between 1,000 and 1,500 lbs. of carbon. The ability to handle successfully this large amount of carbon is believed to constitute a unique difference between this and other cracking processes. The total amount of carbon formed while using Oklahoma crude oil is greatly in excess of the amount formed from the distillate subsequently used. The latter oil averaged only  $\frac{1}{4}$  to  $\frac{1}{2}$  lb. per gal. This

EXPERIMENTS WITH BATTERIES OF TEN TUBES 8 IN. IN DIAMETER  
AND  $11\frac{1}{2}$  FT. LONG

As has been pointed out, the decision to reduce the length of the tubes in the 10-tube furnaces from 14 to  $11\frac{1}{2}$  ft. was due to a desire to reduce mechanical difficulties incident to the operation of the longer stirring rods.<sup>1</sup> It was decided at the same time to decrease the rate of oil feed in order to permit using lower temperature for the same relative amount of conversion. It was determined also to conduct experiments for the purpose of ascertaining whether the pressure previously used (250 lbs. per sq. in.) could not be materially reduced in view of the slower rate of feed. An extensive series of experiments demonstrated that with the distillate a pressure of 150

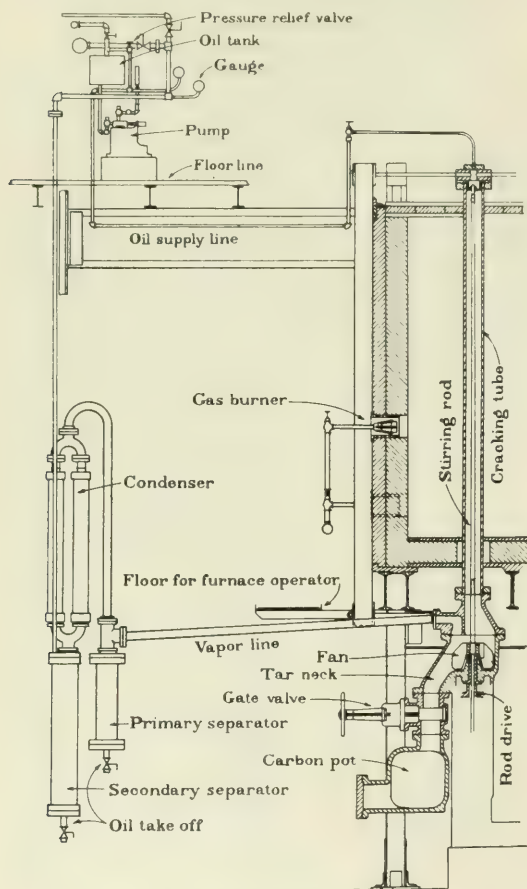


FIG. V—DIAGRAM OF FURNACE CONNECTIONS

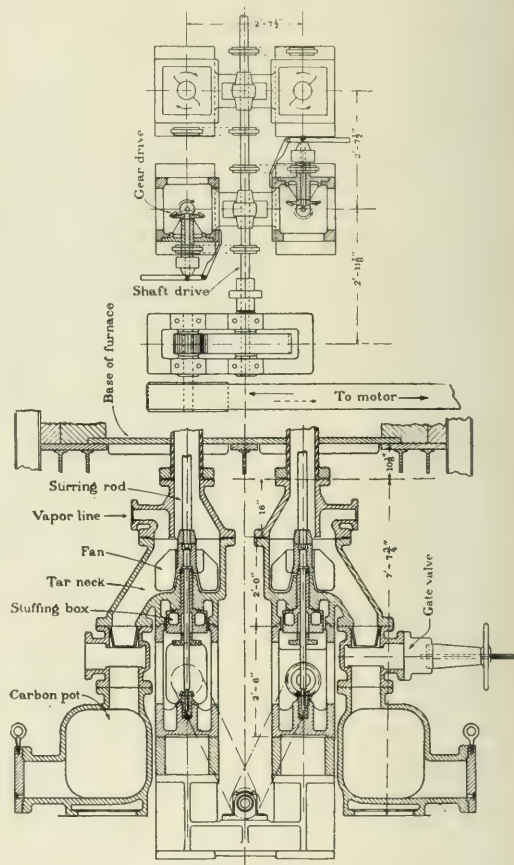


FIG. VI—DETAILS OF STIRRING ROD DRIVE AND TAR NECK

amount has since been reduced to approximately  $\frac{1}{10}$  lb. per gal. of oil.

The results of operations in the large 14-ft. furnaces are given in Table V, and represent the results of more than 3 months of experimentation and operation. Space would not permit the inclusion of all the data for the six furnaces; consequently typical runs and results have been selected.

It will be noted that with the Oklahoma crude oil, the percentage of benzene formed exceeds on an average the percentage of toluene formed. This is in sharp contrast with later results obtained with the use of the distillate oil, in which the percentage of toluene exceeds that of benzene (see Table VI).

to 175 lbs. at the reduced feed gave more satisfactory results than the higher pressures.

The reduction in the length of the tubes from 14 to  $11\frac{1}{2}$  ft. gave an effective furnace length of approximately 10 ft., which is the optimum length as determined by a series of experiments with the single-tube furnaces for an 8-in. diameter.

In considering the total recoveries of benzene and toluene, it should be borne in mind that the percentages shown are not the maximum recoveries that can be obtained from a given quantity of oil. These percentages are based on the amount

<sup>1</sup> The stirring rod is the device employed for keeping the inner wall of the tube free from deposits of carbon.

TABLE V—BENZENE AND TOLUENE FORMED FROM CRACKING OKLAHOMA CRUDE OIL IN 10-TUBE FURNACES (TUBES 8 IN. IN DIAMETER AND 14 FT. LONG) AT VARYING PRESSURES AND RATES OF OIL FEED(a)

(Temperatures varied from 600 to 800° C., and were determined by judging the color of the tubes, aided in some cases by pyrometer inserted in checker-work of furnace. In determining specific gravities for runs in multiple-tube furnaces, covering quantities ranging from 1 to 1,500 gals., the values indicated are correct within 0.02.)

Pressure Oil Lbs. per sq. in. hr.	Gal. Oil Used	OIL RECOVERED		PER CENT IN RECOVERED OIL			Per cent on Basis of Original Oil			
		Per Cent	Sp. Gr.	Ben- zene	Tol- uene	TOTAL B.+T.	Ben- zene	Tol- uene	TOTAL B.+T.	
100	18	1,334	38	0.92	7.9	5.3	13.2	3.0	2.0	5.0
100	18	1,343	34	0.94	8.5	7.9	16.4	2.9	2.7	5.6
150	23	1,461	37	0.93	8.7	7.0	15.7	3.2	2.6	5.8
150	25	1,829	25	0.96	12.8	8.8	21.6	3.2	2.2	5.4
150	27	866	27	0.97	12.6	9.6	22.2	3.4	2.6	6.0
175	26	1,114	31	0.94	11.6	10.0	21.6	3.6	3.1	6.7
175	26	1,286	32	0.94	11.5	10.6	22.1	3.8	3.5	7.3
175	26	1,360	37	0.93	10.8	8.9	19.7	4.0	3.3	7.3
175	26	1,365	37	0.91	8.7	6.2	14.9	3.2	2.3	5.5
175	26	1,393	31	0.93	10.3	9.4	19.7	3.2	2.9	6.1
175	27	961	26	0.94	11.9	9.2	21.1	3.1	2.4	5.5
200	27	1,363	30	0.91	9.7	7.7	17.4	2.9	2.3	5.2
200	28	1,494	25	0.93	12.8	9.6	22.4	3.2	2.4	5.6
250	30	200	33	.....	15.1	7.6	22.7	5.0	2.5	7.5
250	30	200	33	.....	15.1	7.6	22.7	5.0	2.5	7.5
250	30	210	21	.....	30.9	10.5	41.4	6.5	2.2	8.7
250	30	240	33	.....	18.8	7.0	25.8	6.2	2.3	8.5
250	30	252	28	.....	19.6	6.8	26.4	5.5	1.9	7.4
250	30	333	31	0.93	13.9	10.0	23.9	4.3	3.1	7.4
250	30	333	25	.....	24.0	8.8	32.8	6.0	2.2	8.2
250	30	363	23	.....	28.0	10.9	38.9	6.2	2.5	8.7
250	30	382	24	.....	27.1	9.0	36.1	6.5	2.3	8.8
250	30	387	26	.....	23.8	7.7	31.5	6.2	2.0	8.2
250	30	453	20	0.96	17.5	8.0	25.5	3.5	1.6	5.1
250	30	460	25	.....	26.0	10.4	36.4	6.5	2.6	9.1
250	30	483	33	.....	18.8	6.7	25.5	6.2	2.2	8.4
250	30	512	32	.....	20.3	7.5	27.8	6.5	2.4	8.9
250	30	536	22	.....	25.4	10.4	35.8	5.6	2.3	7.9
250	30	580	30	.....	20.0	7.7	27.7	6.0	2.3	8.3
250	30	634	19	.....	34.7	11.6	46.3	6.6	2.2	8.8
250	30	667	24	.....	23.3	7.9	31.2	5.6	1.9	7.5
250	30	725	26	.....	23.1	7.7	30.8	6.0	2.0	8.0
250	30	762	26	.....	24.2	8.9	33.1	6.3	2.3	8.6
250	30	884	24	0.94	12.9	10.0	22.9	3.1	2.4	5.5
250	30	1,070	27	.....	25.2	8.9	34.1	5.8	2.4	8.2
250	30	1,072	22	.....	27.3	9.6	36.9	6.0	2.1	8.1
250	30	1,137	22	0.96	10.0	10.0	20.0	4.4	2.2	6.6
250	30	1,490	24	.....	25.0	8.8	33.8	6.0	2.1	8.1
250	30	1,529	26	.....	24.2	8.8	33.0	6.3	2.3	8.6

(a)Results low, due to insufficient condensation.

of aromatic hydrocarbons in the distillation cut up to a temperature of 175° C. The residue from the 175° C. cut is highly suitable for rerunning through the furnace, and will yield an amount of aromatic hydrocarbons equal to that recovered by the first run (see Table VII). The result is that from a given quantity of oil the maximum recovery on running the oil twice through the tubes will be at least double that reported here. That part of the cut up to 175° C., above the toluene fraction, is even more suitable for rerunning than the cut above 175°, as the former contains the xylenes and solvent naphthas which have been proven to be a most prolific source of both benzene and toluene. In addition, it must be borne in mind that re-

TABLE VI—BENZENE AND TOLUENE FORMED FROM CRACKING A DISTILLATE OIL IN 10-TUBE FURNACES (TUBES 8 IN. IN DIAMETER AND 11½ FT. LONG) AT A CONSTANT PRESSURE OF 150 LBS. PER SQ. IN. (a)

(For distillation analysis of oil used, see Table III)

Gal. Oil Used	OIL RECOVERED Per cent	Sp. Gr.	PER CENT IN RECOVERED OIL			Per cent on Basis of Original Oil		
			Benzene	Toluene	TOTAL B.+T.	Benzene	Toluene	TOTAL B.+T.
242	29.2	0.98	11.7	11.7	23.4	3.4	3.4	6.8
274	30.6	0.95	11.3	11.6	22.9	3.5	3.6	7.1
329	26.1	0.95	12.7	13.0	25.7	3.3	3.4	6.7
368	26.9	0.97	13.7	14.5	28.2	3.7	3.9	7.6
481	33.8	0.91	9.7	11.2	20.9	3.3	3.8	7.1
576	33.1	0.96	12.4	12.9	25.3	4.1	4.3	8.4
578	26.3	0.96	12.3	14.6	26.9	3.2	3.8	7.0
590	28.0	0.97	12.1	13.9	26.0	3.4	3.9	7.3
1,361	29.9	0.91	8.7	11.1	19.8	3.2	4.2	7.3
1,130	28.0	0.94	12.5	13.6	26.1	3.5	3.8	7.3
1,156	32.0	0.95	9.4	9.7	19.1	3.0	3.1	6.1
1,170	25.0	0.97	14.0	13.6	27.6	3.5	3.4	6.9
1,283	25.6	0.97	13.5	14.3	27.8	3.5	3.7	7.2
1,382	37.4	0.91	7.6	8.4	16.0	2.8	3.1	5.9
1,661	29.9	0.94	9.7	11.0	20.7	3.2	3.9	7.1
1,600	24.1	0.98	12.9	13.8	26.7	3.1	3.3	6.4
1,627	30.0	0.94	8.0	9.7	17.7	2.4	2.9	5.3
1,855	31.8	0.94	11.0	11.3	22.3	3.5	3.6	7.1
1,878	25.2	0.96	14.4	14.8	29.2	3.6	3.7	7.3
1,878	25.6	0.95	11.9	13.9	25.8	3.1	3.6	6.7
2,884	27.4	0.93	11.8	12.5	24.3	2.9	3.2	6.1
2,200	34.0	0.92	8.8	10.6	19.4	3.0	3.6	6.6
2,414	29.8	0.96	12.0	12.6	24.6	3.6	3.8	7.4
2,439	25.6	0.96	11.6	12.3	23.9	3.0	3.2	6.2
2,753	34.5	0.92	9.7	11.2	20.9	3.3	3.8	7.1

(a)Results low, due to insufficient condensation.

covery has not been made of the aromatic hydrocarbons mechanically carried in the uncondensed gases. The gases, which in order to maintain uniform pressure were constantly being released during the operation of the process, did not pass through an efficient condenser or scrubber, but into a gas header and thence into a small gas trap, where a portion of their liquid content was removed. These gases mechanically carry over a considerable percentage of the heavier as well as of the lighter oils. Although the gas traps were of great value in indicating qualitatively the amount of liquid product which is mechanically carried by the gases, they did not remove an appreciable quantity of these constituents.

TABLE VII—BENZENE AND TOLUENE FORMED IN A SINGLE-TUBE FURNACE (TUBE 8 IN. IN DIAMETER AND 10 FT. LONG) FROM CRACKING THE RESIDUE ABOVE 175° C. OF AN OIL PREVIOUSLY CRACKED AT VARYING PRESSURES AND RATES OF OIL FEED(a)

No. of Runs	Temp. °C.	Pressure Lbs. per sq. in.	Gal. Oil per hr.	PER CENT IN RECOVERED OIL				Per cent on Basis of Original Oil			
				OIL RECOVERED				T +		T +	
				Per cent	Sp. Gr.	Benzene	Toluene	TOTAL B. + T.	Benzene	Toluene	TOTAL B. + T.
1	600	Atmospheric	14	79	1.035	3.2	3.2	6.4	2.5	2.5	5.0
1	700	"	15	70	1.052	3.3	3.0	6.3	2.3	2.1	4.4
3	650	50	15	49	1.093	9.0	3.7	12.7	4.5	1.8	6.3
1	650	25	15	39	1.085	15.9	7.6	23.5	6.3	3.0	9.3
1	700	25	21	54	1.100	13.0	3.5	16.5	7.1	1.9	9.0
1	650	100	21.2	27	1.048	13.0	5.2	18.2	3.5	1.4	4.9
1	700	100	14.0	21	1.014	14.6	7.5	22.1	3.1	1.6	4.7
1	700	100	22.5	31	1.058	11.5	4.9	16.4	3.6	1.5	5.1
1	700	100	28.8	39	1.060	8.1	3.8	11.9	3.2	1.5	4.7
1	575	150	14	62½	1.034	4.3	3.8	8.1	2.7	2.4	5.1
1	600	150	14	44	1.062	8.3	4.8	13.1	3.6	2.1	5.7
1	650	150	16.5	48	1.042	8.2	5.2	13.4	4.0	2.5	6.5
1	600	200	15.5	41	0.989	7.0	6.0	13.0	2.9	2.5	5.4

(a)Results low, due to insufficient condensation.

#### GENERAL CONCLUSIONS REGARDING MULTIPLE-TUBE FURNACES

Observations of the results obtained in a single-tube furnace as compared with those obtained in the 10-tube furnaces have demonstrated the superiority of the single-tube over the multiple-tube arrangement. No difficulty was experienced in maintaining temperature control over the single tubes, whereas it has been a constant problem to obtain anything like uniformity of heating conditions with the multiple-tube furnace. To get a uniform heat over a small area of the tube it must be heated on more than one side by burners near one plane. This is not possible in the multiple-tube furnace, but is easy of accomplishment in the single-tube type. One side of the tube in the multiple furnace often becomes too hot and the other side too cold. This would not be the case with the smaller installation.

The results of the operations of a new benzene-toluene plant, that of the Benzol Products Co., of Pittsburgh, Pa., has confirmed these conclusions. It has been found possible in this plant to regulate closely the furnace temperatures and to secure a uniformity of product not possible in the multiple-tube furnace, as well as a very large increase in output. In fact, in the newer installations, 4 tubes have as much capacity as 20 tubes in the installation herein described.

#### DESCRIPTION OF AETNA PLANT AS FINALLY CONSTRUCTED

FURNACE CONSTRUCTION—The character of the furnace construction is indicated by Fig. IV. The furnace proper consists of an outer shell of common brick, lined with a single thickness of standard fire



brick. The over-all dimensions of the 10-tube furnace are approximately as follows:

Height of Furnace	12 ft.	5 m.
Clearance between Top and Bottom Plates	11 ft.	
Length of Sides	16 ft.	11 1/2 m.
Clearance between Inner Walls	13 ft.	10 1/2 m.
Width of Furnace	9 ft.	4 1/2 m.
Clearance between Side Walls	7 ft.	11 1/2 m.
No. Gas Burners per Furnace	22	

Any common type of gas burner of sufficient capacity may be used. The consumption of gas per tube averages about 300 cu. ft. per hr. with the present installation, which has not been operated with particular regard to economic heating.

The interior of the furnace is filled with a checker-work of fire brick. The gaseous products of combustion pass through a baffle arrangement from the gas ports, ascend through the checkerwork and are drawn inside the chambers of fire brick in which the tubes are placed. From these chambers the gases pass out through

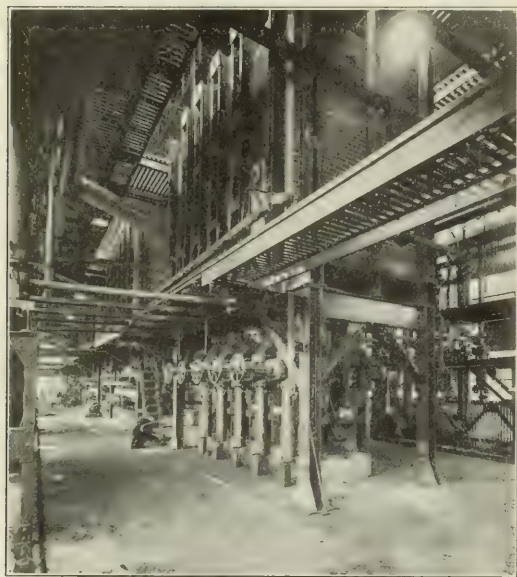


FIG. VII—GROUND FLOOR VIEW OF FURNACE BUILDING, SHOWING ARRANGEMENT AND BUILDING OF FURNACES NOT COMPLETED, AETNA CHEMICAL CO.

two flues at the bottom of the furnace shell and are discharged into the open air through stacks 18 in. in diameter placed at one end of the furnace. The flues are so arranged that the products of combustion of the 11 burners on one side of the furnace pass out through an individual stack. The brick shell of the furnace is strengthened by five steel buck-stays on each side and three on each end, these stays being approximately 15 ft. 8 in. high and 8 in. wide. The tops of the stays are connected with tie-rods so as to give greater stability to the furnace. The burners of the upper row are placed at a height of 3 1/2 ft. above the heater platform, shown in Fig. IV. It has been found necessary to have a double set of burners in order to supply the additional heat required to maintain the tubes at the desired temperature.

The furnaces are set at a height of 10 1/2 ft. above the ground, and rest on 16 in. I beams, supported by 8-in. I beams. The arrangement of the supports is fully shown in Fig. IV. The furnaces were thus elevated because it was necessary to place carbon receptacles immediately under the bottom of the tubes, and to rotate the stirring rod from below. The carbon receptacles and the stirring-rod drive rest on concrete foundations.

**OIL-FEEDING EQUIPMENT**—The general arrangement of the oil feed to the tubes is shown by Fig. V, which is a sketch of a furnace and its connections.

#### APPARATUS FOR REMOVING DEPOSITED CARBON

**USE OF STIRRING ROD**—The most serious problem that was faced at the outset of operations was the removal of carbon formed on the walls of the tubes. It was realized that inability to dispose of the carbon had been the cause of the failure of other processes involving the employment of tubes. The knowledge gained from the laboratory experiments as to the percentage of carbon deposition made evident the necessity of employing some efficient mechanical means for its removal.

**CONSTRUCTION OF STIRRING RODS**—The use of stirring rods was decided on after careful weighing of the probable advantages of a number of possible devices. The location of the rod is shown by Fig. V. Chains are arranged spirally around the rod and are so spaced that they will scrape the entire periphery of the tube where the cracking takes place and carbon is deposited. The chains are thrown out by centrifugal force as the rod is rotated, so that the links strike the inner wall of the tube with considerable force.

The arrangement of the stirring rod in the tube and the manner of its operation are shown by Fig. VI. The lower end of the rod is detachably connected to a vertical shaft that extends upward through a stuffing box in the bottom of the tar neck and has its lower end keyed in a bevel pinion which intermeshes with the corresponding pinion on a short horizontal shaft driven by a chain from below. The entire series of carbon stirrers in a single furnace is operated by a motor-driven line shaft, which is so arranged that the stirring rods on one side of the furnace revolve in one direction while those on the opposite side rotate in the reverse direction. Clutches are attached to each short horizontal shaft, so that any number of stirring rods can be thrown out of gear while the others are being rotated.

This rod has demonstrated its ability to keep the walls of the tube free from carbon, and has made the successful operation of the process possible.

**CONCLUSIONS REGARDING CONDENSERS**—In any new installation for the employment of this process, provision should be made for a condenser of the same type as that used in oil refineries. With the benzene-toluene process, the condensation problem is, however, markedly different from that of the refinery, where all the vapors coming from the still are condensable, as in making benzene and toluene considerable volumes.

of fixed or non-condensable gases are generated. In general, a condensing area of approximately 3 ft. per 1000 cu. ft. of gas generated will be found satisfactory if a gas scrubber is operated in connection therewith. This gas scrubber can be modeled after the benzene scrubbing towers in by-product coke-oven plants, or may consist merely of a large tank filled with a heavy oil, through which the gases are bubbled. This tank should be so enclosed that the fixed gases can be conducted to a gas holder for the purpose of supplying fuel for the furnaces, if desired. In by-product coke-oven practice the introduction of back pressure by forcing gas through a body of oil

than was the physical or chemical nature of the initial material.

The process, however, is not limited to the use of petroleum products, but can be efficiently operated on liquid hydrocarbon material derived from any source. Solvent naphthas, and light oil distillates from water-gas tars and coal tar have been successfully used. These light oils and solvent naphthas are extremely favorable for use in the process as yields two to three times larger than those obtainable from petroleum products can be had in a single operation. The petroleum oils, however, give a wider range of by-products. This fact, together with their greater

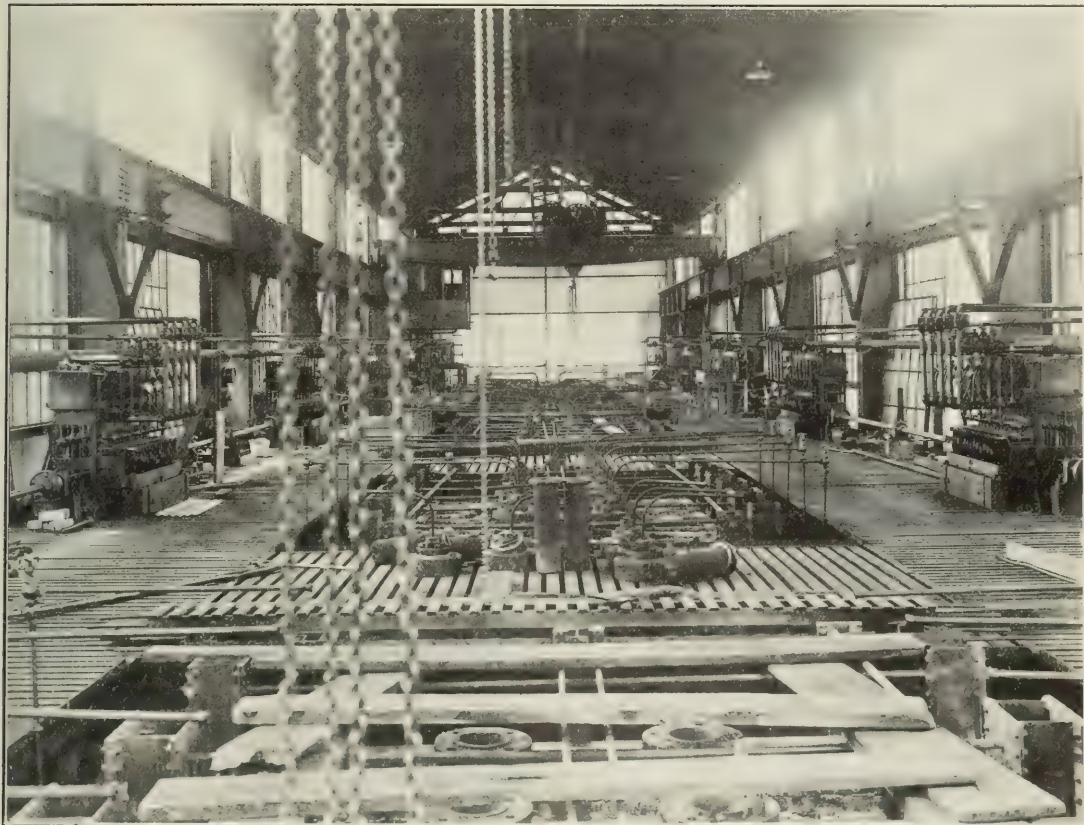


FIG. VIII.—GENERAL VIEW (FROM BALCONY) OF OIL PUMPS AND PRESSURE RELEASE VALVES

would seriously affect the coking products, whereas in the process herein described there is sufficient direct pressure to work against any desired head of oil.

#### OILS SUITABLE FOR USE IN THE PROCESS

In the course of the experiments a large number of petroleum oils have been used, ranging in character from crude oils to gas oils and cylinder stocks. It was found, as was the case in the laboratory experiments, that the reactions desired were in no wise dependent on the character of oil used and that the conditions of operation were of more consequence

availability, as well as lower cost, probably renders them most suitable for use.

The experiments have clearly indicated that the vapor-phase cracking process is not limited to any particular type of oil, and that an asphaltic oil, a paraffin-base oil, oil having a paraffin and asphaltic base, and certain oils obtainable from the destructive distillation of coal, are all suitable for use in the process.

#### GASOLINE PROCESS

During the period of time covered by the bulletin, opportunity was not afforded for testing the gasoline



process on a large commercial scale. At present writing seven refineries in six states are installing plants for the employment of this process. Several of these plants should be ready to operate within a period of a few weeks. On the basis of results obtained

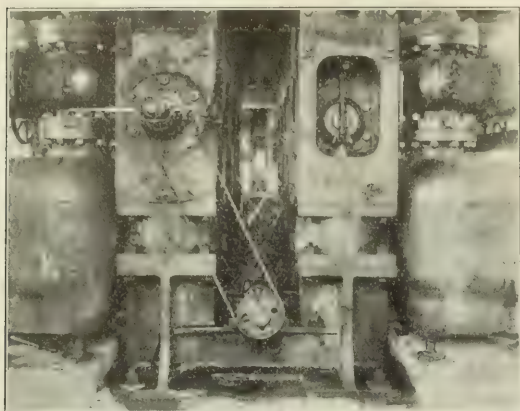


FIG. IX—DETAILS OF STIRRING ROD DRIVE

in the experiments conducted during the progress of the development work on the benzene-toluene process, optimistic belief in the large-scale commercial possibilities of the gasoline process is amply justified.

#### EXPERIMENTS WITH 6-IN. $\times$ 9-FT. TUBE

Table VIII gives the results of runs with the distillate boiling at 250° to 350° C. in a 6-in.  $\times$  9-ft. tube at temperatures ranging between 550° and 650° C. and rates of feed varying from 13 to 26 gal. per hour. Both the percentage of recovered oil and the percentage of gasoline formed are abnormally low, which is due entirely to inefficient condensation. For this reason the figures published are to be regarded as suggestive rather than as definite evidence of the possibilities of the process.

TABLE VIII—GASOLINE FORMED FROM CRACKING A DISTILLATE OIL (a) IN A SINGLE-TUBE FURNACE (TUBE 6 IN. IN DIAMETER AND 9 FT. LONG) AT A CONSTANT PRESSURE OF 250 LBS. PER SQ. IN., WITH VARYING TEMPERATURES AND RATES OF OIL FEED (b)

No. OF RUNS	Temp. ° C.	Gal. Oil per hr.	OIL RECOVERED				GASOLINE PER CENT FORMED			
			Per cent	Sp. Gr.	PER CENT IN OIL	RECOVERED	Sp. Gr.	PER CENT FORMED	ON BASIS OF ORIGINAL OIL	
1	550	17	54	0.800	35.0	0.772			18.9	
2	550	19	85	0.800	20.0	0.730			17.0	
3	550	26	92	0.800	14.0	0.730			12.9	
1	575	13	58	0.815	32.0	0.750			18.6	
3	600	17	79	0.830	36.0	0.760			28.5	
1	600	19	85	0.810	25.7	0.735			21.8	
6	600	23	78	0.810	25.0	2.736			19.5	
3	625	22	76	0.815	27.0	0.740			20.5	
1	650	19	69	0.820	31.0	0.745			21.4	
1	650	21	79	0.816	24.0	0.723			19.0	
1	650	25	86	0.828	20.0	0.740			17.2	

(a) Boiling point 250° to 350° C. (b) Results low, due to insufficient condensation.

#### EXPERIMENTS WITH 8-IN. $\times$ 10-FT. TUBE

The same oil was cracked in a number of experiments in an 8-in.  $\times$  10-ft. tube. The data are assembled in Table IX. The average percentage of gasoline formed is only 18.8 as compared with 19.5 in the smaller tube. In the larger tube the average rate of feed was increased from 22 gal. to 30 gal. per hour. The greater volume of gases generated placed a heavier burden upon the already inadequate condenser, which contributed to the average lower yield obtained.

The low percentage of gasoline formed is, in the majority of yields reported in this table, clearly due to the excessive rate of feed, which did not allow sufficient opportunity for conversion.

When the rate of feed was in proper relationship to the temperatures and pressure, it will be noted that the yield of gasoline, despite the inefficient condensation, is considerably higher than that obtained in the laboratory experiments at Columbia University.<sup>1</sup>

The decrease in gasoline formation at high rates of feed is clearly evidenced by a study of the results for a given temperature and pressure. The tests show that pressure is favorable for the formation of gasoline, an increase of 3 per cent in the yield being obtained at 575° C. and a rate of 24 gal. per hr. by changing the pressure from 200 to 300 lbs. per sq. in.

TABLE IX—GASOLINE FORMED FROM CRACKING A DISTILLATE OIL (a) IN A SINGLE-TUBE FURNACE (TUBE 8 IN. IN DIAMETER AND 10 FT. LONG), AT VARYING TEMPERATURES, PRESSURES, AND RATES OF OIL FEED (b)

No. OF RUNS	Temp. ° C.	Pressure Lbs. per sq. in.	Gal. Oil per hr.	Oil Recovered Per cent	Sp. Gr.	GASOLINE (up to 150° C. cut)			
						Per cent in Recovered	Sp. on Basis of Gr.	Per cent Formed on Basis of Original Oil	
1	550	50	11	81	0.820	22.5		0.74	18.3
1	550	100	25	93	0.808	16.8		0.74	15.7
1	550	150	17	80	0.825	29.25		0.78	23.4
1	550	150	27	[100] (c)	0.810	18.0		0.76	18.0
1	575	200	24	79	0.820	22.8		0.76	18.1
1	550	250	12	81	0.805	26.8		0.76	21.8
1	550	250	22	[98] (c)	0.800	13.8		0.74	13.8
1	550	250	23	70	0.860	38.5		0.75	26.9
1	550	250	55	85	0.835	19.8		0.75	16.8
1	575	250	13	75	0.820	20.5		0.76	15.3
1	575	250	20	70	0.848	32.5		0.76	22.8
1	575	250	26	66	0.825	38.0		0.76	25.3
1	575	250	36	84	0.814	23.3		0.75	19.6
1	600	250	28	75	0.815	29.25		0.76	21.9
1	600	250	57	80	0.839	16.5		0.76	13.0
1	600	250	68	81	0.841	16.3		0.74	13.2
4	650	250	24	70	0.830	28.0		0.74	19.6
2	550	275	26	78	0.815	29.0		0.74	22.6
1	675	275	48	75	0.815	20.8		0.75	15.6
1	675	275	52	75	0.815	19.0		0.74	14.3
1	575	300	24	70	0.820	31.3		0.75	21.9
1	600	300	24	80	0.815	22.0		0.75	17.6

(a) Boiling point, 250° to 350° C.; specific gravity, 0.817 (41.3° B.)

(b) Results low, due to insufficient condensation.

(c) Obviously experimental error.

The highest average conversion figures were obtained in experiments with a distillate fuel oil, data for which are presented in Table X. The average yield of gasoline is nearly 3 per cent greater than in any of the other series of runs. It is to be noted, however, that the average percentage of recovered oil is lower. It is evident that in these runs the rate of feed was too low for the most efficient results.

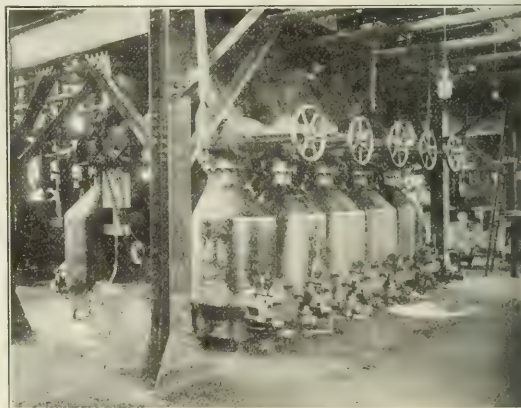


FIG. X—ENLARGED CARBON POTS USED IN NEWER TYPE OF INSTALLATION

CONCLUSIONS AS TO GASOLINE TESTS—In considering the figures assembled in the foregoing tables, it must be remembered that efficient condensation was lacking. The work was carried on during intervals when benzene-toluene experiments were being conducted with equipment erected to obtain indications

<sup>1</sup> W. F. Rittman, *THIS JOURNAL*, 7 (1915), 945.

as to benzene-toluene reactions, and not to determine maximum yields. Accordingly the condensing facilities were of the crudest type. The results can be considered only as suggestive of

TABLE X—GASOLINE FORMED FROM CRACKING A DISTILLATE FUEL OIL IN A SINGLE-TUBE FURNACE (TUBE 8 IN. IN DIAMETER AND 10 FT. LONG) AT A CONSTANT PRESSURE OF 250 LBS. PER SQ. IN., WITH VARYING TEMPERATURES AND RATES OF OIL FEED(a)

Temp. °C.	Gal. Oil per hr.	GASOLINE				Sp. Gr.
		OIL RE- COVERED Per cent	Per cent in Recovered Oil	Per cent on Basis of Original Oil		
575	12	75	30.0	22.5	....	
575	15	79	25.1	19.8	....	
600	12	71	31.3	22.2	0.76	
625	12	77	40.0	30.8	0.72	
625	16	75	38.5	28.9	0.75	
650	12	74	36.3	26.8	0.75	
650	15	88	20.0	17.6	....	
700	15	80	30.5	26.0	0.78	

(a) Results low, owing to insufficient condensation.

Distillation Analysis of Original Oil Used  
[Specific gravity, 0.915 (23° B.); first drop at 300° C.]

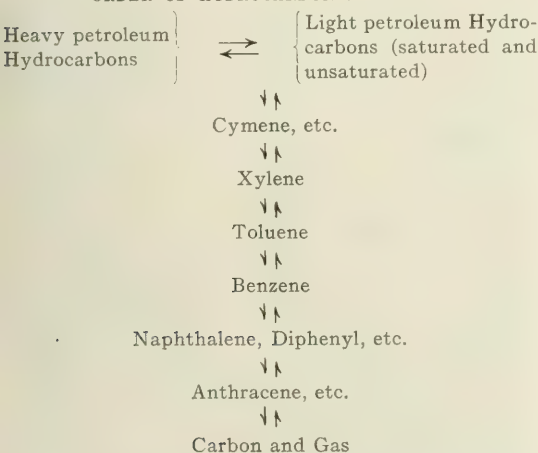
Temperature of Cut °C.	DISTILLATION PRODUCT		
	Volume Cc.	% of Original Oil	Specific Gravity
350	85	42	0.85
400	80	40	Jelly-like

what can be accomplished under proper conditions. Viewed in this light they are of a distinctly favorable character, and justify belief in the commercial possibilities of the process.

#### GASOLINE PROCESS COMPARED WITH BENZENE-TOLUENE PROCESS

In comparison with the benzene-toluene process, the gasoline process is simple in character. This may be more readily perceived by considering the order of hydrocarbon reactions as given below. The relative order is not only based on theory, but is in accordance with the evidence gained as the result of extended series of tests.<sup>1</sup>

#### ORDER OF HYDROCARBON REACTIONS



The conversion from heavy hydrocarbons into lighter hydrocarbons involves only one step, and is easy of accomplishment, whereas the conversion into the lower boiling aromatic hydrocarbons requires that the heavier hydrocarbon molecules undergo a much more extensive series of changes before the desired products are obtained.

Because of the greater ease with which gasoline can be made, the installation used for benzene-toluene production will have double the capacity when used

for conversion of heavy oil into gasoline. The duration of the gasoline reaction is less than half that required for the benzene-toluene reaction if the same size and length of tubes be used. It is manifest, therefore, that by introducing twice the volume of oil to be converted, the effect will be the same as decreasing the time factor by one-half.

#### CONCLUSIONS AS TO GASOLINE PROCESS

The large-scale experiments have fully confirmed the laboratory experiments and established the fact that the conversion into gasoline can be even more satisfactorily accomplished in a tube of greatly enlarged diameter and increased length than in the electrically heated 1½-inch tube. The conditions favorable for gasoline production are shown to be the same in the larger tubes as in the small tube, namely, a temperature of approximately 500° to 575° C. and a pressure of 250 to 300 lbs. per sq. in.

The gasoline process, therefore, can justly be considered as a success so far as conversion in the large tubes is concerned. The adaptation of the unit to refinery conditions is a matter of mechanical detail involving no inherent difficulties.

#### SUCCESS OF BENZENE-TOLUENE PROCESS

In view of the continuous operation of the benzene-toluene process by the Aetna Explosives Co., over a period of nearly one year, as well as the results of the large-scale operations, which have been given in detail, there can exist little doubt as to the success of the benzene-toluene process on a commercially operative scale. It has been proved that benzene and toluene can be produced in large quantities by this process. These products have been shown to be capable of being worked into the nitro-compounds desired for making explosives. Furthermore, these nitro-compounds, or the derivatives thereof, are equally suitable for use in producing dyestuffs.

The claims which were made for the process at the outset have thus been fully verified by commercial results, and its future is dependent alone upon the perfection of the mechanical apparatus and the consequent reduction in labor and operating costs.

BUREAU OF MINES, WASHINGTON

#### A TEST OF A SURFACE COMBUSTION FURNACE<sup>1</sup>

By E. SCHRAMM AND J. R. CAIN

Received February 2, 1916

In an article on "The Design of Surface Combustion Appliances," Prof. C. E. Lucke<sup>2</sup> gives an account of the principles underlying this new process of combustion, and of their application to the development of commercial apparatus. The surface combustion process has aroused considerable interest and given rise to much speculation since its first publication in 1902.<sup>3</sup> For a diversity of views as to its

<sup>1</sup> Published with the permission of the Director of the Bureau of Standards.

<sup>2</sup> C. E. Lucke, *THIS JOURNAL*, 5 (1913), 801-24; *Proc. Amer. Gas. Inst.*, 8 (1913), 420-504.

<sup>3</sup> C. E. Lucke, *Trans. Amer. Soc. Mech. Eng.*, 23, 253-262.

<sup>1</sup> Rittman, Byron and Egloff, *THIS JOURNAL*, 7 (1915), 1019.



nature the reader is referred to papers<sup>1</sup> by Bone, Ellis, Neumann, McCourt, Gray, Jüptner, Kinzbrunner, and to the above-mentioned papers by Lucke. The present work grew out of another investigation<sup>2</sup> in which the authors had occasion to carry out a series of experiments with gas and electric furnaces for the

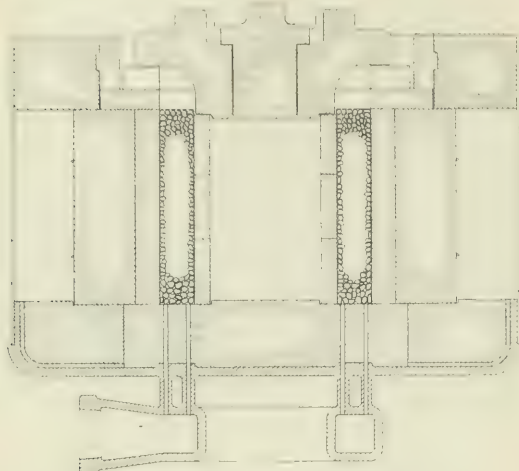


FIG. I—SURFACE COMBUSTION CRUCIBLE FURNACE

production of high temperatures. It was, therefore, not our purpose to consider the many theories concerning surface combustion, but merely to carry out a practical test of a furnace of this type. We are greatly indebted to The Surface Combustion Company, of New York, and to Prof. C. E. Lucke for supplying the furnace and for the assistance and advice they have so kindly given.

The furnace used in this test was the crucible furnace described by Lucke in the first of the papers cited and illustrated in Fig. I. Its crucible chamber is 4 in. in diameter and 6 in. high, and the over-all dimensions are 16 in. in diameter and 14 in. high. Its essential features include a mixing chamber provided with two rings of outlet tubes exposed to the air to permit cooling. The hearth is molded in place by inserting wires of suitable diameter into these feed tubes and filling in with alundum cement, so as to obtain a hearth with perforations registering with the tubes. In operation the gas-air mixture discharges into an annular combustion chamber which is filled with small lumps of electrically fused white alundum. In the original furnace the outer wall of the combustion chamber and the inner wall or muffle were both made of alundum cement. Our experience having shown that this form of muffle would not stand up for any length of time at the high temperatures reached, it was decided to mold a muffle in sections so that failed parts might easily be replaced. At the suggestion of Dr. C. W.

Kanolt, these sections were made of a mixture of 80 per cent white alundum and 20 per cent kaolin, which proved much more refractory than the original alundum cement. Before the second series of tests described below, the furnace was taken apart and provided with a new hearth and new outer and inner muffles.

Figs. II and III show the furnace and accessory equipment assembled for test. A small blower (c) was installed on the gas line to increase the pressure and a gas meter (g), previously calibrated, was placed between the blower and the supply pipe. To permit the collection of the products of combustion and the measurement of their temperature, a sheet-iron chimney (b) was constructed to fit over the furnace. Into this chimney were inserted a thermo-couple (k) and a long piece of flexible copper tubing (i) which, after passing through a can filled with water, was connected to the gas sample bottle (j). The gases were drawn through for a considerable length of time to allow them thoroughly to oxidize the inside of the copper tube before any samples were taken. Furnace temperatures were read by means of a Holborn-Kurlbaum optical pyrometer (a), whose line of sight passed through a small sliding door (l) in the chimney and just under the cover of the furnace (c), and intersected the muffle about 2 in. from the bottom. For the determination of the quantity of air supplied, some sort of flow meter seemed desirable in order that instantaneous readings and prompt adjustment of rate might be secured. The use of a Venturi tube was considered.

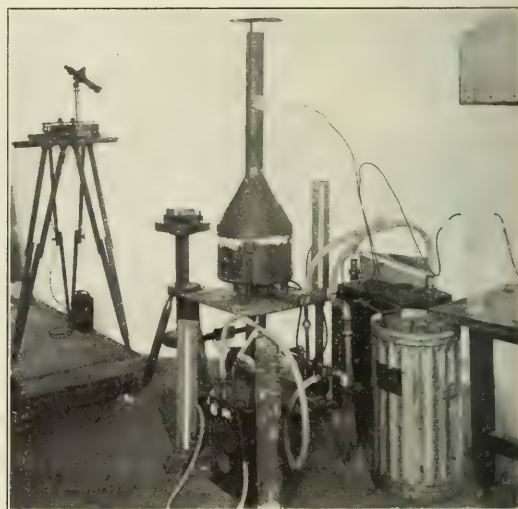


FIG. II—FURNACE EQUIPPED FOR TEST

but because of the low pressure of the air available (1 lb. per sq. in.) and the serious objection to any throttling of the flow, this was rejected in favor of a Pitot tube (h) constructed of copper capillary tubing. The question of the accuracy of small Pitot measurements does not enter here, since it was possible to

<sup>1</sup> W. A. Bone, *J. Gas Lighting*, **106**, 300; *Engineering*, **91**, 487-489; *THIS JOURNAL*, **4**, 77-79; C. Ellis, *Bull. Amer. Inst. Min. Eng.*, **69**, 945-975; B. Neumann, *Stahl u. Eisen*, **33**, 593-599; C. D. McCourt, *Electrician*, **71**, 132-135; H. H. Gray, *J. Gas Lighting*, **126**, 786-789; F. v. Jüptner, *Feuerungstechnik*, **1**, 38-42; C. Kinzbrunner, *Ibid.*, **1**, 62-67, 118-120, 259-262.

<sup>2</sup> J. R. Cain, E. Schramm and H. E. Cleaves, "Preparation of Pure Iron and Iron-Carbon Alloys," *THIS JOURNAL*, **8** (1916), 217.

calibrate the tube in place by means of a large gas meter (*f*) inserted in the air line.

The furnace was operated without a charge. The cover was placed so as almost to close the top of the muffle, thus reproducing normal operating conditions and avoiding loss by radiation from the incan-

with a gas consumption of 3 cu. ft. per min. Failure to maintain this temperature for a longer period was due to the caving in of the alundum muffle.

The curve in Fig. IV gives the rate of cooling of the furnace. This, it will be noted, is very slow, because of the heat storage of the incandescent bed

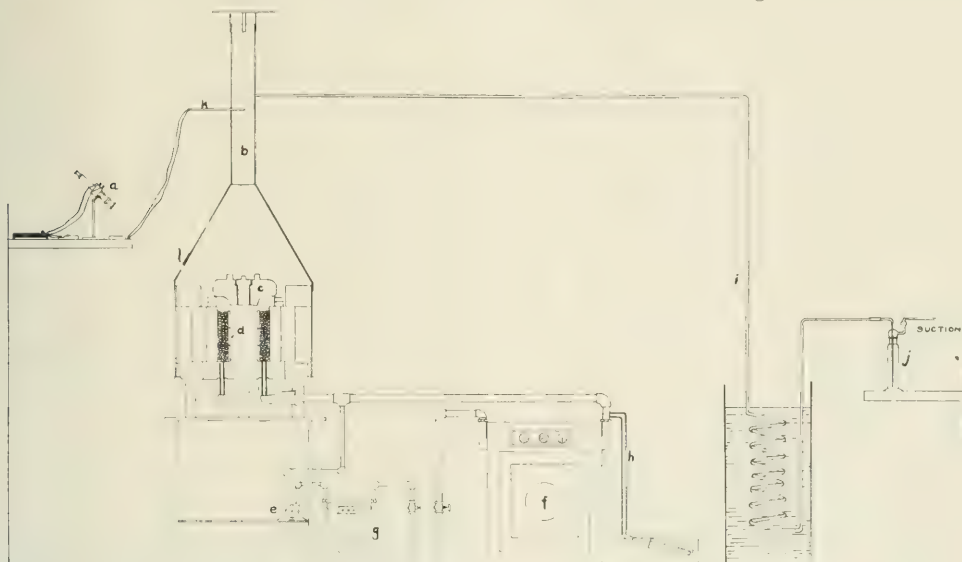


FIG. III—DIAGRAM OF APPARATUS

descent bed. In the later runs, when the composition of the mixture or the rate of combustion were varied, the furnace was allowed to run for half an hour under each new condition so that it might come to equilibrium before temperatures were read and gas samples taken. Experience had shown that at the high temperatures in which we were particularly interested, steady conditions were reached in that length of time.

TABLE I—RESULTS OF PRELIMINARY RUN

Time	Temp. (°C.)	Cu. Ft. Gas Used Total	Per min.	Pressure in Mixing Chamber (Inches of water)
11:20	20	0.0		
11:25	837	11.8	2.35	5.75
11:29	1063	23.6	2.95	6.00
11:32	1237	31.4	2.60	7.50
11:36	1395	43.2	2.95	8.25
11:40	1498	57.0	3.45	13.75
11:45	1528	68.7	2.35	10.50
11:51	1586	84.5	2.65	10.50
11:56	1670	100.0	3.10	10.50
12:00	1645	108.0	2.00	9.75
12:06	1645	125.8	2.95	9.75

Air pressure during run.....43.5 in. water.  
Pressure of gas at meter outlet.....1.75 in. water.  
Total heating value of gas, 670 B. T. U.'s per cu. ft.; net heating value, 620 B. T. U.'s per cu. ft. (60° F., 30 in. Hg. saturated gas).

Table I gives the results of a preliminary trial made before the furnace was equipped for taking flue gas samples or metering the air. Under these circumstances it was impossible to secure the best operating conditions as there was no way of telling when the mixture was properly proportioned. The results are instructive, however, in showing what may be expected in ordinary operation from a furnace of this type. They may be summarized briefly as follows: A temperature of about 1650° C. (3000° F.) was reached in a little over 1/2 hr., and maintained for 10 min.

and the efficient insulation of the walls, a property which should make this type of furnace extremely valuable for certain laboratory operations.

TABLE II

Run No.	Furnace Temp. °C.	Cu. Ft. per Min.	AIR	GAS	Ratio Air : Gas	Gas Pressure In. of Water	Mixture Pressure In. of Water	Flue Gas Temp. °C.	FLUE-GAS ANALYSIS (volume percentages)		
									CO <sub>2</sub>	O <sub>2</sub>	CO
2	1530	16.0	2.95	5.4	...	...	...	690	...	...	...
	1565	16.4	2.40	6.8	...	...	...	610	...	...	...
	1585	15.5	2.40	6.4	3.0	11.0	...	680	...	...	...
	1670	13.7	2.90	4.7	...	...	...	710	12.8	0.0	2.4
	1675	15.0	3.00	5.0	...	...	...	740	...	...	...
	1660	13.5	3.30	4.1	2.9	11.0	...	760	12.1	0.0	2.3
3	1325	16.7	2.45	6.8	1.4	7.6	...	460	...	...	...
	1525	...	...	...	...	...	...	660	...	...	...
	1595	22.7	2.50	8.9	2.0	9.4	...	690	12.3	0.0	3.1
	1635	15.8	3.00	5.2	2.5	9.4	...	720	12.3	0.4	2.3
	1650	15.3	1.85	8.2	3.7	10.2	...	690	11.7	3.5	0.0
	1660	...	...	...	...	...	...	720	...	...	...
	1510	15.6	1.75	8.9	3.9	10.2	...	670	8.3	8.8	0.0
	980	16.3	1.00	16.2	4.5	6.8	...	550	4.3	15.5	0.0
	330	17.3	0.65	25.9	4.7	5.0	...	450	2.3	18.0	0.0
4	1250	6.9	1.05	6.6	4.0	3.4	...	390	...	...	...
	1460	11.5	1.75	6.5	3.5	6.8	...	520	11.0	5.3	0.0
	1555	14.6	2.25	6.5	3.1	10.2	...	650	12.1	3.9	0.0
	1605	16.5	2.60	6.3	2.7	...	...	710	13.0	2.4	0.0
5	1185	4.2	0.80	5.3	4.0	1.6	...	400	...	...	0.0
	1460	7.2	1.30	5.5	3.7	4.2	...	540	14.5	0.3	0.0
	1545	10.2	1.90	5.3	3.4	6.0	...	610	13.2	0.2	1.4
	1630	12.6	2.25	5.5	2.9	8.4	...	670	14.0	0.2	0.3
	1650	14.8	2.65	5.5	2.9	10.2	...	700	13.8	0.3	1.4
6	1155	6.4	1.05	6.0	3.5	2.6	...	370	...	...	...
	1325	7.4	1.40	5.4	3.0	3.4	...	500	13.5	1.4	0.0
	1440	9.2	1.55	6.0	2.9	6.0	...	560	13.7	1.6	0.0
	1525	10.9	1.80	6.0	3.2	8.4	...	590	13.8	1.2	0.0
	1620	13.6	2.25	6.0	2.6	10.2	...	650	13.7	1.0	0.0

Total heating value of gas, 687 B. T. U.'s per cu. ft.; net heating value, 634 B. T. U.'s per cu. ft. (60° F., 30 in. Hg. saturated gas).

Table II represents the results of a number of runs made with the completely equipped furnace. In run No. 3, the furnace was brought up to a high tem-



perature as quickly as possible and the gas cut down in steps to bring out the effect of large excesses of air. The temperatures were therefore read on a cooling furnace, and a comparison of the temperature readings with the figures for gas consumption will make it

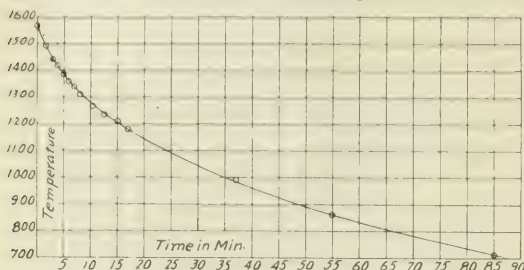


FIG. IV—RATE OF COOLING

apparent that the true equilibrium conditions were not recorded. In the later runs, therefore, all readings were taken with rising temperatures and the unit period of operation was increased from 10 or 15 min. to 30 min. Experience gained in the earlier runs further made it clear that in order to obtain useful comparable data, it would be necessary to regulate air and gas simultaneously so as to maintain constant proportions for varying rates of combustion.<sup>1</sup> This condition was very closely approximated in runs Nos. 4, 5, and 6. In these runs flue-gas analyses corresponding to the lowest rates of combustion are not given, since it was found impossible at these low rates to prevent the mixing of air with the products between the furnace and the flue-gas sampler.

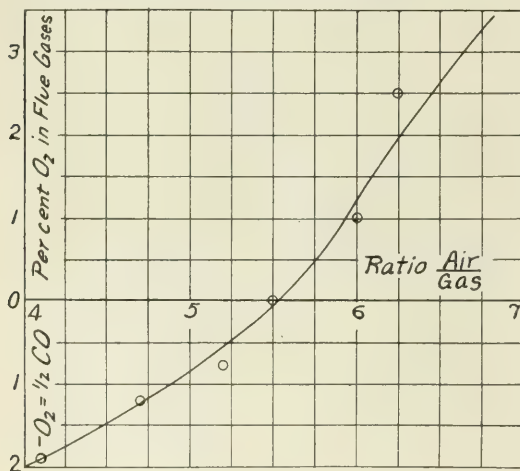


FIG. V

In the curve in Fig. V the ratio of air to gas in the mixture is plotted against the percentage of oxygen in the flue gases. Where carbon monoxide was present in the flue gases, it was considered as representing a deficiency of half its volume of oxygen and the figures were plotted on the curve as negative oxygen. In plotting this curve, two points were obtained from

<sup>1</sup> EDITOR'S NOTE: Commercial surface combustion furnaces are being equipped with automatic proportioning apparatus.

run No. 2, and one from each of the succeeding runs, the values taken corresponding as nearly as possible to the same temperature. The curve and the flue-gas analyses in Table II establish clearly that a ratio of air to gas of 5.5 gives most nearly the ideal condition of perfect combustion without any excess of oxygen. We should therefore expect to obtain with this ratio the most efficient operation, *i. e.*, the highest temperature for any given gas consumption. That this condition was realized is brought out by inspection of

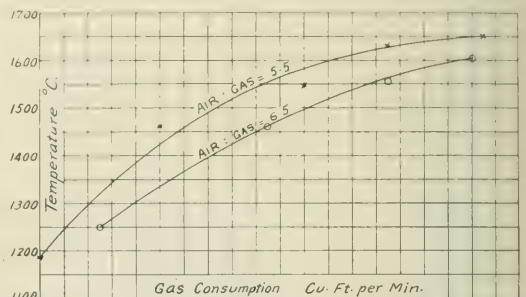


FIG. VI.

the last three runs of Table II and of Fig. VI, in which temperatures are plotted against gas consumption for mixtures in the ratios 5.5 and 6.5.<sup>1</sup> It is seen that a 20 per cent excess of air causes a lowering of furnace temperature of about 100° C. The inconsistency of some of the data taken at low temperatures (see Table II) is due to the difficulty met in regulating the mixture and establishing equilibrium at low rates of gas consumption.

So far as we have been able to ascertain, no previous account has been published of a gas-furnace test of this sort. We are therefore not in possession of any data which would enable us to make comparisons with other types of furnaces of similar dimensions. In a general way, however, it may be concluded that these results demonstrate the importance of close control over mixture proportions with laboratory or industrial gas furnaces. Such control would entail very slight added expense for flow meters and would often result in large economy in gas consumption.

The data obtained, especially those of run No. 5, show that with surface combustion apparatus it is possible to approximate closely the ideal condition of perfect combustion without excess of air. The highest furnace temperature reached during the tests described was 1675° C. (3045° F.). Obviously the temperature of the porous mass must have been considerably higher. It is not suggested that this represents the best that can be done with this type of apparatus, but merely the best with the gas and air supply that happened to be available to us. It should, however, be pointed out that the refractories ordinarily obtainable will not permit the operation of a gas furnace above, or indeed for any length of time, as high as 1650°. Most of the materials with sufficiently high

<sup>1</sup> EDITOR'S NOTE: It was later determined that homogeneity of mixture cannot be secured without special provision for mixing not used here, and that complete combustion without free oxygen requires good mixing.

melting points give trouble from cracking after prolonged operation, and to this is to be attributed our failure to carry the test further. The Surface Combustion Company is at present working on the problem of devising high refractories for these furnaces, and when these are available we hope to resume this work and extend its scope.

#### SUMMARY

A method for studying quantitatively the performance of a gas furnace and for determining the best conditions of operation has been applied to a surface combustion crucible furnace; data are given for the performance of this furnace. A temperature of  $1675^{\circ}\text{C}$ . ( $3045^{\circ}\text{F}$ .) was reached. It has been shown that complete combustion can be attained without excess of air, and that an excess of 20 per cent causes a lowering of furnace temperature of  $100^{\circ}\text{C}$ . ( $180^{\circ}\text{F}$ .).

BUREAU OF STANDARDS, WASHINGTON

#### DESCRIPTION OF A PORTABLE GAS DETECTOR<sup>1</sup>

By GEORGE A. BURRELL<sup>2</sup>

Received January 25, 1916

In this paper is given a description of a portable device for detecting combustible gases in air. Its most important use is for the detection of methane in mine air (fire-damp), but it can also be used for

these endeavors, the safety lamp remains to-day the universally used device for the quick testing of mine atmospheres to determine their methane content. Many other devices have been exploited but the fact that they are not widely used is proof that they do not fulfill the needs.

In working on the problem of gas detection in mines, the author endeavored to develop something that would be superior to the safety lamp, as regards ruggedness, simplicity, weight and accuracy. It is believed that this has been accomplished. The apparatus is 10 to 20 times more accurate than the safety lamp, is lighter in weight, is more rugged and fully as simple of operation. Percentages of methane in air as low as 0.10 per cent can be determined.

A photograph of the device is shown at Fig. I.

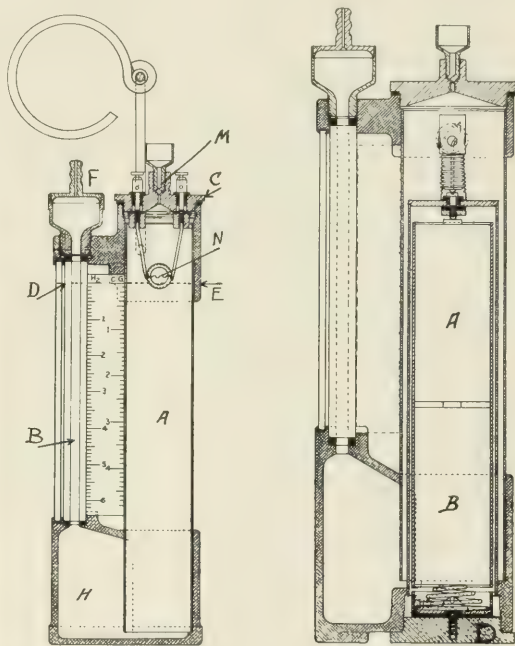


FIG. II

FIG. III

The parts are of aluminum and brass, except the stout gauge glass at the right.

A diagram is shown at Fig. II. The instrument may be considered to be a U-tube, of which the limbs A and B are two branches. Communication is made between the two limbs at a point designated by the arrow.

To start a series of determinations the brass cap C is removed and water is poured into A until it rests in the tube B at the point D, the zero point of the scale. The water will then seek the level E in the tube A.

To make a determination of combustible gas in air, say of methane in mine air, one blows into the tube F, by means of a rubber tube (not shown), thereby depressing the water in B to some point in H and filling the combustion space above E with water. One can tell when this combustion space is filled with water by hearing a slight click when the water strikes the



FIG. I

natural gas in air, coal gas in air, gasoline vapor in air, water gas in air, acetylene gas in air, carbon monoxide in flue gas, and for other combustible gases in air.

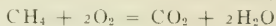
Ever since coal mining has been actively engaged in, technologists have ceaselessly endeavored to perfect methods for gas detection in mines; but despite

<sup>1</sup> Presented by permission of the Director of the Bureau of Mines. Demonstrated before the W. Va. Coal Mining Institute, December, 1915, Fairmont, W. Va.

<sup>2</sup> Chemist in charge, Laboratory of Gas Investigations, Bureau of Mines.



valve *M*. Next, the instrument is raised to the place where the sample is to be collected and the water allowed to seek the former levels at *D* and *E*. The water in falling to *E* sucks in a sample of the air to be tested. Next the valve *M* is closed and the platinum wire *N* electrically heated. The methane in the combustion chamber burns to carbon dioxide and water, thus:



*i. e.*, contraction in volume of the sample occurs corresponding to the amount of methane originally present in the sample. At the end of  $1\frac{1}{2}$  min. the electric current is turned off and the instrument shaken to cool the gases in the combustion space and bring them to the same temperature as the gases were at the beginning of the test. The water in the combustion space will then rise to take the place of the burned-out gas and fall a corresponding distance in the glass tube *B*, *i. e.*, fall to a point on the graduated scale that will show the per cent of methane originally in the sample. A previous calibration, once and for all time, fixes the proper graduations on this scale. The latter carries four graduation columns, one for methane and natural gas, one for hydrogen, one for gasoline vapor, and one for coal gas.

The electrical energy for heating the platinum wire is derived from a miner's electric cap lamp storage battery, thereby providing the electric cap lamp with a gas detector, something it does not possess at present and which has been an objection to the use of electric lamps in gaseous mines.

At Fig. III is shown another gas detector similar in operation except it contains two small dry cells, *A* and *B*, for supplying the electrical energy. These cells cost about 7 cents apiece and will operate the detector for a minimum of 20 determinations. When they are used up, they are as easily replaced (by unscrewing the cap *D*) as the dry cells of the well-known Ever-Ready flashlight batteries.

The author is indebted to several members of the Bureau of Mines for assistance in developing this instrument. Dr. G. A. Hulett, Consulting Chemist, first suggested that an apparatus of this nature be constructed, and O. P. Hood, Chief Mechanical Engineer, rendered valuable assistance in designing it.

Patent claims have been filed by the Bureau of Mines on the above instruments and means for exploiting it are being considered so the best interests of the public will be served.

PITTSBURGH

## AN APPARATUS FOR DIGESTING CRUDE FIBER

By J. M. PICKEL

Received May 28, 1915

In an article<sup>1</sup> by the author several years ago, it was stated that round-bottom flasks, through which cold water is passing, set on the beakers in which crude fiber is digesting, prevent evaporation and hold frothing in check. The apparatus pictured here is the outgrowth of that idea. The distinctive feature of it is the round-bottom reflux condenser.

<sup>1</sup> THIS JOURNAL, 2 (1910), 280

**THE CONDENSERS**—In Fig. I eight of the condensers are shown resting on the beakers. Two are shown suspended above the beakers. One is suspended, giving a view of the tube, through which the cooling water passes out of the condenser. Another, lying on the heating plate, affords a top view. The parts of a condenser (see Fig. II) are: (a) a zinc or copper—in this case it chanced to be zinc—shell (hemisphere) 7.6 cm. in diameter; (b) a copper ring, similar to those used on water baths, about 10 cm. in diameter, the circular opening in the ring being about 5.7 cm. in diameter, this ring is soldered to the shell; (c) a copper cone whose big end is about 5.7 cm. in diameter, small end about 1 cm. in diameter (1.5 cm. would be better) and vertical height about 4.5 cm.; this cone is soldered to the ring; (d) a copper tube about 1 cm. in diameter (1.5 cm. would be better) and about 11 cm. long, soldered to the cone; in the side of this tube near its top is a small hole, by means of which the condenser may be suspended on a catch or hook on the influx tube; (e) an elbow-shaped exit, or overflow, tube, about 4 mm. in inside diameter (1 cm. would be better), length (horizontal) to the elbow

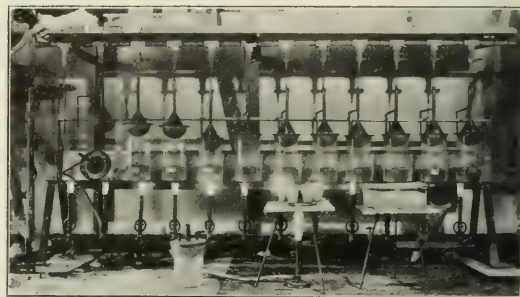


FIG. I

about 7.5 cm., length (vertical) about 10 cm.; this tube is soldered to the tube (d) about 3.5 cm. above the cone.<sup>1</sup>

**THE DELIVERY TUBES**—The cooling water is delivered into the condensers from the water-main by branch tubes each provided with a stop-cock. These cocks are ordinary brass gas-cocks, in the nozzles of which are soldered copper tubes about 4 mm. inside diameter and 24 cm. long. The adjustment should be such that the lower ends of these tubes are about 4 mm. above the bottoms of the condensers when they are suspended and about 1 to 2 cm. below the top of the cone when the condensers rest on the beakers. The condensers are suspended from a little catch or hooks soldered to the delivery tubes. Whether the condensers be suspended above the beakers or be resting on them, the water circulates through them freely and spills into a trough back of the beakers—no rubber connections. A horizontal strip with holes in it, through which the overflow tubes pass, keeps the exit ends of these tubes centered over the trough. It is important that these ends should always be visi-

<sup>1</sup> Since writing the above, an ordinary glass flask, whose neck is provided with a suitable side-tube, has been used quite satisfactorily for several months instead of one of the metallic condensers.

ble so that one may at any time know that there is ample flow of water through the condensers. These tubes should not, therefore, dip into the trough. The trough (galvanized sheet iron) is about 3.5 cm. wide, about 13 cm. deep and, of course, extends along the entire length of the "plant."

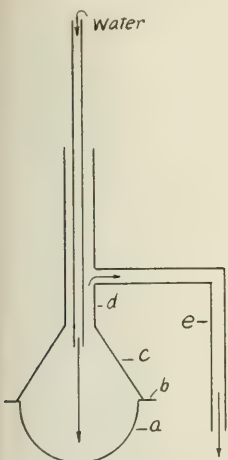


FIG. II—REFLUX CONDENSER  
FOR USE ON BEAKERS IN  
CRUDE FIBER DETER-  
MINATION  
(1/4 Size)

These condensers prevent completely loss of liquid by evaporation, and suppress, or hold sufficiently in check, frothing. But the boiling must be started gently and conducted gently; violent ebullition is not at all necessary and is to be avoided. Frothing is due to bubbles filled with steam—and doubtless to some extent with hot air; condense the steam and the bubbles or froth collapse. The upper region of the beakers is kept cool by the condensers; hence there is no need of a cold blast of air—it is the *coldness*, not the *blast*, that checks the frothing. A cold air-

blast could, however, be easily introduced through these condensers. Such a condenser is shown on a beaker in the foreground of Fig. I.

Beakers of 500 cc. capacity, 7.5 cm. inside diameter and 14 cm. high, Jena glass, are preferred; but beakers of 600 cc. capacity, 8 cm. diameter, 15.5 cm. high, can be used interchangeably with the smaller ones. The beakers can be given a rotary shaking without lifting them from the heating plate. After the boiling has been gotten under way and the beakers have been rotated a time or two, the apparatus may be left to itself.

The heating plate (wrought iron) is about 4 mm. thick and has a top surface about 9.5 cm. wide. Along its entire length is turned a flange about 2.5 cm. wide. The object of the flange is to give rigidity and prevent sagging or buckling.

LABORATORY OF THE NORTH CAROLINA  
DEPARTMENT OF AGRICULTURE, RALEIGH

#### A FURNACE FOR CRUDE FIBER INCINERATION

By J. M. PICKEL

Received May 28, 1915

If the chemist have at his disposal the requisite electric current and \$50 to \$100, he will be apt to invest in an electric furnace. If he have but a dollar or two, he can, with that capital and with materials ready to hand in the laboratory, construct a wonderfully efficient incinerating furnace. Such a furnace, occupying on the table a space 20 × 20 cm. (8 × 8 in.), is shown in Fig. I in the previous article (page 366), at the left uncovered, at the right as it appears when performing. Twelve crude fiber incinerations are made in 15 to 20 min. on, or in, this furnace

by the heat of one small Bunsen burner; and the ash is as nearly perfect as the writer and designer of the furnace has ever seen.

A piece of asbestos board 0.7 × 19 × 19 cm., in whose center is cut a circular opening 9 cm. in diameter, is laid on an ordinary laboratory tripod. On this board is set a disc of wrought iron (cast iron would probably be better) about 2.5 mm. thick and 13.5 cm. in diameter (14.5 cm. would be better since it would furnish space for several more incinerations). The disc is supported on three legs, 1 cm. long, screwed into it. On the disc are set 12 crucibles, alundum RA 98, 3.8 cm. high and 3.7 cm. in outside diameter, in which the fiber has been filtered, washed, dried and weighed. On the asbestos board is placed an asbestos cylinder 15.5 cm. in diameter and 6.5 cm. deep. The cylinder is covered with a piece of asbestos board of the same dimensions as the one previously described, but having in its center a hole only 3.5 cm. in diameter. A small Bunsen burner, whose gas tip has been widened somewhat by inserting the point of a penknife blade, furnishes the heat. The burner should be set on a block so as to bring its top close to the iron disc, thus causing the flame to spread over the under surface of the disc. In a few minutes (6 or 8) the disc and the crucibles will be brought to a bright glow.

The cylinder is easily and quickly made. Strips of suitable width (about 6.5 cm.) are cut from asbestos board of suitable thickness (about 7 mm.) and their ends beveled by shaving with a sharp knife. These strips are saturated with water, and, while wet, are wound, two or three thicknesses, around a suitable core (an empty 2-kilo ether can or a piece of sheet-iron stovepipe), bound in place by two or three bands of wire and allowed to dry out at room temperature and finally on or near a steam radiator. The core is removed and the lapped ends of the strips riveted.

LABORATORY OF THE NORTH CAROLINA  
DEPARTMENT OF AGRICULTURE, RALEIGH

#### A GAS PRESSURE REGULATOR

By J. R. POWELL

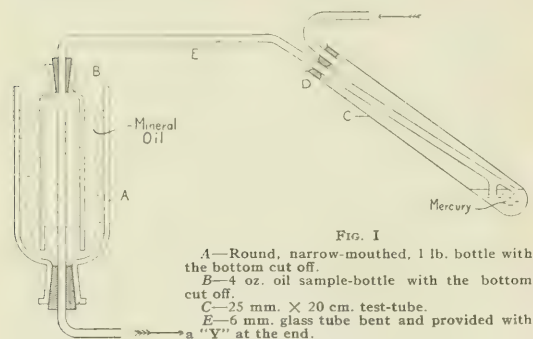
Received November 15, 1915

Occasion arose in this laboratory to make use of a gas-heated thermostat, but a great deal of inconvenience was experienced because of varying gas pressure. In casting about for some simple pressure regulator, the apparatus described below and illustrated in Fig. I was finally hit upon as a practical solution of the trouble. It will be noted that the apparatus is constructed from material readily obtainable in almost any laboratory; also that there is no great skill required for its assembly. Practically every chemist has the rudimentary knowledge of glass-blowing necessary, to make the one "Y" required.

A and C are rigidly fastened, in the position shown, to a board which acts as a mounting for the whole apparatus. B is suspended inside of A on the end of E by a rubber stopper. E is so arranged that it may



have a slight lever movement about the point where it passes through the rubber stopper *D*, as a fulcrum. The rubber stopper *D* is cut very short and, to give the tube *E* still greater freedom of movement, the hole cut for it may have the edges grooved on both sides. The "Y" on the end of *E* should be constructed with a rather small branch (about 2 mm.) as the extension of *E*, while the branch looking down should have the full opening of *E* (6 mm.). When *B* is depressed the small branch of the "Y" should be raised just above the surface of the mercury that fills the lower end of *C*, the larger branch of the "Y" remaining below the surface. When *B* rises slightly, both



openings of the "Y" will submerge in the mercury. With the assembly made as described, *A* is filled about  $\frac{2}{3}$  full of mineral oil and the apparatus is ready for use.

Gas flows into *C* through the tube connection shown, from there through *E* to *B* and out through the tube from *A*. As soon as the pressure builds up sufficiently on the delivery side the bell *B* floats up slightly, plunging the end of *E* below the mercury and shutting off the gas till consumption again slightly reduces the pressure under *B*. As the end of *E* rises from the mercury the slug of mercury that has closed the small branch of the "Y" is forced up into *E*, but is permitted to flow back through the lower branch of the "Y." The gas pressure on the delivery side can be regulated by the weight of *B* or the length of *E*. Once set up and adjusted, this simple apparatus will automatically deliver gas at a reduced but constant pressure, irrespective of variations of the initial pressure.

ARMOUR GLUE WORKS, CHICAGO

#### A NEW FORM OF ABSORPTION BOTTLE FOR USE WITH EITHER CALCIUM CHLORIDE OR SODA LIME IN THE ELEMENTAL ANALYSIS OF CARBON AND HYDROGEN IN ORGANIC SUBSTANCES<sup>1</sup>

By HARRY L. FISHER

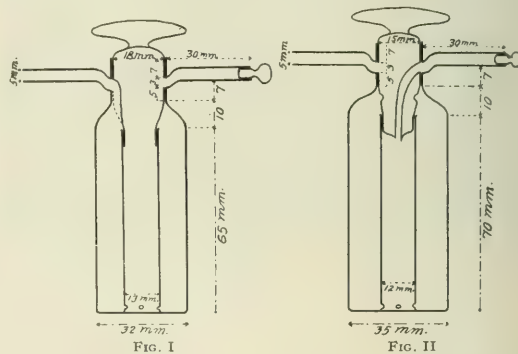
Received February 29, 1916

The U-tube as a container of calcium chloride or soda lime for the absorption of water and of carbon dioxide, respectively, has been in use for many years. In general it is efficient, but on account of its shape it has many disadvantages in that it is fragile and unwieldy, and presents difficulties of support during

the combustion and weighing and of filling and emptying which do not make it very popular, especially with students. The addition of ground-in stoppers, and of a brace and support for hanging as suggested by McIntire,<sup>1</sup> were very acceptable improvements. The tendency, however, has been to use a bottle form of apparatus because this is easier to handle in every way.

This new style of absorption bottle has an inner tube fused to the bottom of the bottle and a single, hollow, ground-in stopper which makes a gas-tight joint in the neck of the bottle and the top of the inner tube. Two kinds of stoppers have been designed as shown in the accompanying diagrams.

In Fig. I, opposite the hole in the hollow stopper there is a narrow longitudinal depression about 2 mm. deep and 3 mm. wide. This is to allow communication with the outer chamber and the side tube at the same time that the inner chamber is in communication with the other side tube by means of the hole in the stopper. When the stopper is turned, communication is then entirely shut off from both tubes at the same time. Around the bottom of the inner tube there are four small holes. The two arms or side tubes are bent upwards slightly where joined to the



neck in order that in the collection of moisture any droplets that may remain in the arm will not easily run out when the apparatus is being disconnected. One arm is provided with a small ground-in stopper to prevent loss of moisture when the bottle is not connected in the absorption train. Only a minimum amount of grease should be used on this stopper so as not to introduce any chance of loss with consequent error in weighing. The upper edge of the neck is beveled and smooth to allow thorough cleaning. The bottle has a total available capacity of 30 cc., 6 cc. for the inner chamber and 24 cc. for the outer chamber. By way of comparison an ordinary 11 cm. U-tube has an available capacity of 22 cc. A larger stopper cannot advantageously be made because of the difficulty of drawing it out and lining it up for the grinding.

The bottle represented in Fig. II has a small curved tube in the stopper which connects the opening in one arm with the large inner tube of the bottle. The gas passes through the inner tube as in the other bottle

<sup>1</sup> Presented at the Seattle Meeting of the American Chemical Society, September, 1915.

<sup>1</sup> J. Amer. Chem. Soc., 33 (1911), 450-1.

and into the outer chamber through the small holes at the bottom and then into the inside of the stopper through the two holes and on into the opposite arm.

#### NOTES

**FOR WATER**—Calcium chloride is used and the gas passed through the inner tube first. The small amount of calcium chloride in the inner tube becomes exhausted first and can be replaced at any time, whereas the larger amount in the outer chamber will last for many combustions. By greasing the inside of the inner tube, the caked calcium chloride will not stick to the walls, and can easily be removed. When filled, the bottle weighs approximately 55 g.

**FOR CARBON DIOXIDE**—The inner tube is filled with calcium chloride or small pieces of solid potassium hydroxide, and the outer chamber with moist soda lime. The gas is passed through the *outer* chamber first. When the bottle is filled in this manner an extra weighed guard bottle containing soda lime and calcium chloride is not necessary although it is recommended for careful work since it gives an indication of the efficiency of the absorption. When filled, the bottle weighs about 65 g.

**FILLING**—The inner tube is filled first, a plug of cotton or glass wool being put at the bottom to protect the holes, and the absorbing reagent covered with another plug of cotton or glass wool. A loose plug of cotton is then put on top to act as a cap while the outer chamber is being filled and then removed, leaving the ground surface clean and ready for greasing. The ground joint in the inner tube should be well greased, because if this joint becomes "frozen," there is no opportunity of getting at it by the usual methods. A piece of copper wire and a pair of narrow forceps are a great help in filling and emptying the bottle.

In order to prove that the ground joints of the apparatus are gas-tight, before using, add some water,

and while passing air through the inner tube, close the stopper. The liquid should remain at its high level.

When inserting the stopper, it is well to see that the holes are coincident in order to avoid any excess of pressure in the bottle.

#### ADVANTAGES

1—The apparatus can be easily and thoroughly cleaned.

2—It has only one hollow stopper and one turn of this shuts off both openings.

3—It will stand upon the balance pan and needs no hangers when joined in the absorption train.

4—It makes no difference which way the bottle is connected up, since the course of the gas is controlled by the single stopper. In the determination of moisture, it is of course advisable to pass the gas through the arm fitted with the small ground-in stopper.

5—It is provided with a small stopper as recommended by Dennstedt to prevent loss of any moisture remaining in the arm.

6—The arms are bent upward at the neck in order to prevent in a measure any droplets of water which may remain from being lost when the bottle is being disconnected.

7—The upper edge of the neck is beveled and smooth so that the excess of grease can be easily removed.

The bottle shown in Fig. I is of more general use because it has a wide stopper which is open and can be easily cleaned. The stopper of the bottle represented by Fig. II is more difficult to clean but was designed with the idea of catching the condensation liquid in a drip cup. Both forms of absorption bottles have been in use for almost a year. They were made by Emil Greiner and Co., New York.

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## ADDRESSES

### THE SEATTLE WATER SUPPLY<sup>1</sup>

By JOHN WEINZIRL

Like the water supply of any large city, the Seattle supply has had an interesting evolutionary history; much of this history is not essentially different from that of other supplies, but parts of it are quite unique if the writer is correctly informed. This paper will sketch the history in outline only, give the present status of the supply, dwell upon the unique features, and draw one or two conclusions.

In the early days when Seattle occupied one or two streets along the water front, the numerous springs from the hills furnished the water supply. As these sources became dangerous or inadequate, pumping from Lake Washington was begun; this supply served for 20 years, or until 1900. The pumping was regarded as expensive and the plant installed was not adequate for fire protection, as the great fire of 1887 demonstrated. It was apparent, too, that the Lake would be polluted in time, and that either the supply would have to be purified or a new one found. In 1890 the latter plan was adopted,

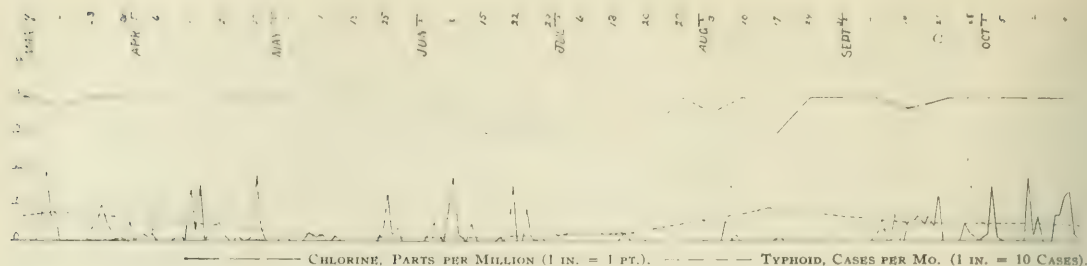
and 10 years were spent in putting the present Cedar River supply in operation. In making the change from the lake supply to the mountain supply, private ownership gave way to public ownership, and with it prices have fallen to approximately one-third the former cost. At the present time \$0.50 per month is the minimum rate for homes with meters, and the cost exceeds this rate only when irrigation or some other cause increases the consumption. With respect to this phase, and all the engineering and economic problems involved, the city has published a most valuable and interesting book entitled "The Seattle Municipal Water Plant;" it furnishes a wealth of detail to those interested in this aspect of the water problem.

#### CEDAR RIVER SUPPLY

Cedar River drains an area of approximately 150 sq. mi. in the Cascade Mountains. Most of the area is covered with primeval forest, and the soil is largely glacial drift. The intake of the gravity system is at Landsburg, 28.57 mi. from Seattle, and two pipe lines carry the supply. From Landsburg to Cedar Falls where the municipal power plant is located, the Milwaukee Railroad follows the river in close proximity for 12 mi. Midway at Barnston, on the left bank of the river is a logging camp

<sup>1</sup> Address before the Water, Sewage and Sanitation Section at the 51st Meeting of the American Chemical Society, Seattle, August 31 to September 3, 1915.





occupied by perhaps 350 persons. Taylor's logging camp is a small outfit with perhaps 200. There is also some logging being done about Cedar Lake. The construction of the Railroad in 1907-8 and the building of the large dam for power purposes in 1913-14 introduced special difficulties in keeping the supply pure. In general 1000 to 1500 people occupy the watershed at all times.

With respect to the water supply specifically, this is at its source practically snow or rain water, and consequently is very soft and pure. The following analysis by Mr. A. Jacobson, city chemist, is taken from the book previously referred to:

	Parts per million
Color.....	None
Turbidity.....	None
Odor.....	None
Total solids.....	60.00
Volatile solids.....	14.84
Nitrogen as free ammonia.....	0.015
Nitrogen as albuminoid ammonia.....	0.030
Nitrogen as nitrates.....	None
Oxygen consumption.....	0.160
Chlorine.....	4.00
Total hardness in degrees.....	13.84

The bacterial content is not quite so satisfactory, but it is still good when compared with most natural waters. The bacteriological analyses are made essentially according to the standard methods of the A. P. H. A. and cover a period of half a dozen years or more. The data do not vary greatly and it has not seemed worth while to include tables covering the same; in lieu of such tables the accompanying graph presents a set of curves covering: (a) rainfall in tenths of inches; (b) chlorine as parts per million; (c) bacterial count per cc. using agar at 37° for 48 hours; and (d) typhoid cases per month. This graph covers a period of 15 months beginning with March, 1914, and is fairly representative of the whole time. The total count averages about 50 per cc. and has gone above 100 only 4 times in the period; the highest count reached was 950 in September. *B. coli* was present in 1 cc. sample three times, but more recently it has been found quite frequently. Dr. Simpson, the city bacteriologist, informs me that he is not certain of the organism being true *B. coli*; he describes it as of the "coli type." This organism has been found on the weeds growing about Cedar Lake and its significance has not been fully determined.

Comparing the typhoid and bacterial curves, there is no obvious relation between the two. The highest typhoid rate was 9 during August of last year; this is not high for a city of 300,000 and can readily be explained in other ways. It must be noted, however, that this highest typhoid rate did occur during the period when the bacterial curve was abnormally high and when *B. coli* was present three times in two months. The Health Department maintains that there is no relation.

One other comparison seems desirable, and that is between the rainfall and bacterial count. July and August comprise the dry season when little or no rain falls; the remainder of the year is almost a continuous rainy season. During the dry season such excretions as may be deposited on the surface of the ground

accumulate and the fall rains wash them into the water course. In the graph the highest count occurred immediately following a heavy rain of 1.2 in. during September. After the surface has been thoroughly washed, the bacterial count settles down to a nearly constant figure. This fact that the beginning of the rainy season is a danger point for the water supply in all regions having a dry season should be thoroughly appreciated by all who have charge of water supplies located in them.

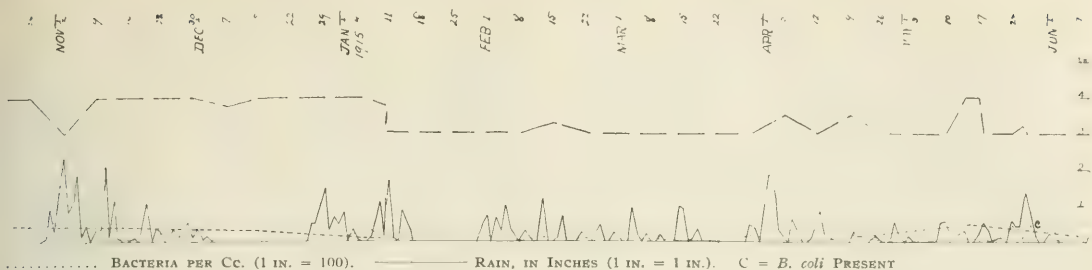
A chemical engineering problem of quite a serious character involves the lasting property of the conducting pipes. The first pipe line installed was of wood with a 15-year lasting period. For the second line cast iron was chosen because it was expected to have a 45-year service period. The electric transmission lines cause the iron to be heavily charged and electrolysis has caused serious trouble. It appears that wooden pipes will prove much cheaper and give more satisfaction after all.

#### SPECIAL SANITARY MEASURES EMPLOYED

The construction of the Milwaukee Railroad, which parallels the Cedar River for 12 mi. above the intake, presented a critical time for the water supply. During this period construction camps with upward of 200 men were located practically on the banks of the stream. The railroad authorities were compelled to keep these camps sanitary, and the State Board of Health took charge of enforcing the regulations. Under the agreement, the members of the construction crews were compelled to deposit all excreta in the privies provided for them. The excreta were received into iron vessels which were emptied daily into an incinerator constructed for that purpose. The privies were fly-proof, as were also the mess rooms where the meals were served. All kitchen and stable refuse was incinerated in order to discourage flies from breeding. As a result of this régime, only two cases of typhoid occurred during the entire construction period; these were imported, and detected within a short time when they were immediately sent to the hospital. During the entire construction period the city typhoid rate remained normal.

The railroad company was also compelled to take certain measures to guard the water supply subsequent to construction. It is obvious that cases of typhoid or other intestinal diseases transported on the trains would endanger the water supply. To guard against this emergency, the company constructed a dike along the road bed between it and the river, and at suitable places this dike enclosed natural filter beds of sufficient area to take care of surface drainage. The bridges across the river were made water-proof and their drainage led into similar filter beds. In this way it was hoped to prevent any unfiltered drainage from reaching and polluting the river. As an additional precaution, the company is compelled to lock all of its toilets while running through the watershed, and no stations are permitted within this area.

So far as the writer is aware these sanitary measures are unique in that they were employed here for the first time. That they have been effective, is indicated by the favorable typhoid



curve. It is perhaps unnecessary to state that similar measures are enforced in subsequent construction camps, such as that which built the \$1,700,000 power dam when several hundred men were employed for a couple of years.

The city also polices the water shed and hunting, fishing and parties are not permitted on the grounds. The camp crews are examined for typhoid carriers, and as far as possible all persons employed in them are immunized against typhoid.

Seattle prides itself in its water supply and has attempted to provide a "certified" water, to borrow a phrase from milk lore. But certified water like certified milk is subject to accidents. We can never be quite certain that a tramp infected with typhoid is not infecting the water supply while passing through the shed or stopping for a time in one of the camps. The seepage from the reservoir has also introduced an uncertain factor. To guard against these uncertainties the city maintains an emergency hypochlorite plant, but it is a question whether more elaborate protective measures should not be taken. A certain amount of protection is afforded by the reservoirs, but these are not constructed with a view to holding all the water for a definite time. Three other protective measures suggest themselves:

(1) The pipe lines might be extended to a point above the railroad; this would mean twelve miles farther up the river; from that point the city already has two lines up to the power dam. Doubtless the expense would be heavy and the line would be difficult to maintain, but perhaps additional power might be generated to offset the expense; at any rate nearly all of the present danger would be eliminated.

(2) Another possibility would be the construction of filter beds. This, too, would be expensive, and it is doubtful whether the citizens would vote the funds necessary without first passing through a severe typhoid epidemic.

(3) The simplest, cheapest and, indeed, the safest method would be to install a chlorination plant. This might take the form of an emergency plant to be used only when the water showed danger signs.

UNIVERSITY OF WASHINGTON  
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## HIGH-TEMPERATURE INSULATION<sup>1</sup>

By P. A. BOECK

Received February 4, 1916

The problems of conservation of heat and prevention of thermal losses have been the subject of considerable investigation and research in certain industries, more especially in the application of cold storage installations for low temperatures, and of steam lines and electric furnaces in high temperature work. It has not been until recently, however, that this subject, as applied to general industrial purposes, has received the attention of designers and engineers that its importance deserves.

Heat flow is a rather difficult factor to measure under the working conditions of an industrial furnace. It was not until the

comparatively recent introduction into certain operations of the heat balance sheet, with a systematic attempt to account for the discrepancies in the totals, that the various causes of heat losses and the reasons for their existence were brought to light. Moreover, such rapid advancement and radical changes in the design of equipment, especially in metallurgical lines, have occurred, that practice has apparently outdistanced the theory of design. In the modern tendency toward greatly increased size of units, effort has seemingly been made to utilize the heat of fuel gases without proper attention having been paid to conserving heat energy and confining it strictly to the points of maximum activity.

The work of several of the Government Bureaus, notably that of the Bureau of Mines and the Bureau of Standards, and the systematic investigation of the thermal properties of structural materials by a number of the technical societies are forming the basis for more intelligent and consistent work in the economically important subject of the prevention of fuel waste. We would refer to the recent excellent paper of L. B. McMillan<sup>1</sup> before this society. Here the point is made that it is not alone the efficiency of the insulator nor its initial cost, but a factor consisting of both of these items, together with the factors of durability or permanence, which form the ultimate criteria of the most effective insulator for any specific purpose.

It should be unnecessary in this practical and utilitarian age to call attention to the need of preventing heat losses, but the consistent and intelligent application of insulation to high temperatures has brought out other advantages in addition to the saving in fuel. The most important of these advantages, from an industrial point of view, is that of increasing the furnace capacity, it not being uncommon to add as much as 10 to 15 per cent to the furnace capacity without increasing size of the equipment, fuel consumption or overhead expense. This is more evident when dealing with higher temperatures, considering that no matter how much fuel is consumed to produce a given product, the results are not obtained until the temperature attained is high enough to bring about the reaction. Any increase in the temperature and heat capacity of the equipment above that necessary to get results, produces an increase in output equivalent to many times the actual temperature difference. The insulation of hot blast stoves, for instance, is being advocated for the heat saved. This is a large and important factor which has been frequently brought out but it is of minor importance when compared with the advantages of increased tonnage produced. Therefore, when reference is made in this discussion to heat-saving and increased capacity, we have in mind the effect of adding increased energy at the point of maximum effectiveness without additional fuel.

### ADVANTAGES OF INSULATION

In any high-temperature apparatus, if the heat can be prevented from being dissipated from the outside of the furnace,

<sup>1</sup> Presented before the Chicago Section of the American Society of Mechanical Engineers, January 14, 1916.

<sup>1</sup> L. B. McMillan, "The Heat Insulating Properties of Commercial Steam Pipe Coverings," *Trans. Am. Soc. Mech. Eng.*, 1915.



the temperature of the furnace is made more uniform and the zone of the reaction, and consequently the capacity, are manifestly increased without additional fuel consumption. Furthermore, overheating at the source of heat in the effort to bring as much of the furnace as is possible into the zone of reaction, is materially reduced by preventing the loss through the furnace walls. This has the ultimate effect of lowering the temperature at the source of heat, greatly increasing the life of the refractories and the capacity of the furnace. It is evident, also, that in furnaces which are surrounded by metal casings, deterioration and damage caused by overheating may be many times as great as the cost of installing the proper insulation. The advantages gained by the protection of workmen from unhealthy and unsanitary conditions, incident to their laboring under overheated conditions, are also apparent. In general, then, the question of insulation does not concern itself so much with the saving in fuel, which, of course, is an important item, as with the general effect produced by confining the heat generated to points of maximum effectiveness. The higher the cost of fuel, the more necessary it is to look closely to the preventable losses to gain an economically operated furnace.

#### HEAT FLOW

Without going into a detailed consideration of the laws governing the nature and quantity of heat flow, which are familiar

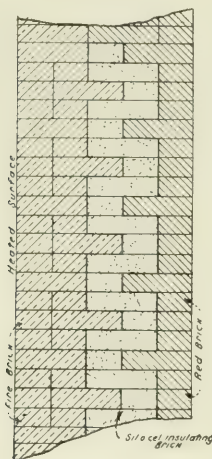


FIG. I—TYPICAL WALL CONSTRUCTION, SHOWING INSULATING BRICK LAID IN WALL

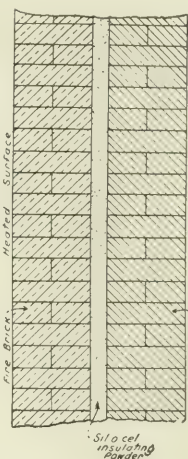
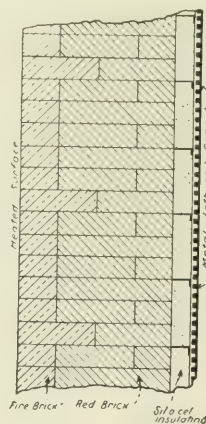
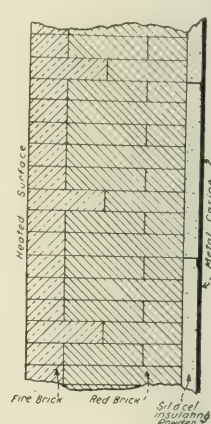


FIG. II—TYPICAL WALL CONSTRUCTION, SHOWING POWDER IN HOLLOW WALL



FIGS. III AND IV—TYPICAL WALL CONSTRUCTION, SHOWING INSULATING POWDER SUPPORTED BY METAL LATH, CEMENT FINISH, AND POWDER SUPPORTED BY METAL CASING



available in other forms. That portion, however, which is transferred to the walls of the furnace setting by any of the three methods mentioned, is conducted through the setting and lost by radiation or convection from the outer surface of the setting if means are not provided to prevent. It is the heat lost in this manner and methods for its prevention that will be especially considered in this discussion.

The selection of a boiler setting to illustrate the various methods for heat propagation was taken as that most familiar to general practice, but the selection is, unfortunately for the illustration, one in which the heat losses through the settings are comparatively low.

#### RATE OF HEAT FLOW

The rate of transfer of heat under various conditions, by both conduction and radiation, shows the relative importance of these

<sup>1</sup> Henry Kreisinger and Walter T. Ray, "The Transmission of Heat into Steam Boilers," U. S. Bureau of Mines, *Bull.* 18 (1912).

to you, it would be well to review briefly the mechanics applying to this in a general way. Heat was formerly believed to be caused by an indestructible material fluid called "caloric." It is now known to be not a substance but the energy of molecular motion, consisting, in the case of a gas, of nearly uniform rectilinear motions with sudden changes of direction and velocity when the molecules come near enough to one another; in the case of a liquid, of irregular wanderings of its molecules; and in the case of a solid, of orbital or oscillatory motions.

Inasmuch as the amount of heat conducted by a body is one of the principal sources of loss in high-temperature equipment which we have under consideration, it will be of interest to inquire into this in order that we may control the flow of heat by this method as far as possible. Since heat is a form of energy consisting of molecular vibration of a periodic character, and subject to the general laws of wave motion, it can be reflected, refracted and dispersed by creating the proper conditions. In other words, by the proper mechanical manipulation we can

two methods in influencing heat losses.<sup>1</sup> The amount of heat conducted through a unit area from one part of the body to another is proportional to the difference in temperature of the two parts, directly proportional to the thermal conductivity of the body through which the heat passes and inversely proportional to the distance between the two parts of the body. In other words, the conduction of heat through a solid body from one place to another is a direct function of the conductivity of the body and the difference in temperature of the two planes, and an indirect function of their distance apart.<sup>2</sup> This is identical with Ohm's law for transfer of electrical energy.

**RADIATION**—The heat transferred from one body to another by radiation is proportional to the difference of the fourth powers of the absolute temperatures of the two bodies. While this is strictly true, only of the ideal "Black bodies," the variation is so small that for all practical purposes this relation holds good in ordinary procedure.<sup>3</sup>

#### HOLLOW WALL CONSTRUCTION

This relation indicates why a hollow wall space is an effective insulator in low-temperature work, such as refrigeration, etc.,

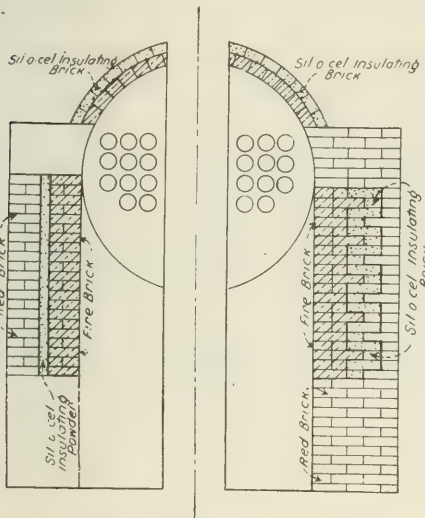


FIG. V—SIL-O-CEL INSULATING POWDER IN HOLLOW WALL CONSTRUCTION APPLIED TO BOILER SETTING

FIG. VI—SIL-O-CEL INSULATING BRICK APPLIED TO BOILER SETTING

whereas, in high-temperature operations, the loss of heat by radiation through a hollow wall space is so great that its insulating effect is less than if this wall space were filled with material of rather high thermal conductivity. This has been brought out by Ray and Kreisinger who demonstrate that the hollow wall space type of wall construction is much less effective as a means for preventing the loss of heat than a solid wall of any ordinary construction material of equal thickness. This is especially true if the air space in the hollow wall is near the furnace side and becomes highly heated. This is entirely contradictory to the general belief that, since air is a poor conductor of heat, air spaces built into the walls of a furnace will greatly reduce heat loss by radiation. While the heat does travel very slowly through the air by conduction, it leaps over the air space readily by radiation, because the quantity of heat which passes

<sup>1</sup> Irving Langmuir, "Convection and Radiation of Heat," *Trans. m. Electrochem. Soc.*, **23** (1913), 299.

<sup>2</sup> Walter T. Ray and Henry Kreisinger, "The Flow of Heat through Furnace Walls," U. S. Bureau of Mines, *Bull.* **8** (1912).

<sup>3</sup> Harold P. Gurney, "Heat Radiation," *This Journal*, **3** (1911), 807.

across the hollow space is a function of the fourth power of the absolute temperatures of the surfaces enclosing it, so that the loss is thus enormously increased by rise in temperature.

#### FURNACE WALLS

In general, in high-temperature furnace construction, there are two separate and distinct factors which must be considered to produce an effective wall: (1) to provide a material having the ability to resist the action of high temperatures, sufficient mechanical strength, and, possibly, the property of resisting corrosive slags, gases, etc., without spalling or being eroded; (2) to prevent the excessive loss of heat due to conduction from the interior of the furnace to the outside where it is lost. Only rarely is a good refractory material an insulator; usually it is necessary to augment or back up the refractory with some material having a much lower heat-conducting capacity.

#### REQUIREMENTS OF INSULATORS

The requirements of the insulating backing for the more refractory lining are rather severe. An ideal material would have the following properties: it should have an extremely high insulating value, and be sufficiently refractory so that no fusing or excessive shrinkage would take place in that portion which is in direct contact with the highly heated refractory

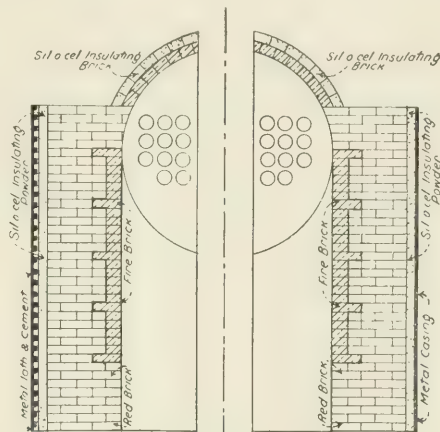


FIG. VII—SIL-O-CEL INSULATING POWDER AND METAL LATH CONSTRUCTION APPLIED TO BOILER SETTING

FIG. VIII—SIL-O-CEL INSULATING POWDER AND METAL CASING APPLIED TO BOILER SETTING

wall. It should not be decomposed or be changed greatly in volume at the temperature, and it should, furthermore, be of light weight, unaffected by moisture, of convenient form, readily applied by unskilled labor, and low in cost. It should be of such composition as not to react upon or attack either the refractory material or the metal shell of the container, even in the presence of moisture; *i. e.*, it should contain no free acid radicals, and should not be broken or caused to settle by vibration or heat. It should not have high expansion and it should be sufficiently elastic to take up strains between the lining and the shell produced by temperature changes. While this is a rather formidable array of requirements, there are products upon the market which fulfill practically all of them. Such materials as are being commonly applied to steam-temperature insulation, of which magnesia and asbestos are best known, are, of course, eliminated from consideration in the great majority of cases mentioned here on account of decomposition, shrinkage and settling. The lack of more extended practice in high-temperature insulation must be attributed to the fact that



effective high temperature nonconductors have not been generally available.

#### AMOUNT OF INSULATION

When the kind of refractory material that is best suited to the surface has been determined, the next most important item is the thickness of the walls and the nature of the insulating material most suitable, and it is necessary to determine the degree of insulation which will produce the most effective results.

In attempting to obtain perfect insulation, it is entirely possible to overinsulate, causing a serious damage to the refractories in the high-temperature zones of the furnace. To maintain the inner walls, it may be necessary to permit a considerable flow of heat through the wall, with a corresponding decrease in the temperature of the refractories at the heated point, in order to prevent their destruction. It would be manifestly impracticable to insulate the roof of an electric steel furnace or open-hearth furnace, for instance, with a heavy layer of insulating material, because the cost of the refractory lining which

In an electric-furnace practice, where extremely high temperatures are encountered and where effective insulation is necessary, because of the relatively high cost of current, the question of insulation, or rather overinsulation, has been given more attention than in other lines. F. T. Snyder<sup>1</sup> has presented a detailed study of the nature and amount of insulation which is permissible under various conditions and presents many valuable data which might with advantage be applied to other industries.

#### DESCRIPTION OF CELITE

The requirements of an ideal insulator have been outlined, and in order to show the various methods of application which have been worked out, it will be well to select the insulator which apparently most nearly meets the requirements and use this as an example of methods of construction. In the applications shown, attempt was made to cover as wide a field of use as possible, to show the scope of possible applications.

The mineral known as celite, on account of its extremely cellular nature, is of a highly siliceous composition and of very light weight; it occurs on the Pacific Coast<sup>2</sup> in an exceptionally pure state. It is composed of numerous hollow cells, and weighs in its natural rock form, air-dried, from 25 to 30 lbs. per cu. ft. When this material is ground properly, it weighs but 8

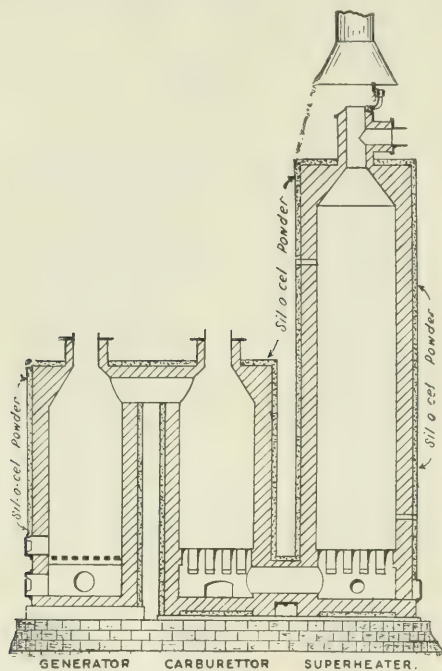


FIG. IX—GAS-GENERATOR SET INSULATED

would be destroyed would be considerably greater than the cost of the heat which would otherwise be lost.<sup>1</sup> However the issue in some instances may be met by other practical methods such as increasing the working capacity of the unit in order to make use of the additional heat available, rather than to let this valuable heat at the critical point escape to save the refractory lining. In calcining celite, the product which we will consider further this evening, the temperatures are controlled entirely by the working load imposed on them without allowing the oil burners to ever fall below their lightest working capacity and highest heat. To produce celite calcined to 2500° F., an average kiln has a daily capacity of about 20 tons. When celite is wanted which has been calcined at 2000° F., the kiln is pushed to approximately 30-tons capacity and for a product treated to even less heat, the capacity is increased to as much as 40 tons, the heat utilized being the same in all cases.

<sup>1</sup> D. A. Lyon, B. M. Keeney and R. F. Cullen, "The Electric Furnace in Metallurgical Work," U. S. Bureau of Mines, *Bull.* 77 (1914).

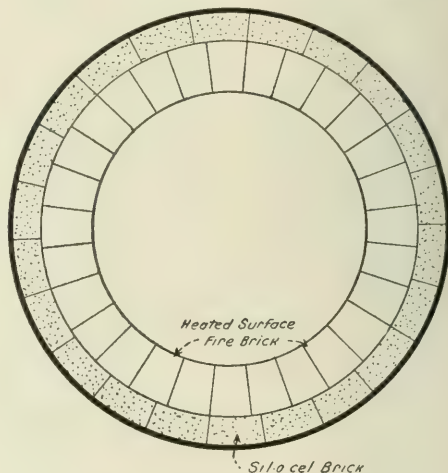


FIG. X—HIGH-TEMPERATURE FLUE INSULATION

lbs. to the cubic foot, and has a thermal insulating power about 9 to 12 times the insulating power of ordinary fire brick. In other words, a 1 in. layer of this material is the equivalent in insulating value of from 9 to 12 in. of fire brick. Being almost pure silica, its melting point is high, 2930° F. (1610° C.) as reported by the Bureau of Standards, and it can be subjected to high temperatures without fear of alteration. It has been found advisable, however, not to use celite as a refractory at extremely high temperatures without some direct protection which is readily accomplished by using it as a backing material for more refractory and highly conducting bodies. Owing to its remarkable nonconducting properties, the accumulation of heat on its face is so great, due to the fact that the surface is not cooled by conduction, that a "flash" of flame or gases might easily exceed the melting point of silica and cause failure. If it is protected, however, only modified and uniform temperatures are encountered, and these are maintained without damage.

<sup>1</sup> F. T. Snyder, "The Flow of Heat through Furnace Walls," *Trans. Am. Electrochem. Soc.*, 18 (1910), 235.

<sup>2</sup> Deposits worked by the Kieselguhr Company of America, New York, Chicago, San Francisco and Los Angeles.

It is possible further to prepare bricks and blocks of various sizes and shapes by sawing the natural material by means of gang saws. Standard 9 in. straight Sil-O-Cel brick made from natural celite weigh from  $1\frac{1}{2}$  to 2 lbs. each and are equivalent in insulating value to many times their thickness of ordinary fire brick. In crushing strength these brick withstand over 100 lbs. per sq. in., and are sufficiently strong to stand transportation and handling.

The high insulating value of Sil-O-Cel bricks can be shown by applying the heat of a blast lamp or torch upon their surface for hours, the unheated surface remaining cool enough to allow handling with ease. Powdered Sil-O-Cel can be tested in the same way by packing it into a shallow paper box of convenient size.

The cost of these insulating bricks is but little more than that of fire brick and that of the powder about one-third as much, so that the first cost of insulation is comparatively low. In fact, instances are on record where the entire cost of insulation has been saved in fuel in the first few months of operation, saving the gain in equipment efficiency and increased output capacity as a clear profit.

#### TYPICAL WALL INSULATION

Because of the variation in form in which Sil-O-Cel products are supplied—that of brick, blocks of various shapes, in powdered

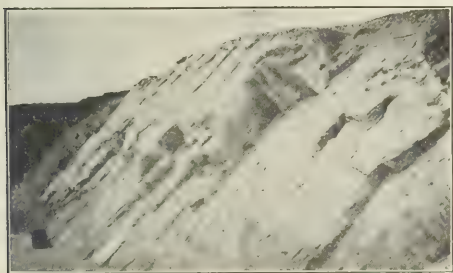


FIG. XI—A LEDGE OF CELITE

Celite, from which Sil-O-Cel is produced, is found in giant ledges in California. These ledges have been protected from foreign substances and present walls of absolutely pure material.

form and as a plastic cement—this material is adaptable to most any form of thermal insulation, as will be shown in the following typical examples.

In general, there are four forms of construction for high-temperature insulation which can be adapted to almost any character of equipment.

Fig. V indicates the usual method of using Sil-O-Cel brick overlaid between a course of fire brick and red brick for the prevention of heat leakage through walls. This form of construction is largely used in boiler settings, bakers' ovens, reverberatory furnace walls and roofs, etc., and is generally applicable where strong, solid nonconducting wall is desired.

Fig. VI indicates one of the methods of construction of an insulating wall in which an otherwise hollow space is filled with insulating powder. From 2 to 4 in. are usually sufficient. The powder is packed slightly to a density of approximately 12 lbs. per cu. ft. at which point it attains its maximum insulating value and is not subjected to settling or contraction, due to either vibration or heat. Where this form of construction has been in severe service in high-temperature furnaces for a period of years no contraction or settling has taken place.

Figs. VII and VIII indicate the methods of insulating brick walls which are already in place. This form of insulation can be ap-

plied to old construction as well as new. In this method, expanded metal lath is erected on an angle iron at the required distance from the outer wall and coated on the outside with one or more coats of Portland cement plaster, to which a small amount of Sil-O-Cel powder (approximately 20 per cent by volume) has been added to give greater plasticity and ease of working and to increase the heat-resisting properties of the cement. Sil-O-Cel powder is packed to a density of 12 to 15 lbs. per cu. ft. between the brick wall and the expanded metal lath. This form of construction is relatively inexpensive and permits as much insulation as is required and furthermore, gives an absolutely permanent surface of excellent appearance, which can be applied to almost any character of equipment.

#### INSULATION OF HOT-BLAST STOVES

Hot-blast stoves and mains serving a blast furnace give an interesting application of high-temperature insulation, a number of these having been insulated in the Pittsburgh and Cleveland districts with excellent results. The detailed figures relating to the increased capacity and the thermal data are being compiled and will form the subject of another paper. At the present time, complete figures are not available. Both insulating brick and powder have been used for this purpose with apparent equal beneficial effect.

The advantages derived from the effective insulation of stoves and high-temperature flues have been pointed out by Maccoun,<sup>1</sup> Johnson,<sup>2</sup> Mathesius,<sup>3</sup> Wysoz,<sup>4</sup> and others, it being estimated

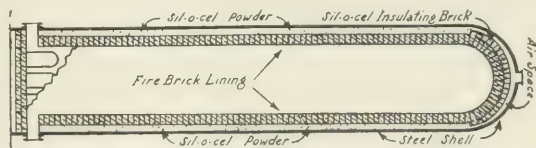


FIG. XII—HOT-BLAST STOVE INSULATED WITH SIL-O-CEL POWDER AND BRICK

that preventable heat losses from surface radiation varies from 8 to as much as 20 per cent.

Hot-blast stoves provide an excellent example of the requirements of an insulation for high-temperature work, not so much because of the high temperature to which they are subjected, but more especially because of the size, expansion and contraction of lining and shell, settling, shrinkage, elasticity and corrosion of the insulator and protection to the shell itself, the constant change in temperature and other factors.

In a 20 × 100 ft. stove, for instance, the column of brick in the lining may expand through heat as much as 6 or 8 in. in height from cold to maximum heat. Therefore, the insulator may be considered at all times as being subjected to a certain amount of stress and friction requiring an elastic medium which will take up these continued strains without that injury or danger of being crushed, such as would be the result in case of granular slag in constant settling, the accumulation of fine material causing occasional bulging of the shell at the base of the stove on account of its inelastic nature. Two principal requirements of the insulator are, then, elasticity with still sufficient strength to give the proper support to the brickwork and shell, and secondly, the proper amount of cohesion or high internal coefficient of friction and light weight to overcome any tendency toward settling under the movement or vibration of the stove.

KESSELGUHR COMPANY OF AMERICA  
11 BROADWAY, NEW YORK CITY

<sup>1</sup> "Blast Furnace Advancement," *Trans. Am. Iron and Steel Inst.* (1915) *Iron Age*, 96.

<sup>2</sup> *Am. Inst. of Min. Eng.*, Bull. 99, March (1915)

<sup>3</sup> "Measurement of the Temperature Drop in Blast Furnace Hot-Blast Mains," *Trans. Am. Inst. Min. Eng.*, 1916.



## CURRENT INDUSTRIAL NEWS

### A NEW SOURCE OF ANTIMONY

The high price of antimony in 1915, says the *Mining Journal*, led to the mining of over 800 tons of stibnite ores in Alaska. The greatest part of this, 700 tons in all, was produced in the Fairbanks district, the remainder coming from Seward Peninsula. An exact valuation of the stibnite ore from Alaska is difficult to be arrived at, but from facts to hand it would appear that the producer received from \$1.25 to \$1.75 per unit of stibnite. It may be reasonably estimated that the Alaska shipments sold for \$86 per ton in San Francisco, which would give a total value of about \$70,000 for the shipments made in 1915. Four antimony properties were operated in the Fairbanks district during 1915—the Scrafford in the Treasure Creek basin, the stibnite in the Eva Creek basin, the Gilmer in the Vault Creek basin and the Chatham Creek mine. All the operations were on a small scale. The mining consisted chiefly in making open cuts and digging out the ore which occurs in shoots, kidneys and irregular masses along zones of fissuring. Most of the ore was broken and hand-sorted and none carrying less than 50 per cent antimony was shipped. The antimony content probably averaged something like 58 per cent. Considerable prospecting was also carried out in a number of other stibnite lodes in the Fairbanks district. The ore was hauled to the railway by wagons and then sent by rail to Fairbanks and over the all-water route to San Francisco. The transportation companies offered a low freight rate to encourage the new industry. Developments were continued in the Sliscovitch mine. The ore from this property carries some gold and the mine has been worked for gold. In 1915, however, the energies of the operators were directed towards getting out the stibnite ore. The total ore shipped from Nome is reported to be 132 tons and there is reason to believe that a considerably greater quantity was mined. Stibnite is not an uncommon mineral in Alaska. The recent demand for antimony has led to the prospecting of a number of stibnite deposits within the territory. Such work is reported in the Kantishna district, in Prince William Sound and in Kenai Peninsula.—McMILLAN.

### MINING IN PORTUGAL

The south of Portugal, says the *Mining World*, is rich in minerals, particularly copper and iron. Official statistics omit all mention of marble, slate and other stone quarried in the country. The principal antimony mines are in Gondomar within the Porto district; the ore likewise occurs in the Braganza district. The four chief mines which produced coal are in the districts of Coimbra, Aveiro and Oporto.

A deposit of copper-bearing pyrites is found at San Domingos in southern Portugal and there are, besides, important mines producing cuprous iron pyrites at Aljustrel and Sierra de Caveira and in Grandola, in Beja and Lisbon districts. Auriferous quartz exists in the district of Porto and alluvial gold has been found in the districts of Lisbon, Santarem and Castello Branco. Gold is at present worked in a mine near Oporto and also in a mine in the Lisbon district.

Deposits of iron ore of a rich variety are found, the producing mines being in the districts of Beja, Evora and Aveiro. Portugal possesses many beautiful varieties of white statuary marble. The annual value of salt exported from Lisbon is about \$20,000. There are slate quarries at Valongo which produce large slabs for billiard tables, tanks and cisterns. Uranium ore is worked in the districts of Guarda and Castello Branco. Tin ore and wolfram occur in Vianna do Castello, Braga, Braganza, Guarda, Vizeu, Villa Real and Castello Branco districts. The supply of tin is derived chiefly from one

mine, the ore yielding 60 per cent of metal. Alluvial tin is also worked to some extent. Many wolfram mines are in operation, Portugal being one of the most important producers of wolfram in Europe.—M.

### BRITISH PROJECTILE FACTORIES

The January number of *Engineering* gives a description of one of the new British projectile factories. The article is illustrated by several good photographs showing some of the shops. The nine bays of the factory cover about 196,600 sq. ft. and are arranged so as to reduce to the minimum the distance which the shell has to travel in the process of manufacture. From the entry of the rough bar to the finished shell ready to be put into the breach of the gun, the distance is only 40 yards. There are nearly one hundred operations in making a shell and many of these take but little time, hence it is important that the time spent in moving the shell from one operator to another should be as short as possible. Small shells are machined in the factory by female workers and there are 1800 women in this department. The girls are able to work the machines in three days and are efficient in seven days; the highest efficiency can be attained after two months' experience. One skilled worker suffices for setting the machines for twelve female operators. The accuracy demanded is 0.004 in. and it speaks well for female labor that the rejected shells do not amount to more than one per cent.—M.

### AUTOMOBILE CYLINDER COOLING

In a paper on the cylinder cooling of internal combustion engines delivered before the Institution of Automobile Engineers, London, Mr. F. W. Lanchester said that investigation of the standard type of honeycomb radiator gave its total weight per square foot of surface with complement of water as 0.8 lb. For motor car work about 3 sq. ft. must be supplied per H. P. and thus its weight per H. P. comes out at about  $2\frac{1}{2}$  lb. When cylinder jackets, jacket water pumps, etc., are included it is with difficulty that less than 3 lb. per H. P. can be reached in the motor car or 1 lb. per H. P. in the flying machine, and, for the latter, in Mr. Lanchester's opinion, it will not be found possible to get below 0.75 lb. per sq. ft. (approximately per H. P.). Further, the lecturer thought that with cylinder diameters of 300 mm. and upwards, air cooling offered little or no advantage on the score of weight. But with diameters of 100 mm. or 110 mm. such as are usually made use of for aeronautical work, the weight of the gills per H. P. is about 2 oz. as against very little less than 1 lb. if water cooling be adopted. It was an open question whether direct air cooling might not yet have a more important part to play in the future of the automobile, and first in its aeronautical application and later in motor car engines of high power the problem of direct air cooling should be given the attention to which it was entitled.—M.

### RUSSIAN PLATINUM INDUSTRY DEVELOPMENT

The British Vice-Consul at Ekaterinburg reports that an interesting development is to take place in the near future in the mining of platinum. The new development will take the form of a practical experiment in the crushing and washing of the matrix rock-bearing platinum (similar to the crushing of gold matrix by Chilean mills). The rock in the present case takes the form of a huge lode of dunite which is stated to carry platinum amounting to approximately 0.0852 oz. Troy per ton. This at the present price of platinum is about \$4 per ton and is

seemed sufficient to pay cost of treatment. Should this experiment prove a success, researches will probably be made in other parts of the country for similar lodes.—M.

### ALUMINUM

A French metallurgist is said to have solved the problem of giving aluminum a coating that will take a high polish and will safeguard it against the effects of air and of certain foods. By successive baths of boiling lye, cyanide of potassium and hydrochloric acid containing ferrous chloride, a surface can be produced which takes a plating of nickel so perfectly that the metal can be rolled into plates, drawn in wires or hammered into any shape without in any way injuring the film of nickel.—M.

### PALLADIUM INSTEAD OF PLATINUM

Palladium, says a contemporary, is already taking the place of platinum in the making of jewelry, thus proving that its value is not confined to those special properties for which this metal has chiefly been distinguished in scientific laboratories. So far, it has been familiar as a member of the platinum group possessing similar catalytic powers but with a remarkable absorbent faculty for hydrogen, its most striking quality being to allow hydrogen to pass through it under certain conditions, though ordinarily impervious to this gas and to all others of larger molecule. Being untarnishable and capable of high polish, palladium has found a use in the construction of delicate instruments. In price, general properties and appearance, it is almost identical with platinum.—M.

### REDUCTION OF METALLIC OXIDES

A paper on "Reduction of Metallic Oxides with Hydrogen at High Pressures" was recently read before the Royal Society, London. Metallic oxides were heated to temperatures of 500° C. in dry hydrogen at pressures up to 150 atmospheres, water vapor being removed by metallic sodium. The following oxides were reduced to metals:  $\text{Cr}_2\text{O}_3$  to Cr and  $\text{MnO}_2$  to Mn. The following oxides were reduced to the lower oxides:  $\text{O}_3$  to VO;  $\text{Nb}_2\text{O}_5$  to NbO;  $\text{U}_3\text{O}_8$  to  $\text{UO}_2$ ;  $\text{TiO}_2$  to TiO; and  $\text{CeO}_2$  to  $\text{Ce}_2\text{O}_3$ . The following were unchanged:  $\text{Al}_2\text{O}_3$ , MgO,  $\text{ZnO}$ ,  $\text{Y}_2\text{O}_3$  and  $\text{ThO}_2$ . Of the metals obtained, Cr and Mn are probably the purest samples of these metals that have been prepared up to the present. This supposition is supported by the sharp nature of their melting points, a feature not observed in other specimens.—M.

### COPPER INDUSTRY IN AUSTRALIA

The Electrolytic and Smelting Co. at Porto Kembla, says the *Mining Journal*, have started excavating for the building of additional works to be erected at a cost of about \$500,000. Last year the works produced about 24,000 tons of refined copper, the chief supplies coming from Mount Morgan, Mount Well, Hampden and Cloncurvy mines. The capacity of the present smelter which treats copper, gold and silver ores is 50,000 tons per annum. Since the outbreak of the war and the consequent suspension of German competition, blister copper and matte have been received from different parts of Australia for treatment. The additional works are in response to an appeal of the Commonwealth Government to have all such ores treated entirely in Australia and also the copper and products well. The Queensland Government, it is understood, has acquired the Box Flat and Park Head properties for state coal purposes at a price between \$375,000 and \$500,000. A second site is also believed to have been secured in the Ipswich district.—M.

### CHESHIRE SALT EXPORTS

According to the annual statistics computed by the Salt Union Ltd., the exports of salt from the Liverpool and Man-

chester ship canal ports reached a total of 401,977 tons which was greater than that for 1914 and was not much less than that for 1913. The shipments to the coast show a decrease which is due to the small fisheries. The amount exported to the United States had to be somewhat curtailed, due to the lack of ship-room. The export figures to British North America are practically alike for the past three years. There is an increase in the export trade to the West Indies and South America and a great increase in the South African trade, the total exceeding that of any of the ten previous years. The quantity shipped to Asia was very much the same as for 1913, while that to Australia showed a decrease, due to the difficulties of transportation. The exports to Europe for 1915 were less than for 1914 which, however, had had the largest total for many years.—M.

### COPRA FROM QUEENSLAND

Coconut cultivation, says *Nature*, though still a small industry in Queensland, is rapidly extending. Hitherto it had been supposed that copra from Queensland coconuts did not contain enough oil to be of commercial value, but the examination of a sample of copra from these nuts at the Imperial Institute, London, has now established that the oil content is normal and the copra of good quality, and brokers state that shipments would be readily salable in this country at good prices. It is interesting to note that, before the war, the bulk of the copra shipped to Europe from Ceylon, India and elsewhere was crushed in Germany and France. Urgent representations on this subject were made by the Imperial Institute on the outbreak of the war to the oil-seed crushing firms in the United Kingdom, some of whom have now started to work copra with the result that there is a new and good market for the product in this country which is likely to expand when the new factories now building start work.—M.

### INDIAN JUTE INDUSTRY

The Indian Jute industry formed the subject of a lecture before the Royal Society of Arts, London, recently. Illustrations were given showing the cultivation and mode of preparation of jute. In Bengal, Cooch Behar and Assam more than 3,350,000 acres are under jute cultivation and the value of raw jute exported in 1913 amounted to £20,000,000. It was not until 1855 that a jute mill was started at Calcutta and now the mills there turn out nearly 3000 tons of the manufactured article per day.—M.

### PROHIBITION OF EXPORTATION OF WOOD PULP

The threatened prohibition of Sweden, says *Nature*, of the exportation of wood pulp awakens political interest in an important branch of the British cellulose industries. The paper-making industry of Great Britain is chiefly dependent on imported raw materials of which about 80 per cent are the wood pulps. In evidence of the growth of the industry as of its collateral dependence upon exotic supplies, the importation of these wood pulps shows a tenfold increase for the period 1887 to 1915, i. e., £500,000 to £5,000,000. The value of total imports is about six million Sterling which includes esparto grass (£700,000), rags, and rag pulps, also miscellaneous raw material. As to the distribution of the sources of supply of the wood pulps, a large part of the total—60 to 70 per cent—is derived from Scandinavia, Norway sending a large proportion of mechanical pulp which is the basis of our newspapers, and Sweden sending the larger part of our chemical pulp, which is used in higher class printings and also writings. The chemical pulps of the American continent, including Canada, are little exported while some come from Newfoundland. Our dependence on Scandinavia is, therefore, reciprocal; their wood-pulp industry, which is now a very important means of ex-



plottation of their pine forests, is certainly of primary importance to them. The general conclusion of specialists is that Sweden cannot afford to enforce any such prohibition. It is probably a card played in *haute politique* and the solution of the matter is to be found in some form of license to export similar to that granted in Britain for sulfur and other products ranking directly or indirectly as munitions.—M.

### PHOSPHORESCENT CALCIUM SULFIDE

In *Comptes rendus*, 161 (1915), 732, P. Breteau describes a method by which a highly phosphorescent calcium sulfide may be obtained. A mixture of 100 g. pure precipitated calcium carbonate and 30 g. powdered roll sulfur is heated to a dull red heat for an hour in a covered crucible. When cold, the white calcium sulfide obtained as above is impregnated with 1 : 1000 of bismuth. For this purpose a solution of 0.3 g. of basic bismuth nitrate in 200 cc. of absolute alcohol containing a few drops nitric acid is employed: 10 grams of the calcium sulfide are made into a paste with absolute alcohol and 1 cc. of the bismuth solution is added to it and mixed very thoroughly. After drying, the mixture is carefully heated in a covered crucible to a cherry-red heat for two hours, and then allowed to cool in the furnace. The powdery product obtained has a fine violet phosphorescence. Molybdenum may be used in place of bismuth to produce the phosphorescence, as may also tungsten and vanadium. The phosphorescence does not seem to be due to traces of alkali chlorides as suggested by Verneuil. A very fine phosphorescence is obtained by the addition of 1 per cent sodium sulfide, although it is not more intense than that given by the calcium-bismuth sulfide alone.—M.

### TOBACCO CULTIVATION

The improvement of tobacco cultivation in Behar, says *Nature*, is one of the subjects which has engaged the attention of Mr. and Mrs. Howard at the Agricultural Research Institute, Pusa, and their account is published as a Bulletin from the Institute. Attention has been mainly concentrated on the improvement of indigenous varieties of tobacco and a type has been discovered of light color and good texture suitable for cigarette tobacco. Green manuring with Sunn hemp has also been found valuable in light, high-lying, well-drained soils. The importance of growing only one kind of tobacco and of growing even fields of the crop is insisted upon, the value of a single variety being evident since cross-fertilization is common in tobacco. The Bulletin contains useful information on seed-sowing, transplanting, manuring and the principles of curing, for it is largely on the curing that the value of the tobacco depends.—M.

### SEASONING OF TIMBER

A process of treating timber which is intended to obviate the necessity for prolonged periods of stocking, has been introduced by Mr. Owen, Liverpool. The plant is simple and the process can be carried out by unskilled workmen. The method consists in placing unseasoned timber in cylinders or chambers and subjecting it to the action of steam under pressure. The steam is then cut off and a vacuum produced. It may be necessary to repeat the process two or three times according to the nature of the wood. Hot air conjointly with certain gaseous products obtained from a distilling apparatus are then introduced into the cylinder, the gaseous products being varied for different woods. When the operations are finished, the wood is seasoned and is found to be quite as good as after long stocking and to retain its "life" quite as well.—M.

### THE DEARTH OF DYESTUFFS

The Imperial Institute, London, recently issued a circular on the dearth of dyestuffs. It states that the shortage of

synthetic dyes in this country and the United States has greatly increased the demand for vegetable dyestuffs which have accordingly risen in price and in some cases are difficult to obtain. In particular, mention is made of the scarcity of logwood. In the past, the chief British sources of supply have been Jamaica and British Honduras but, some years ago, the Imperial Institute investigated the possibility of exporting logwood from Mauritius. A trial shipment was found to be of excellent quality, and in 1912 offers were made by a leading British dye firm to take considerable quantities. At that time the price was not high enough to warrant cost of export but, in view of the higher price, the Imperial Institute has arranged for the export of large supplies of Mauritius logwood.—M.

### NEW LABORATORY

A recent number of the *Electrical Review* contains an illustrated article on the laboratory for heating and ventilation which has been opened at University College, London. The equipment described consists mainly of apparatus for measuring temperature radiation and the effectiveness of gas and electrical radiators, for testing hot water pipes, for determining the slope of temperature through the walls to the outside and for measuring the resistances of air ducts. This laboratory seems to be the first established by any university for the special study of heating and ventilation but some important work in the scientific problems of heating and ventilation was done by Sir Napier Shaw in the Cavendish Laboratory, Cambridge, some twenty years ago. The inclusion of this work within the sphere of the University is a welcome innovation and it is to be hoped that those who have the arranging of such matters will see that the scientific study of problems underlying every-day life receive due consideration.—M.

### INSULATING MATERIAL

A fusible insulating material for electrical purposes and adapted to be sold in powdered form, patented by H. Grossman, Switzerland, consists of a mixture of powdered colophonium and gypsum preferably in about equal proportions. Powdered paraffin wax may be added in order to render the mixture less brittle when fused. In this case suitable proportions are 45 per cent gypsum, 45 per cent colophonium and 10 per cent paraffin wax.—M.

### BRITISH BOARD OF TRADE

During the month of February the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply of the following articles. Firms that may be able to give information regarding these things are asked to communicate with Board of Trade, 73 Basinghall Street, London.

Anodes, nickel for plating purposes	Chromite
Asbestos, rope, also roofing sheets, corrugated	Cotton fiber, sheets for beer filtering
Bone, shavings, turnings and borings	Diatomite
Bottles with metal tops	Files
Brass rod joints for perambulators	Fireclay "flattening" stones for use in window-glass factories
Capsules, lead for bottles	Flints or friction metal for tinder
CHEMICALS	Cigar lighters
Amyl acetate	Forks, iron, cheap
Amyl alcohol for paint making	Lamps, acetylene, for miners
Amyl formate	Lenses for flash lamps
Barium peroxide	MACHINERY
Bleaching powder	Presses for cattle food
Calcined magnesias	For winding silk cocoons
Calcium phosphate, precipitated to contain 1/100 arsenic per lb., 5 per cent sulfate and only traces of iron	For making chlorine for sterilizing water
Methyl acetone	ONLS
Phosphorus pentoxide	Kapok oil
Potassium ortho-quinoline sulfate (chinosol)	Olive oil
Sodium hydrogen phosphate	Oilcloth
Sodium peroxide	Plant for coating cloth with nitro-cellulose
Sodium salicylate	Plant for recovering acetone from water
Sodium dichromate	Papier-mâché pots for cream, etc.
Trichlor-ethylene	Ramie yarn for mantles
Valerianic acid	Soap, soft, odorless
Washing soda	Syringes
Chrome ore	Thermometers
	White metal, of specified design

## WILLIAM H. NICHOLS MEDAL AWARD

The Nichols Medal, awarded by the New York Section of the American Chemical Society for the best original contribution to the publications of the Society during the year 1915, was conferred upon Dr. Claude Silbert Hudson, of the Bureau of Chemistry, in recognition of his research in the field of organic chemistry, at the regular meeting of the Section, in Rumford Hall, Chemists' Club, March 10, 1916.

Dr. T. B. Wagner, Chairman of the Section, presented the medal. The presentation address and the medal address are printed in full below.

Claude Silbert Hudson was born in Atlanta, Georgia, January

6, 1881. His early education was obtained in Mobile, Alabama, at the public schools and in the University Military School of that city. Entering Princeton University, he graduated from the chemistry course in 1901 with the degree of B.S. and was awarded the Class of 1860 Fellowship in Experimental Science, which gave him the opportunity to take post-graduate work the following year and to begin an investigation on the mutarotation of milk sugar under Prof. William Magie. He was awarded the degree of Ph.D. at Princeton and in 1902 went to the University of Göttingen and studied one semester under Prof. Nernst, continuing physico-chemical studies on milk sugar. During the spring recess of the University he carried out an investigation under Prof. Tamann on the mutual solubility of nicotine and water. Removing from Göttingen to Berlin, he studied one semester under Prof. van't Hoff in the latter's private laboratory at Charlottenburg, continuing investigations on milk sugar. Returning to America in 1903,

he worked one year as Research Assistant in Prof. A. A. Noyes' newly established Research Laboratory of Physical Chemistry at the Massachusetts Institute of Technology. In 1904-5 he was employed at Princeton as Instructor in Physics, and 1905-7 at the University of Illinois in similar duties.

In June, 1907, he received the degree of Ph.D. from Princeton, his major subject having been physics, and after short employments in the Geological Survey and at the New York Testing Laboratory, he entered the Bureau of Chemistry at Washington in 1908, where he has since been engaged, except for the year

1912-13, when he was acting professor of physical chemistry at Princeton during a year's absence of Prof. Hulett. He is at present Chemist-in-Charge of the Carbohydrate Laboratory, Bureau of Chemistry, U. S. Department of Agriculture.

Dr. Hudson's principal contributions have dealt with the application of physico-chemical principles and methods to the chemistry of the sugars. Some of the more prominent articles which he has published in this field deal with the following subjects:

"The Mutarotation of Milk Sugar."

"The Significance of Certain Numerical Relations in the Sugar Group."

"A Relation Between the Chemical Constitution and the Optical Rotatory Power of the Sugar Lactones."

"The Estimation of Cane Sugar and of Raffinose by Enzymotic Hydrolysis."

"The Preparation of New Acetyl Derivatives of the Sugars."

### PRESENTATION ADDRESS

By T. B. WAGNER<sup>1</sup>

Research has become the watchword of the day. One might almost be led to believe that research was a product of the 20th century—something unknown heretofore and newly created by a universal desire to mobilize our industries. Yet, the present highly developed state of the chemical industries was brought about chiefly by the painstaking, patient and quiet research work in the laboratory, conducted primarily from love of and for the sake of research and based upon a desire to obtain more light—in short, work undertaken in search of the truth. It was in recognition of such work that the William H. Nichols Medal was



C. S. HUDSON—WILLIAM H. NICHOLS MEDALIST, 1916

founded in 1902. It is interesting and instructive to observe the specific character of chemical research represented by the different awards of the William H. Nichols Medal in past years:

1903	AGRICULTURAL CHEMISTRY	E. B. VOORHEES
1905	RARE EARTHS	C. L. PARSONS
1906	ORGANIC CHEMISTRY	M. T. BOGERT
1907	ANALYTICAL CHEMISTRY	H. B. BISHOP
1908	CHEMICAL ENGINEERING	W. H. WALKER
1909	PHYSICAL CHEMISTRY	W. A. NOYES and H. C. P. WEBER
1910	ORGANIC CHEMISTRY	L. H. BAERLAND
1911	PHYSICAL CHEMISTRY	M. A. ROSANOFF and C. W. BASLEY
1912	ORGANIC CHEMISTRY	C. JAMES
1914	ORGANIC CHEMISTRY	M. GOMBERG
1915	PHYSICAL CHEMISTRY	I. LANGMUIR

<sup>1</sup> Chairman of the New York Section of the American Chemical Society.



The William H. Nichols Medal jury made this year's award to a chemist who has distinguished himself in research work in the field of organic chemistry: carbohydrates, more especially the sugars. Dr. Hudson, to whom the honor goes this year, is connected neither with the industries nor the universities, as were most of his predecessors, but fills with distinction an important post in an institution the work of which commands the admiration of the scientific world—the Bureau of Chemistry in the United States Department of Agriculture.

TO DR. HUDSON:

Dr. Hudson, it is a very great pleasure to me to be permitted to confer upon you, in behalf of the New York Section of the American Chemical Society, this coveted endowment—the William H. Nichols Medal. May I ask you to receive it as an expression of the appreciation with which your work in the field of chemical research is being regarded by your colleagues and may I add the wish that it may serve to stimulate you to further efforts in your chosen field.

### THE ACETYL DERIVATIVES OF THE SUGARS MEDAL ADDRESS

By C. S. HUDSON

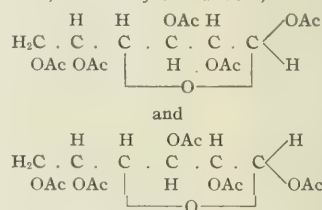
The forty-five crystalline acetates of the sugars that are exhibited this evening take their origin from the pioneer experiments of Berthelot<sup>1</sup> fifty-six years ago, who combined glucose with glacial acetic acid to form an oil-like ester. No one of these crystalline substances was discovered, however, by Berthelot and the investigations of many chemists during the intervening years have been required in the development of the methods that have led to their production.

Schützenberger<sup>2</sup> introduced the use of acetic anhydride in place of acetic acid and with this stronger reagent prepared the first crystalline acetate of a carbohydrate, mannite hexacetate, but was unable to obtain any crystalline acetates of the sugars proper. The employment of catalytic agents to aid the action of acetic anhydride in this reaction was introduced by Liebermann,<sup>3</sup> who used sodium acetate. By Liebermann's reaction the first crystalline acetate of a sugar was prepared from glucose in 1879 by Franchimont;<sup>4</sup> the substance was undoubtedly what is now known as the beta pentacetate of glucose, but Franchimont made an error of 6 per cent in its quantitative saponification and considered it to be an octacetate of a hypothetical diglucose sugar. By the further application of Liebermann's reaction Herzfeld prepared the crystalline octacetates of lactose and maltose in 1880,<sup>5</sup> and of sucrose in 1887.<sup>6</sup> Liebermann's reaction has also led to the preparation of the following other fully acetylated sugar derivatives: beta galactose pentacetate by Erwig and Koenigs<sup>7</sup> in 1889; beta melibiose octacetate by Scheiber and Mittelmeier<sup>8</sup> in 1890; the beta octacetate of glucoheptose by Fischer<sup>9</sup> in 1892; beta xylose tetracetate by Stone<sup>10</sup> in 1893; beta cellose octacetate by Maquenne and Goodwin<sup>11</sup> in 1904; and beta gentiobiose octacetate by Zemplen<sup>12</sup> in 1913.

In 1889, Erwig and Koenigs<sup>13</sup> made a contribution to the subject which has developed into a matter of prime importance. Using as a catalyst of the acetylation reaction, zinc chloride

(ZnCl<sub>2</sub>), which had been suggested by Franchimont,<sup>4</sup> they prepared from glucose and acetic anhydride a crystalline substance which is now known as alpha glucose pentacetate. The importance of their work lies in their establishment of the fact that two crystalline acetates may be prepared from the acetylation of glucose with acetic anhydride, according as sodium acetate or zinc chloride is used to catalyze the reaction. It is true that the correct composition of the product which Franchimont had obtained through the employment of sodium acetate, his so-called octacetyl di-glucose, was not at that time understood, nor did the researches of Herzfeld and of Erwig and Koenigs improve the situation since they obtained analytical results identical with Franchimont's and joined with him in his erroneous conclusion. It was indeed Franchimont<sup>2</sup> himself who showed in 1892 that his di-glucose octacetate is in reality a glucose pentacetate which is isomeric with the one which Erwig and Koenigs prepared. It may be mentioned at this point that the use of zinc chloride as a catalyst of the acetylation has yielded four other crystalline acetates of the sugars, namely, trehalose octacetate,<sup>3</sup> alpha hexacetyl glucoheptose<sup>4</sup> and a tetracetate and pentacetate of fructose.<sup>5</sup> The use of pyridine as a catalyst of the acetylation has yielded beta mannose pentacetate<sup>6</sup> and the use of sulfuric acid has given alpha cellose octacetate,<sup>7</sup> and a second fructose pentacetate.<sup>8</sup>

Returning to the isomeric glucose pentacetates, the first explanation of their structure was Fischer's<sup>9</sup> suggestion that they have the  $\gamma$ -cyclo ring configuration which Tollens<sup>10</sup> had proposed some years before for glucose itself. With such ring structure the end carbon atom is asymmetric and two isomeric forms are possible, which may be indicated,



This explanation was soon supported by the isolation of two isomeric methyl glucosides,<sup>11</sup> and by C. Tanret's<sup>12</sup> discovery of a second isomeric form of glucose itself. Indeed, the structural relationships between the two forms of glucose and the two methyl glucosides were brought out strongly by E. F. Armstrong's<sup>13</sup> experimental proof in 1903 that the enzymotic hydrolysis of  $\alpha$ -methylglucoside yields  $\alpha$ -glucose while the  $\beta$ -methyl glucoside yields  $\beta$ -glucose. It has also been shown that the slow acetylation of  $\alpha$ -glucose at low temperature with either pyridine or zinc chloride as catalyst yields principally  $\alpha$ -glucose pentacetate, while the  $\beta$ -pentacetate is produced under similar conditions from  $\beta$ -glucose.<sup>14</sup>

It is now known that the two pentacetates of glucose change easily in solution one into the other provided a suitable catalyst, such as zinc chloride, is present. Sulfuric and hydrochloric

<sup>1</sup> Ber., **12** (1879), 2059.

<sup>2</sup> Rec. trav. chim., **11** (1892), 106.

<sup>3</sup> Maquenne, Compt. rend., **112** (1891), 947.

<sup>4</sup> Fischer, Ann., **270** (1892), 64.

<sup>5</sup> Hudson and Brauns, J. Am. Chem. Soc., **37** (1915), 2736.

<sup>6</sup> Fischer and Oetker, Ber., **46** (1913), 4029.

<sup>7</sup> Skraup and Koenigs, Ibid., **34** (1901), 1115.

<sup>8</sup> Hudson and Brauns, J. Am. Chem. Soc., **37** (1915), 1283.

<sup>9</sup> Ber., **26** (1893), 2400.

<sup>10</sup> Ibid., **16** (1883), 923.

<sup>11</sup> Fischer, Ber., **26** (1893), 2400; Van Ekenstein, Rec. trav. chim., **13** (1894), 183.

<sup>12</sup> Bull. soc. chim., **15** (1895), 195.

<sup>13</sup> J. Chem. Soc., **83** (1903), 1305.

<sup>14</sup> Behrend and Roth, Ann., **331** (1904), 369; Behrend, Ibid., **353** (1907), 109; Hudson and Dale, J. Am. Chem. Soc., **37** (1915), 1267.

<sup>1</sup> Ann. chim. phys., [3] **60** (1860), 93.

<sup>2</sup> Compt. rend., **61** (1865), 485; Ann. chim. phys., [4] **21** (1870), 235.

<sup>3</sup> Ber., **11** (1878), 1618.

<sup>4</sup> Compt. rend., **89**, 713; Ber., **12** (1879), 1940.

<sup>5</sup> Ber., **13** (1880), 265.

<sup>6</sup> Z. Ver. Zuckerind., **24** (1887), 422.

<sup>7</sup> Ber., **22** (1889), 2207.

<sup>8</sup> Ibid., **23** (1890), 1438.

<sup>9</sup> Ann., **270** (1892), 64.

<sup>10</sup> Am. Chem. J., **15** (1893), 653.

<sup>11</sup> Bull. soc. chim., [3] **31** (1904), 856.

<sup>12</sup> Z. physiol. Chem., **85** (1913), 402.

<sup>13</sup> Ber., **22** (1889), 1464.

acids are also catalysts of this isomerization but sodium acetate is not. Erwig and Koenigs<sup>1</sup> observed that the substance which is now termed beta glucose pentacetate may be changed to the alpha form by heating with acetic anhydride and a trace of zinc chloride, but since they regarded the first substance as an octetyl-di-glucose they looked upon the change which zinc chloride brings about as one of hydrolysis rather than of isomerization, and the correct interpretation of this change was first indicated by Fischer.<sup>2</sup> It is important to note that Erwig and Koenigs<sup>3</sup> sought to change maltose octacetate, which in their view was isomeric with the so-called di-glucose octacetate, into alpha glucose pentacetate by heating it with acetic anhydride and zinc chloride, without success, and they stated that the substance remained unchanged. With present knowledge such a hydrolysis would not be expected, but on the other hand it is difficult to understand what experimental tests could have led Erwig and Koenigs to believe that the maltose octacetate remained unchanged, because we now know that it changes under such conditions almost completely into an isomeric octacetate. This point will come up again; it is here mentioned to indicate that although in fact Erwig and Koenigs were the first to change sugar acetate to its isomer by the use of zinc chloride, they did not interpret the change correctly nor apply it further. An important study of this reaction from the physico-chemical standpoint was made by Jungius,<sup>4</sup> who showed that the beta octacetate of glucose does not change completely to the alpha form in acetic anhydride solution containing zinc chloride, but that a balanced reaction between the two substances exists and that when equilibrium is attained 90 per cent of the alpha and 10 per cent of the beta form are present. The quantitative measurements of Jungius show why the alpha form crystallizes readily from the transformed beta modification, and a consideration of his results led me sometime ago to inquire whether other sugar acetates could be rearranged similarly to give an equilibrium mixture in which a new isomer might so predominate that its crystallization could be accomplished. The first experiments were made by Dr. Johnson and myself<sup>5</sup> on lactose, but we considered it desirable to start with the pure octacetate of lactose rather than with the sugar itself in order to avoid the presence of by-products that may be produced during the acetylation. It was found that the specific rotation of a freshly prepared cold solution of the lactose octacetate of Herzfeld in acetic anhydride containing a trace of zinc chloride was +4° and that on heating, this value rapidly changed, becoming constant at +52°. From the transformed solution a new crystalline octacetate of lactose was separated. Its specific rotation in acetic anhydride was found to be +64, which indicates that about 81 per cent of the new isomer was present in the equilibrium mixture from which it was crystallized. In a similar manner we found that the heating of a solution of maltose octacetate in acetic anhydride containing zinc chloride changed its specific rotation from +60° to +110° and from the transformed solution a new octacetate was crystallized. A pentacetate of galactose and of mannose, and a tetracetate of xylose have been prepared similarly, with the assistance of Dr. Johnson, Dr. Dale and Mr. Parker.<sup>6</sup>

In naming the pairs of isomeric acetates we have followed the plan that I suggested some years ago,<sup>7</sup> according to which the more dextrorotatory substance of a given pair is named the alpha form and the more levorotatory the beta. While it might seem at first thought that such naming is wholly arbitrary, experience has shown that there does exist in the sugar group

a relationship between optical rotation and chemical structure upon which such a rule of nomenclature may be based. Thus, it has been shown in the articles cited that considerations of structure lead to the conclusion that the difference in molecular rotation between the alpha and beta forms of the fully acetylated derivatives of glucose, lactose, maltose, and cellose should be equal, and experiment has confirmed the conclusion. The rotations of the acetates of galactose, mannose and xylose do not agree so well with those of glucose, but conform sufficiently for a basis of nomenclature.

	Glucose pentacetates	Lactose octacetates	Maltose octacetates	Cellose octacetates	Xylose tetracetates	Galactose pentacetates	Mannose pentacetates
Alpha form	+39,600	+36,500	+83,000	+27,800	+28,300	+41,600	+21,400
Beta form	+1,500	— 2,900	+42,500	—10,200	— 7,900	+ 8,900	— 9,800
Difference	38,100	39,400	40,500	38,000	36,200	32,700	31,200

This numerical relationship extends to many other sugar derivatives; two recent tests of it may be presented from the measurements by Irvine and Hogg<sup>1</sup> of the rotations of the alpha and beta forms of monomethyl glucose and those by Bourquelot<sup>2</sup> on the alpha and beta forms of glycol glucoside. It is to be expected that the difference of the molecular rotations of the two monomethyl glucoses should equal that of the two forms of glucose, while the sum of those of the two glycol glucosides should equal that of the two glucoses.

$$\alpha\text{-Glucose: } (M)_D(a) = 20340 = +A + B$$

$$\beta\text{-Glucose: } (M)_D(a) = 3420 = -A + B$$

$$\text{Monomethyl } \alpha\text{-glucose: } (M)_D = 20874 = +A + B(a)$$

$$\text{Monomethyl } \beta\text{-glucose: } (M)_D = 4733 = -A + B(a)$$

$$\text{Glycol } \alpha\text{-glucoside: } (M)_D = 30347 = +A(a) + B$$

$$\text{Glycol } \beta\text{-glucoside: } (M)_D = -6843 = -A(a) + B$$

	Molecular Rotations Sum (2B)	Difference (2A)
$\alpha$ - and $\beta$ -Glucoses.....	23760	16920
Monomethyl Glucoses.....	23504	16141
Glycol Glucosides.....	23504	.....

(a) These values are based upon +113 and +19 for the specific rotations of  $\alpha$ - and  $\beta$ -glucose, as recently measured by Dr. Dale, Dr. Yanovsky and myself.

The acetates which have been mentioned so far are those of the aldose sugars, such as glucose, and of the nonreducing sugars, sucrose and trehalose. Since the nonreducing sugars do not occur in alpha and beta forms, only one fully acetylated derivative is to be expected for each of them, and only one is known. The rotatory powers of sucrose and trehalose octacetates in acetic anhydride solution are not affected by heating in the presence of zinc chloride, showing that there is no transformation to isomers.<sup>3</sup> It is only recently that the behavior of any acetate of a ketose sugar towards isomerization has been investigated. Starting with a crystalline tetracetate of fructose which Dr. Brauns discovered some years ago, we<sup>4</sup> have prepared from it two crystalline isomeric pentacetates of fructose which appear to constitute an alpha and beta pair. Neither of these pentacetates changes, however, to the other form when heated with acetic anhydride and zinc chloride and it may be, therefore, that the establishment of an equilibrium between the alpha and beta acetates is limited to the derivatives of the aldose sugars.

Steps in the advancement of chemical theory have often occurred as the result of the discovery of more isomers than could be accounted for by accepted principles. Thus, the discovery of two pentacetates of glucose, two methyl glucosides and two forms of glucose caused the acceptance of the Tollens  $\gamma$ -cyclic structure for the sugar in place of the older aldehyde formula. A similar overgrowing of the bounds of the past is now in progress, having had its start in the discovery of a third form of methyl glucoside by Fischer.<sup>5</sup> The substance is amorphous and prob-

<sup>1</sup> Ber., **22** (1889), 1464.

<sup>2</sup> Ibid., **26** (1893), 2400.

<sup>3</sup> Loc. cit., p. 2213.

<sup>4</sup> Z. physik. Chem., **52** (1905), 101.

<sup>5</sup> J. Am. Chem. Soc., **37** (1915), 1270.

<sup>6</sup> Ibid., **37** (1915), 1276, 1280, 1589, 2748.

<sup>7</sup> Ibid., **31** (1909), 66.

<sup>1</sup> J. Chem. Soc., **105** (1914), 1386.

<sup>2</sup> Ann. chim., [9] **4** (1915), 338.

<sup>3</sup> Hudson and Johnson, J. Am. Chem. Soc., **37** (1915), 2752.

<sup>4</sup> Hudson and Brauns, Ibid., **37** (1915), 1283, 2736.

<sup>5</sup> Ber., **47** (1914), 1980.

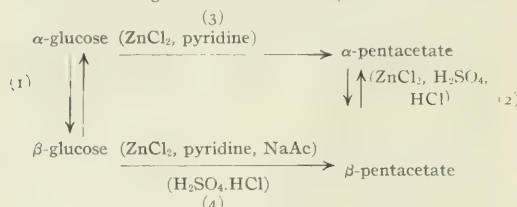


ably consists of a mixture of isomers, and its difference from the two known methyl glucosides lies in the fact that it is distillable. Fischer considers that its existence is to be accounted for on the ground that the ring is formed on some other than the  $\gamma$ -carbon atom. Recently while studying the acetylation of galactose with acetic anhydride and sodium acetate, I noticed the crystallization of a substance which proved to be a third pentacetate of galactose.<sup>1</sup> By the treatment of this third substance with acetic anhydride and zinc chloride it has been rearranged<sup>2</sup> to a fourth crystalline pentacetate of galactose. The first and second isomers establish an equilibrium in the rearranging solution, and the third and fourth forms do likewise, but it has not been possible to rearrange a member of the one pair into a member of the other. This fact leads to the view that the four pentacetates consist of the alpha and beta forms of two pairs and that the pairs differ in structure by the position of the internal ring.

It is possible at the present time to summarize fairly well the numerous reactions which have been observed in the acetylation of the sugars. For this purpose the sugar group may be divided into three classes, the nonreducing sugars, such as sucrose and trehalose, the aldoses, and the ketoses:

I—The acetylation of the nonreducing sugars gives only one fully acetylated derivative independent of the catalyst used.

II—Selecting glucose as an illustration of the aldose class for the reason that its reactions have been thoroughly studied, the known steps in the acetylation of an aldose sugar may be indicated in the diagram as four reactions, two of which are re-



versible and two irreversible. The acetylation of either  $\alpha$ - or  $\beta$ -glucose with acetic anhydride and sodium acetate requires

warm temperature and as a result the isomerization of the sugar [reaction (1)] precedes its acetylation and the beta pentacetate is produced because  $\beta$  glucose (and the other  $\beta$  aldoses) acetylate more readily than the  $\alpha$  form. It is evident why the final product by this method of acetylation consists largely of the  $\beta$  pentacetate, no matter whether  $\alpha$  or  $\beta$  glucose is used at the start. When zinc chloride is used as the catalytic agent, two cases have to be considered, depending upon whether the temperature is kept low ( $0^\circ$ ) or high. If it is low, reactions (1) and (2) are very slow and reactions (3) or (4) can be produced without the occurrence of isomerization. Starting with the pure form of either  $\alpha$ - or  $\beta$ -glucose, the correlated pentacetate can be produced in this way. At low temperatures the same correlation is produced by acetylating with acetic anhydride and pyridine. On the other hand, if the temperature is warm, reaction (2) proceeds rapidly when  $\text{ZnCl}_2$  or  $\text{H}_2\text{SO}_4$  or  $\text{HCl}$  is the catalyst and as a result the equilibrium mixture of  $\alpha$ - and  $\beta$ -pentacetate is obtained no matter which form of the sugar is acetylated; and since this equilibrium is far towards the  $\alpha$ -acetate in the case of glucose and all other aldoses which have been tested, the  $\alpha$ -pentacetate is the substance which forms the crystalline product of the reaction.

III—The acetylation of the ketoses is only vaguely understood at present and only one representative of the class (fructose) has been investigated. It appears that reaction (2), the isomerization of the pentacetates, does not take place and the whole scheme is thereby made different. Further investigations will be required before the acetylation of the ketoses is fully understood.

The fully acetylated derivatives of the sugars are the most accessible materials for the preparation of many important sugar derivatives—thus glucose pentacetate yields acetobromoglucose and from it many synthetic glucosides, as well as glucose tetracetate, may be obtained—and it is reasonable to suppose that the present knowledge of the mechanism of the acetylation reaction will permit in the future its control and efficient utilization in the production of new substances.

BUREAU OF CHEMISTRY, WASHINGTON

## NOTES AND CORRESPONDENCE

### AMERICAN CHEMICAL SOCIETY—SPRING MEETING UNIVERSITY OF ILLINOIS, URBANA-CHAMPAIGN APRIL 18 TO 21, 1916

A number of special features in the way of entertainment will be provided for visitors to the American Chemical Society meeting at the University of Illinois, April 18 to 21, 1916. These will include excursions to the campus and entertainment by student organizations, a trip to the industrial plants in the vicinity of Danville, Illinois, the dedication of the new chemical laboratories of the University, and an Exposition of chemical products and apparatus of American make. In addition, there will be a smoker, the equal of any in the past, a subscription dinner, and special entertainment for the ladies, the nature of which has not been divulged at the present time. Before the smoker in the evening there will be a complimentary concert by the First Regiment Band.

LOCAL EXCURSIONS—These will be held on two different afternoons. On Tuesday, the 18th, the buildings and grounds of the College of Agriculture will be visited. The Easter Flower Show of the Department of Horticulture will be in the best shape at this time; it will consist of eight glass houses filled with flowering plants, in addition to a special display of cut flowers. A

special fine stock show will be given in the new Stock-judging Pavilion, and the Agronomy and Plant-breeding laboratories and plots will be visited. Following this excursion will be a review of the University cadet brigade of two regiments with their military bands, battery, signal, engineer and hospital companies—an excellent show of preparedness.

On Thursday the special excursions will be to the buildings of the College of Engineering, where the various engineering laboratories, shops and power plant will be seen.

DEDICATION OF THE CHEMICAL LABORATORY—Laboratory instruction in chemistry has been given at the University of Illinois since its organization in 1868. The present laboratory building was erected in 1902, and contains about 77,000 square feet of floor space. The addition now being completed will give the building the form of a hollow square with 166,288 square feet of available floor space. The building is 231 feet long and 202 feet deep. The addition is absolutely fireproof, and will contain both research and student laboratories.

The dedicatory ceremonies will be in the form of a University Convocation, with Governor Edward F. Dunne presiding. Addresses will be delivered by President Edmund J. James of the University, Professor Alexander Smith and Doctor W. R. Whitney.

EXPOSITION OF CHEMICAL INDUSTRIES—Much interest is being displayed at the present time in the product of American Chem-

<sup>1</sup> *J. Am. Chem. Soc.*, **37** (1915), 1591.

<sup>2</sup> Hudson and Johnson, forthcoming publication.

al Manufacturers, and it seems particularly fitting that such an exhibition should accompany the dedication of this building devoted to the teaching of chemistry. The exhibition will be held in the large first floor laboratories, and will be of easy access to all visitors. To date, March 11th, forty-two firms (listed below) have signified their acceptance of the invitation to take part. Among others, the Research Laboratory of the General Electric Company is sending intact its exhibit from the Panama-Pacific Exposition at San Francisco.

Abbé Engineering Company  
Blakiston's Son & Co.  
Muloid Zapon Co.  
Central Scientific Co.  
Carbide Chemical Co.  
Airion Castings Co.  
Mer and Amend  
Gryia Enameled Products Co.  
Inverful Fluorspar Co.  
General Electric Co.  
Harry Holt & Co.  
International Instrument Co.  
Trey Dewitt Co.  
Dumble-Durand Glass Co.  
Laboratory Supply Co.  
Eds and Northrup  
Hess and Naumann  
Obsey Glass Co.  
Ingmans, Green & Co.  
Paul E. Lungwitz  
Jacobeth-Evans Glass Co.

Manhattan Rubber Co.  
McGraw-Hill Book Co.  
McIntosh Stereopticon Co.  
Metallurgical and Chemical Engineering  
Mojonier Bros. Co.  
National Carbon Co.  
National Lead Co.  
Norton Company  
Paudler Company  
Schaeffer & Budenberg Mfg. Co.  
Schutte-Koering Co.  
Scientific Materials Co.  
Sowers Mfg. Co.  
E. R. Squibb & Sons  
Standard Calorimeter Co.  
Sweetland Filter Press Co.  
Thermal Syndicate  
Thwing Instrument Co.  
Toch Bros.  
U. S. Bottlers Machinery Co.  
John Wiley & Sons

INDUSTRIAL EXCURSIONS—On Friday, April 21st, special cars over the Illinois Traction System will take the visitors to Danville to visit the industrial plants in that vicinity. The Carbon Hill mine of the Two Rivers Coal Company will show the surface mining of coal by the stripping method. The soil is stripped with a steam shovel having an eight-yard bucket, exposing the vein of coal, which is then broken down and loaded to cars. There are four mines of this type in the vicinity of Danville, and the Carbon Hill mine is one of the two largest. The Western Brick Company, one of the largest plants in the United States, manufactures wire-cut shale brick and building blocks. The shale and coal are both obtained from the tip mine of the company at the plant.

Hegeler Brothers operate one of the largest and best equipped lead smelters in the country. The ore comes from the Missouri district chiefly and is roasted in Hegeler roasters and then smelted. Muriatic acid is manufactured in lead chambers from the gases from the roasting.

While in Danville the party will be the guests of the Danville Chamber of Commerce, and will be entertained at luncheon by them.

The General Committee on Arrangements wishes to emphasize the fact that excellent accommodations will be provided for all visitors at the meeting. It is desirable, however, that reservations be made as early as possible.

## A CRITICISM OF THE OBJECTIONS RAISED BY W. C. MOORE TO THE FORMATION OF A CHEMISTS' PROTECTIVE ASSOCIATION

*Editor of the Journal of Industrial and Engineering Chemistry:*

The objections recently raised by W. C. Moore [THIS JOURNAL, (1915), 1000] to the formation of a Chemists' Protective Association may be placed under four headings:

I—That the American Chemical Society "is intensely practical" and will ultimately raise the salaries of "its members as chemists."

II—That the attempt to define a chemist as a person \* \* (see the writer's original article in Sept., 1915 issue of THIS JOURNAL) "is doomed to sure and certain failure."

III—That the proposed salary scale "is artificial, academic and impractical."

IV—That the effect of raising wages should be left to the employer, he being the one to decide the worth of the chemist.

The writer has made a critical study of these objections. The criticisms to follow are an answer to them:

I—It is very questionable whether the American Chemical Society increases the practical efficiency of chemists. The writer's experience and that of others whom he has talked with, strongly indicates that practical efficiency is the effect (a) of a systematic and careful training in the didactic and laboratory side of chemistry; (b) of hard practical work in laboratories; and (c) of love of one's work. In addition to this the writer can cite the example of more than one chemist who was not a member of the American Chemical Society, and whose increase in practical efficiency was proven by an increase of wages. What is more to the point is that the American Chemical Society has been in existence since 1876 and that wages have changed but little and in some cases have actually decreased, which indicates that its influence on practical efficiency has been greatly exaggerated and at times wholly absent. On the basis of Mr. Moore's own argument, then, it may be concluded that the American Chemical Society is not "intensely" practical and will not fatten materially the pay envelope. Indeed, the writer conceives the American Chemical Society to be a scientific organization and not directly interested in purely practical considerations.

II—To the writer's view the second objection is nonsense. Why attempt to define anything? Are the chemists such a degraded lot of individuals, that any attempt to define what they are becomes abortive and is to be criticized? Is it not highly probable that this very tendency to deprecate any attempt to define what the chemist is, acts as a cause in lowering the dignity as well as the earning power of the chemical profession? Is it not strange that Mr. Moore should use the word chemist at all? Why would not laborer be preferable? Has my critic supported his objection? He has not! Suppose some chemists are unsuccessful, and suppose it is granted that some laboratory boys do make efficient workers, what has this to do with the attempt to define? *Definition is at the basis of all exact language and classification.*

III—Three interpretations of this objection appear to be possible:

(1)—If it is assumed to be "artificial, academic and impractical" for assistant chemists to receive less than their chiefs, then the contrary proposition would appear to hold true, *vis.*, assistant chemists should receive an equal or greater salary than their chiefs. Manifestly this last proposition is false, since it does not agree with experience. Neither is the first proposition true, since *it is natural* for assistant chemists to receive less than their chiefs; *it is unacademic*, in that it is realizable in experience; and *it is practical*, in that it has stood the test of time.

(2)—If it is asserted that the proposed salary scale is "artificial, academic and impractical" in respect to the minimum wage, then my critic has betrayed himself into error again. Firstly, because within certain limits, employers themselves have set a minimum wage for chemists; secondly, because the United States Government expressly states in its civil service bulletins what it will pay Junior or Assistant and Chief Chemists, thus establishing a minimum wage for chemists in its employ; and thirdly, because in general the trades unions define what the minimum wage is for their members and in addition have actually increased this wage from 25–50 per cent in a number of instances.

(3)—In respect to the maximum wage, this would not appeal so much to chemists or any other workers. The writer placed an upper limit to wages for two principal reasons: one to make his arguments more definite, and the other to invite criticism and arouse discussion. Personally, *he does not believe in fixing an upper limit for wages.* Even in this case, however, a maximum scale is not artificial and impractical. In fact, the statements made in respect to the minimum wage scale would appear to be true for the maximum wage scale also.



IV—The last objection deals with the standardization of the chemist's worth by the employer; worth according to Mr. Moore being expressed in earning capacity, *i. e.*, in dollars and cents. This infers that the judgment of the business operator is a correct one, since the remuneration for the employee's service is controlled directly by him. But, and here is the crux of the whole discussion, *the employer is directly interested in getting a maximum of advantage for a minimum outlay of capital.* Is it not barely possible that selfish motives may be active in his estimation of a chemist's worth? Is it to be expected that a business man or employer will be inclined to allow either generosity or even justice to influence his balance sheet?

The hackneyed phrase, "that a man will get what he is worth," and used by my opponent, is entirely evasive and expresses nothing, unless clearly defined. It is a generality and is truly academic, and certainly artificial. Could the worth of the Panama Canal builder be expressed in money? Is the President worth his hire? Can coin or currency measure the worth of these men? And yet my critic maintains that salaries are in proportion to worth! Are or were these men's responsibilities to their country comparable to those of corporation heads? And how do the salaries compare? The President of this great nation is paid a yearly salary of \$75,000, while the head of the steel trust gets more than this amount. Assuming that the President, whose responsibilities are infinitely greater, receives in salary full value for his worth, then, obviously, the steel trust magnate is paid far more than his worth. It necessarily follows that all attempts of the employer to *fairly estimate the chemist's worth* by a money standard must fail, if for no other reasons than those of expediency or those of economic pressure. The former and the latter to a certain extent are the tools of the business man, with which he regulates his employee's wages. But economic pressure may also be a weapon in the hand of the employee, and if properly used can mould the expediency of the employer. Hence the need and value of a Chemists' Protective Association which would not only check avaricious employers, but would in addition protect its members, by upholding them in their demands for a higher and a more just emolument.

My critic considers low-grade routine work as deserving of only slight remuneration and not worthy of the attention of the chemist, meaning, apparently, that it is of little value. But this routine work is of vital necessity to the manufacturer, otherwise, it would not be required; and this vital necessity is left too often in the care of the laboratory boy. Therefore, the manufacturer is getting a maximum of value for a minimum of outlay. But is it not reasonable to expect that the value of this work could be greatly enhanced by placing it in the hands of trained men? And could not chemists be found willing, if the salary were commensurate with the training? Why not try it out?

Summing up, then, the arguments presented by my critic are inconclusive, since by the use of ambiguous words and phrases he attempts to evade the real issues. He shows an entirely selfish attitude in objecting to the use of a method tending to give the chemist a voice in the settlement of wages, a method, moreover, which even employers permit with respect to the trades unions. Does my critic assume that the interests of the chemists will be most satisfactorily promoted by making them always subservient to the arbitrary and selfish ruling of the employer?

TULANE UNIVERSITY

ROLLIN G. MYERS

NEW ORLEANS, January 17, 1916

## AMERICAN CHEMICAL INDUSTRIES MUST BE BUILT UP BY AMERICAN METHODS

*Editor of the Journal of Industrial and Engineering Chemistry:*

The wide-spread interest which is now being taken in the establishment of the coal-tar dye industry is certainly most

gratifying. It proves that we have at last awakened to the realization that we shall be badly handicapped in industrial development, and in the race for our just position in our home market, as well as in the world's trade, without a fully adequate chemical industry.

I have read with absorbing interest Dr. Pratt's masterly address on the subject published in the *Journal of the Society of Chemical Industry* of December 15th last. His views certainly deserve the most serious consideration.

The name of coal-tar dye industry is unfortunately a misnomer. It implies too much, but signifies too little. It really is no more nor less than the applied chemistry of synthetic organic compounds. As such, it is the crowning effort of a systematically developed chemical industry. Economically, as well as technically, it is utterly impossible without the foundation of a general chemical industry in all its branches. Any competent chemist can produce aniline dyes, if the materials for its production are furnished to him. But none, even the highest skilled one, can do so on an economical basis, if his raw materials, *viz.*, *inorganic and organic chemicals*, are not at his command in quality and at cost permitting him to produce the dyes at a figure at which they can find a profitable market. Any attempt at the manufacture of dyes must invariably lead to economical disaster if it is not preceded by the coal-tar refinery, the manufacture of intermediates, and a full line of inorganic chemicals. The importation of highly skilled experts from Europe should be preceded by calling to our aid experts in refining coal tar and in the manufacture of intermediates. And even then it is doubtful whether the immediate results would be satisfactory. These men acquired their high efficiency under different conditions from those prevailing here. Our raw materials are often of a different nature. Labor conditions are radically different. Engineering methods are different on account of the widely different conditions prevailing here. Before these experts have mastered the situation fully, it is bound to undergo a radical change again, after the deplorable European war permits us to return to normal conditions.

The marvelous success of the German chemical industry has not been achieved by the employment of "experts" trained by somebody else. The Germans long ago came to the conclusion that in the chemical industry the competent chemist is the paramount factor. They did not want their colleges to train the students to be manufacturers of soda-ash, cyanide, phenol or methyl violet. They insisted upon the graduates of their colleges being "chemists." Such men find their place as readily in acid works as in a sugar factory; in a soap factory as in dye works. They do not work according to recipes nor according to standard methods. They produce the desired article by applying the best possible methods to the given conditions. Many of our American chemists are fully equal to the occasion, if given the opportunity. We certainly would not expect a civil engineer, no matter how "expert" he may be, to tell us off-hand what kind of a bridge should be constructed over a river and what its cost would be, without giving him an opportunity to make his surveys and soundings and finish his plans. The chemist called upon to erect a chemical plant must have the same opportunity to study the local conditions before he can tell whether the problem is feasible, and before he is expected to proceed with the manufacture.

No foreign dye industry bodily transplanted into the United States will serve our purposes. This has long been proven by the steel, sugar and cement industries. If we wish to achieve a lasting success in the manufacture of coal-tar dyes, the industry must be an American one, developed under American conditions and by American chemists. Our chemists are second to none; they will certainly rise to the occasion, if given the opportunity and sustained by judicious help from a few who already have had practical experience.

The prospects for an American chemical industry, topped by synthetic organic chemicals, are certainly very bright, especially since we are justified in believing that we shall obtain a reasonable tariff protection to start with. The field is as wide as the United States. It can be exploited as well in the east as on the Pacific Coast. It needs, however, the indomitable energy of a few captains of industry who are willing to exercise a little patience in reaping the large reward which is sure to be theirs. Our chemists will surely do their part.

LOS ANGELES, CALIFORNIA  
March 4, 1916

JULIUS KOEBIG

## THE PAIGE BILL ON COMPULSORY WORKING OF PATENTS IN THE UNITED STATES

*Editor of the Journal of Industrial and Engineering Chemistry:*

IN THIS JOURNAL, 7 (1915), 304, there was published a paper by Dr. B. C. Hesse on "Compulsory Working of Patents in the United States, Germany and Great Britain," and also a "Symposium on Compulsory Working of Patents and Designs in England."

It may interest your readers to know that Mr. Paige, of Massachusetts, has introduced in the present Congress, a Bill known as H. R. 11967, 64th Congress, 1st Session, copies of which can be obtained on application to the Document Clerk, House of Representatives. This Bill adds to Section 4886 of the present law, the following proviso:

"That no patent shall be granted on any application filed subsequent to the passage of this Act upon any drug, medicine, medicinal chemical, coal-tar dyes or colors, or dyes obtained from alizarin, anthracene, carbazol, and indigo, except in so far as the same relates to a definite process for the preparation of said drug, medicine, medicinal chemical, coal-tar dyes or colors, or dyes obtained from alizarin, anthracene, carbazol, and indigo."

It also adds to Section 4887, a "Compulsory Working" proviso, which reads as follows:

"That in case any drug, medicine, medicinal chemical, coal-tar dyes or colors, or dyes obtained from alizarin, anthracene, carbazol, and indigo, on which a patent for a definite process or the preparation thereof has been granted on any application filed subsequent to the passage of this Act is not manufactured in the United States by or under authority of the patentee within two years of the granting of said patent, and after the commencement of said manufacture the same is not continuously carried on in the United States in such a manner that any persons desiring to use the article may obtain it from a manufacturing establishment in the United States, then said patentee shall have no rights under the patent laws of the United States as against any citizen of the United States who may import such drug, medicine, medicinal chemical, coal-tar dyes or colors, or dyes obtained from alizarin, anthracene, carbazol, and indigo into the United States, or who may produce or manufacture the same in the United States or who may handle for sale or use such article so imported or manufactured."

The disastrous effect on the interest of chemical inventors, which would be produced by the passage of this proposed law, is self-evident; but, none the less, it is important that chemists and manufacturers who would be affected should write to their Congressmen and Senators protesting against the passage of any such law.

Dr. Hesse's articles above referred to contain a full discussion of the reasons why the law should not be passed, and an readily be referred to by your readers.

WASHINGTON  
February 29, 1916

J. H. BRICKENSTEIN

## ANALYSIS AND TESTING WORK OF THE NATIONAL BUREAU OF STANDARDS

*Editor of the Journal of Industrial and Engineering Chemistry:*

It has come to my attention that there is still some misunderstanding as to the conditions under which the Bureau of Standards will make chemical analyses of materials. Although various publications of the Bureau should make this matter clear to the reader, it is desired to correct any misapprehension as to the facts by this statement.

The Bureau performs tests of materials and apparatus for the general public in cases where the Bureau is asked to serve as referee by the parties between which differences exist, or where an authoritative or official test is demanded by the nature of the case. Tests are also made for the public where the results are of value to the Bureau as a part of a general investigation, and tests are also made if there are no other consulting or general laboratories that have facilities for carrying out the work or in cases where the establishment of standards is desired. However, in all cases the Bureau will determine what tests will be undertaken according to the circumstances, and it reserves the right to make such use of the results of these tests as is deemed desirable. It should be clearly understood that this work is not done by the Bureau in any way in competition with consulting or other laboratories. When other laboratories have facilities for making the tests the Bureau declines to carry them out unless the results are of direct value to the Bureau as well as to the person for whom the tests are made.

The Bureau is glad at all times to coöperate, in so far as facilities permit, with investigators, manufacturers, testing laboratories, and others, not only by executing tests properly within its jurisdiction, but also, on request, by furnishing any information at its disposal concerning materials or methods of testing.

NATIONAL BUREAU OF STANDARDS  
WASHINGTON, March 15, 1916

S. W. STRATTON, *Director*

## RUSSIAN TREASURY DEPARTMENT COMPETITION ON THE INDUSTRIAL USES OF ALCOHOL

On January 1, 1916, expires the term for presenting declarations in the competition announced by the Russian Ministry of Finance for finding out new ways of utilizing alcohol (wine spirits) and for discovering new denaturants of the same. In view of the insignificant quantity of statements received, the Ministry of Finance gives notice that the term in which to present declarations for the above mentioned competition has been extended to September 1, 1916, and the adjudging of the prizes accordingly put off until March 1, 1917.

V. ANANIEFF, *Secretary*

COMMERCIAL ATTACHÉ TO THE IMPERIAL RUSSIAN EMBASSY  
NEW YORK CITY, March 4, 1916

## LIME REQUIREMENT METHODS—CORRECTION

In the article under the above title, THIS JOURNAL, 8 (1916), 243, the following correction should be made:

Page 245, Table III, last line: "None" should read "None + Lime."

WOOSTER, OHIO J. W. AMES AND C. J. SCHOLLENBERGER  
March 15, 1916

## PERSONAL NOTES

Dr. Charles Geiger Carroll, head of the department of chemistry at the University of Arkansas, died on February 22nd, after an illness of several months. Dr. Carroll was born in Ashland, Ky., October 15, 1875. In 1895 he entered Southwestern University, receiving the A.B. degree in 1896, and the

A.M. degree a year later. After his graduation Dr. Carroll remained at the university as an instructor in languages and science, and in 1898 was promoted to an assistant professorship in chemistry. In 1901 he entered Johns Hopkins University as a graduate student in chemistry and in 1904 the de-



gree of Ph.D. was conferred upon him. Dr. Carroll then returned to the Southwestern University as professor of chemistry, and in 1905 was called to a similar position at the University of Arkansas, where he remained to the time of his death.

Dr. L. H. Backeland, member of the Naval Consulting Board, delivered an illustrated address on "Chemistry in Relation to the War" before a meeting of the Washington Academy of Sciences held on March 23rd.

The United States Civil Service Commission announces the following open competitive examinations: *Specialist in agricultural, biological and physiological chemistry*, for men only, salary \$1,500 to \$1,800 a year, on April 5, 1916; *assistant chemist, for men only*, salary \$1,320 a year, on April 5-6, 1916.

Charles Weisman, of the United States Public Health Service, has been transferred to Pittsburgh, which is the new headquarters of the Service for work on industrial hygiene.

The Puget Sound Section of the A. C. S., in coöperation with the Manufacturers' Association, have planned a series of open meetings to outline possibilities for the establishment of new industries. The first of this series was held on February 26th at which there were short talks on the following subjects: "The Electrical Fixation of Nitrogen," by J. D. Ross; "Fisheries Products," by G. H. Stillson; "Potash from Kelp," by I. F. Laucks and H. Mahschmedt; "Potash from Mineral Sources," by G. A. Newhall; "Phosphate Rocks," by G. E. Weaver.

The University of Washington has decided to establish a Bureau of Industrial Research, the first institution of its kind on the Pacific Coast. The plans for the bureau were developed by members of the faculty and business men of the northwest. Dr. Henry K. Benson, professor of industrial chemistry in the university, has been appointed director.

The managing geologists of The Associated Geological Engineers take pleasure in announcing the opening of a New York office at 3112 Equitable Building, 120 Broadway, in charge of Frederick G. Clapp, managing geologist of the Petroleum Division. They will continue the practice of geological engineering in all its branches, with special reference to examinations and reports on oil and gas properties.

Mr. Nathan Owitz, formerly in the sales department of the Wheeler Condenser & Engineering Company, Carteret, N. J., has been elected sales manager of the J. P. Devine Company of Buffalo, N. Y. Mr. Owitz will be located at the main office and works in Buffalo.

W. A. Neill, for many years engineer of the mining department of Allis-Chalmers Company, has moved to Denver and become associated with The Dorr Company, successors to The Dorr Cyanide Machinery Company, as mechanical engineer.

Dr. George Sarton, a graduate of the University of Ghent, Belgium, and editor of "Isis," an international journal on the history of science, published in Belgium, but which had to be discontinued during the war, and who is now lecturing in this country, has been honored by the Académie des Sciences, of Paris, with the "Prix Binoux," for his researches on the history of science. Dr. Sarton recently gave a lecture to the chemical students of the College of the City of New York, at which several prominent educators and chemists were present.

Dr. Ludwig A. Thiele announces his establishment as an independent consulting chemical engineer, in the Hartman Building, Columbus, Ohio. Dr. Thiele has had seventeen years' practical experience as chief chemist, superintendent and director in the chemical industry of Germany and America.

Dr. Charles Baskerville has been appointed official representative of the American Chemical Society on the Joseph Holmes Memorial Committee. This committee is taking steps to see that a suitable memorial of the late Director Holmes,

of the Bureau of Mines, is placed in Washington. Dr. S. S. Voorhees is the alternate representative.

Dr. L. D. Ricketts, president and general manager of the Canadian Consolidated Copper Company, has been elected president of the American Institute of Mining Engineers.

A. L. Blomfield, for many years in the employ of Bewick-Moring & Company as metallurgist, and for the last eight years mill superintendent of the Golden Cycle Mill at Colorado Springs, has become associated with The Dorr Company, successors to The Dorr Cyanide Machinery Company. Mr. Blomfield has taken charge of the metallurgical consulting work for the company, with headquarters at Denver. He retains connection with the Golden Cycle Mill as general superintendent.

J. T. McGill presented a paper on "The Utilization of Waste in the Manufacture of Copper," at the February 18th meeting of the Nashville Section of the A. C. S.

Prof. M. Mason spoke on "The Electron Theory" at the March 8th meeting of the Wisconsin Section of the A. C. S.

Samuel P. Sadtler & Son, consulting and analytical chemists, have removed their office and laboratory to 210 South 13th Street, Philadelphia, Pa.

The lecture of Dr. T. H. Norton, commercial agent, U. S. Department of Commerce, entitled "The Emancipation of American Chemical Industries," which was scheduled to be delivered at the College of the City of New York, May 5, 1916, has been cancelled by orders received from the U. S. Department of Commerce.

Frederick J. Falding, the well-known chemical engineer, died in New York City on February 7, 1916.

W. H. Nichols, Jr., has been elected president of the General Chemical Company, in place of S. H. Steele, who now fills the new office of general counsel for the same firm. J. M. Goetchius has been elected vice-president to fill the vacancy caused by the advancement of Mr. Nichols.

Benjamin M. Ferguson, chemical engineer, has taken charge of the Chicago office of the Permutit Company of New York City, specialists in water rectification problems.

H. E. Howe has become associated with Arthur D. Little, Inc., of Boston. For the past eleven years he was with the Bausch & Lomb Optical Company. Mr. Howe is a chemical engineer, and is chairman of the Division of Industrial Chemists and Chemical Engineers of the A. C. S.

Mr. A. M. Douglass, formerly chemist in charge of the laboratories of the Merrimac Chemical Company and the New England Manufacturing Company, of Boston, is now engaged in the installation of the plant and process of the American Bromine Company, located at Midland, Mich.

Dr. Julius Nelson, professor of biology at Rutgers College and State biologist of New Jersey, died suddenly from pneumonia at his home in New Brunswick, N. J., on February 15th, at the age of fifty-seven years. Dr. Nelson had been a professor at Rutgers since 1888. He was called upon by the State to investigate oyster culture and bovine tuberculosis, and was a member of the New Jersey Tuberculosis Commission. He was also vice-president and consulting adviser of the Lederle Laboratories, New York City.

Among the members of the Assay Commission for the coming year, appointed by President Wilson, are Prof. James L. Howe, Washington and Lee University; Prof. Andrew C. Lawson, University of California; and Dr. F. W. Clarke, U. S. Geological Survey. The commission met February 9th to test the weight and fineness of the coins reserved by the several mints of the country during the past year.

# GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

## BUREAU OF MINES

**The Compressibility of Natural Gas at High Pressures.** GEORGE A. BURRELL AND I. W. ROBERTSON. Technical Paper 131. 12 pp. Paper, 5 cents. This paper reports on two series of compressibility tests on the natural gas which is supplied in the city of Pittsburgh. The results show that this gas differs from an ideal gas sufficiently so that the compressibility is 15 per cent greater than the theoretical at 35.5 atmospheres. The commercial significance of this is evident when one knows that many commercial measurements are made with pressures as high as 450 lbs. (30 atmospheres).

**Graphic Studies of Ultimate Analyses of Coals.** OLIVER C. RALSTON. Technical Paper 93. 37 pp. Paper, 10 cents. "This paper presents the results of a study of the most reliable published analyses of coal. The analyses are studied from several different angles, a special type of trilinear coordinates based on that proposed by Groul<sup>1</sup> for this purpose being used for plotting the ultimate analyses of coals in terms of the recalculated percentages of carbon, hydrogen, and oxygen, and the nitrogen and sulfur being ignored, as they are known to be, to some extent, organic constituents of the coal substance, but in very small amounts and varying according to no known laws."

The conclusions which are of particular industrial significance are as follows:

"The plotting of all the coal analyses available, considered as 'pure coal' (carbon, hydrogen, and oxygen), on an ash-, moisture-, nitrogen- and sulfur-free basis, on such a diagram, reveals the fact that the various grades of coal and the accepted classification fall into definite fields on the diagram.

"From the direction of evident change in composition of coals with age, it is possible to draw many deductions that agree with the experimental work of others.

"Connecting the points representing coals of equal calorific value and those of coals having equal volatile matter gives a series of lines called 'isocals' and 'isovols,' respectively, which plainly show a relation between the ultimate analysis and each of these two entities. Considerations of the probable errors in the determinations, of the plotting of the points representing the coal analyses, and of these two entities, show that the errors in plotting are probably within the total experimental errors to be encountered. A combination diagram, with the isocals and isovols crossing each other, shows the possibility of predicting the ultimate analysis from a knowledge of the calorific value and the volatile matter of a sample of coal, or *vice versa*.

"The author discusses the possibility of applying the same method to the representation of the moisture in coal, and points out the hopelessness of looking for a relation between the ultimate analysis and either the ash, sulfur, or nitrogen.

"The ternary diagram may be applied to a study of the residues from the heating of coals, etc., and to studying the problem of distillation of fuels and coking. Several new facts have been

<sup>1</sup> E. F. Groul, "The Composition of Coals," *Econ. Geol.*, **2** (1907), 225-241.

observed as to the relation of pressure, heat, and time to the analysis of the residue from heating a coal.

"An application of the diagram to the study of the oxidation and weathering of fuels results in valuable conclusions."

**Some Engineering Problems of the Panama Canal in Their Relation to Geology and Topography.** DONALD F. MACDONALD. Bulletin 86. 88 pp. Paper, 45 cents.

## GEOLOGICAL SURVEY

**The Data of Geochemistry.** F. W. CLARKE. Bulletin 616 (3rd Ed.). 821 pp. This is a revision of this well-known bulletin and includes some of the more recent data not found in the previous editions.

**Preliminary Report on the Economic Geology of Gilpin County, Colorado.** E. S. BASTIN AND J. M. HILL. Bulletin 620-M, from Contributions to Economic Geology, 1915, Part I, pp. 295-323.

**A Reconnaissance for Phosphate in the Salt River Range, Wyoming.** G. R. MANSFIELD. Bulletin 620-O, from Contributions to Economic Geology, 1915, Part I, pp. 331-49.

**Oil and Gas near Basin, Big Horn County, Wyoming.** C. T. LUPTON. Bulletin 621-L, from Contributions to Economic Geology, 1915, Part II, pp. 157-90.

**Geology and Oil Prospects of Cuyama Valley, California.** W. A. ENGLISH. Bulletin 621-M, from Contributions to Economic Geology, 1915, Part II, pp. 191-215.

**Structure of the Berea Oil Sand in the Summerfield Quadrangle, Guernsey, Noble, and Monroe Counties, Ohio.** D. D. CONDIT. Bulletin 621-N, from Contributions to Economic Geology, 1915, Part II, pp. 217-31.

**Structure of the Berea Oil Sand in the Woodsfield Quadrangle, Belmont, Monroe, Noble, and Guernsey Counties, Ohio.** D. D. CONDIT. Bulletin 621-O, from Contributions to Economic Geology, 1915, Part II, pp. 233-49.

**Shorter Contributions to General Geology, 1915.** DAVID WHITE. Professional Paper 95. 120 pp. This bulletin comprises the following papers: "Potash-Bearing Muds from Columbus Marsh, Nevada; Eocene Glacial Deposits in Southwestern Colorado; The Relation of Cretaceous Formations in Colorado and New Mexico to the Rocky Mountains; An Ancient Volcanic Eruption in the Upper Yukon Basin; The Evaporation of Artificial Potash Brines; Erosion Intervals in Eocene Time in the Mississippi Embayment; The Diffusion of Solids; The Geology of Gravina Island, Alaska; The Age of the Ocala Limestone."

**Evaporation of Brine from Searles Lake, California.** W. B. HICKS. Professional Paper, 98-A, from Contributions to General Geology, 1916, 8 pp.

**Non-Metals.** Mineral Resources of the United States, 1914, Part II. This is the consolidation of 34 advance chapters giving the statistics of production of nonmetalliferous mineral substances in the United States during 1914. The several chapters have been previously reviewed in this section.

**Gold and Silver in 1914.** H. D. McCASKEY. (General Report.) Separate 23, from Mineral Resources of the United States, 1914, Part I, pp. 829-65. Published January 20, 1916. The production of gold in 1914 totaled 4,573,000 fine ounces valued at \$95,000,000. The silver production in the same period was 72,500,000 ounces valued at \$40,000,000. These represented an increase of \$5,000,000 in the value of gold production but a decrease of approximately one-quarter million dollars in the silver value.



"In addition to the production of gold and silver from domestic sources in 1914, the domestic smelters and refineries produced as refined bullion from foreign ore, matte, and unrefined bullion, 875,250 fine ounces of gold and 39,789,129 fine ounces of silver."

The average price for silver during the year was \$0.55312.

"The figures show a steady increase of the total world's output, from \$327,702,700 in 1903 to \$466,136,100 in 1912, followed by a decrease to \$454,942,211 in 1913, and a probable further decrease to about \$453,000,000 in 1914. The indications, however, do not point to a continued decrease in 1915, for increased activity at the great Rand mines, in the Transvaal, South Africa, promises to offset the decrease probable elsewhere due to shortage of labor because of the European war or for other reasons."

**Zinc.** C. E. SIEBENTHAL. (General Report.) Separate 24, from Mineral Resources of the United States, 1914, Part I, pp. 867-919. Published February 1, 1916. "The production of primary spelter from domestic ores in 1914 was 343,418 short tons, valued at \$35,028,636, based on the average St. Louis price, as compared with 337,252 short tons, valued at \$37,772,224, based on the average St. Louis price in 1913—an increase of 6,166 tons, equal to about 2 per cent in quantity, and a decrease of \$2,743,588, equal to 7 per cent in value.

"The total production of spelter from both domestic and foreign ores in 1914 was again the largest in the history of the zinc-smelting industry of the United States, being 353,049 tons, as against 346,676 tons in 1913, an increase of 6,373 tons, or about 2 per cent. The domestic consumption was below normal, so that the stocks of 40,569 tons at the beginning of the year had increased to 64,039 tons by the middle of the year. The war in Europe, which resulted in practically shutting off their previous supplies of spelter from the allies, soon led to larger exports from the United States which amounted to 72,542 tons during the latter half of the year, and the large spelter stocks were reduced to 20,095 tons at the close of the year.

"If the average annual capacity of a retort were four tons of spelter, the production of spelter in 1914 would represent the output of 88,262 retorts, running steadily throughout the year. A canvass of the zinc smelters in December, 1913, showed 85,051 retorts then in operation on ore; there were 94,468 retorts effective for ore at the close of 1914. The mean of these two numbers would give 89,760 retorts as operating in 1914, which is very close to the number reached from the assumed retort capacity."

A full discussion of production and resource statistics is included and trade conditions as to quality are discussed. Methods for metallurgical treatment of zinc are described.

**Cadmium.** C. E. SIEBENTHAL. (General Report.) Separate 24, from Mineral Resources of the United States, 1914, Part I, pp. 921-2. Published February 1, 1916. "The chief output of cadmium comes from the zinc-producing regions of Silesia, where it is recovered as a by-product in the distillation of zinc. No cadmium is recovered in the United States in the distillation of zinc ores, but most of the output is gained from bag-house fumes of lead smelters which treat lead ores containing more or less zinc. In England a little cadmium is recovered in the purification of the solution of zinc sulfate in the manufacture of lithopone, and some has been recovered in the same way in the United States for several years. Another source of cadmium is the residues left after the manufacture of zinc chloride from low-grade zinc ores and from zinc ashes and drosses.

"The domestic production was considerably larger in 1913-14 than in any previous years and as a result the imports of cadmium were the smallest since 1903.

"The price of metallic cadmium in sticks throughout the first seven months of the year varied from 85 to 95 cents per lb. With the commencement of the war retail prices in small lots rose to \$1.15 per lb. and during the last quarter of the year some

sales were made at \$1.35 per lb. The average price per pound as based on sales was about 90 cents."

**Cobalt.** FRANK L. HESS. Separate 25, from Mineral Resources of the United States, 1914, Part I, pp. 923-4. Published February 26, 1916. No cobalt is known to have been produced from domestic ores in 1914. Most, if not all, of the cobalt used by steel manufacturers is thought to have been imported. The imports of the cobalt oxide, ore and zaffer amounted to 300,000 lbs. valued at \$275,000. No record is kept of the imports of metallic cobalt. The price of the metal appears to have varied but little during the last three years, ranging from \$1.50 to \$2.00 per lb.

**Molybdenum.** FRANK L. HESS. Separate 25, from Mineral Resources of the United States, 1914, Part I, pp. 925-6. Published February 26, 1916. "The production of molybdenum minerals in the United States has never been large, but the demands of buyers in 1914 were more insistent than before, and although the production was still comparatively small, the interest in molybdenum mining was much greater.

"The price of molybdenite reached \$2.00 per lb. for choice hand-picked material that probably carried more than 90 per cent MoS<sub>2</sub>. Poorer material sold at half the price. Wulfenite seems to have sold at 50 to 60 cents a lb. for the molybdenum oxide it contained. Marketable wulfenite ores should carry at least 25 per cent molybdenum oxide and be free from copper, vanadium, tungsten, and chromium. It is difficult to find ores free from all these impurities."

**Nickel.** FRANK L. HESS. Separate 25, from Mineral Resources of the United States, 1914, Part I, pp. 927-930. Published February 26, 1916. "No nickel ores are known to have been mined as such in the United States in 1914, but an equivalent of 845,334 lbs. of metallic nickel, valued at \$313,000, is understood to have been saved as a by-product in the electrolytic refining of copper. A part of this nickel was marketed in the form of sulfate and a part as electrolytically deposited metal. During the year the price of nickel ranged from about 35 cents to 45 cents a lb." The imports in 1914 were divided into the groups indicated below.

	Quantity	Value
Nickel, alloys, pig, bars, etc.....	106,019	\$ 42,678
Ore and matte (nickel content).....	34,989,745	4,956,448
Nickel oxide.....	3,194	1,468
Total.....	35,098,958	\$5,000,594

The United States refines much more nickel than it can use, so that, though not a large producer, it is a large exporter. The exports during 1914 amounted to 27,000,000 lbs. valued at \$9,500,000.

There is included a discussion of Canadian production which is of particular interest because of the dependence of the industry upon Canada for much of its nickel supply.

**Tin.** FRANK L. HESS. Separate 25, from Mineral Resources of the United States, 1914, Part I, pp. 931-934. Published February 26, 1916. "The only domestic production of tin in 1914 was made in Alaska and, except a small quantity produced from the lodes on Lost River, was stream tin.

"The United States is the greatest user of tin among the nations, and the imports are of course large. A very large part of the tin imported comes by way of England and Holland from the Malay Federated States and the Dutch East Indies, though at least one American company finds it advantageous to keep a buyer in the Far East to avoid payment of European profits, charges for extra shipping and handling, and possibly excessive prices due to manipulation of the market."

The world's production of tin during 1914 is estimated to have been 120,000 short tons. The price of Straits tin in New York during the year averaged 35.70 cents per lb., ranging from an average for October of 30.395 cents to an average for August of 50.595 cents.

**Titanium.** FRANK L. HESS. Separate 25, from Mineral Resources of the United States, 1914, Part I, pp. 935-936. Published February 26, 1916. "The only rutile produced in the United States in 1914, so far as known to the United States Geological Survey, was, as heretofore, that put out by the American Rutile Company at Roseland, Nelson County, Va. The company produced 94 tons of rutile carrying 95 per cent of titanium dioxide and, as a by-product, 89 tons of ilmenite, carrying about 55 per cent of titanium dioxide.

"Concentrated rutile sells for \$50 to \$400 a ton, its price depending on its purity, its form, whether crushed or pulverized, and the quantities purchased.

"A little ilmenite has been used in making ferrotitanium, but no figures showing the quantity consumed are at hand. Ilmenite is used also in electrodes for arc lamps.

"Rutile is used in electrodes for arc lamps, for making ferrotitanium for use in cast iron and steel, in ceramics, in chemicals (the principal of which is titanium potassium oxalate), and in dyeing leather and wool. Some cuprotitanium for use in copper, brass, and bronze castings has been manufactured."

**Tungsten.** FRANK L. HESS. Separate 25, from Mineral Resources of the United States, 1914, Part I, pp. 937-942. Published February 26, 1916. The returns received from the several producers indicate that an equivalent of 990 short tons of concentrates carrying 60 per cent of tungsten trioxide,  $WO_3$ , valued at \$435,000, was mined and sold in 1914. This was a reduction of 647 tons in quantity and of about \$237,000 in value from 1913.

"During the earlier part of the year prices were low, about \$6.50 per unit (a unit is 1 per cent of a ton in tungsten trioxide), and as most of the known, easily mined surface ores had been extracted, such a price offered slight inducement to the miner, so that the year's production was very low. The breaking out of the European war nearly paralyzed tungsten mining for a little while, but toward the end of the year the demand began to quicken, offers of \$9 a unit were made, and inquiries for ore became more insistent. But throughout the year prices depended on quality and quantity of ore and the urgency of the needs of buyers and sellers.

"If the countries from which statistics are unavailable produced quantities about equal to those produced during the last year for which their statistics are available, the world's production for 1914 was about 7,650 tons.

"During 1914, as shown by the figures compiled by the division of statistics, Bureau of Foreign and Domestic Commerce, the imports of tungsten-bearing ores for consumption amounted to 299 tons, valued at \$139,687, and 218 short tons of tungsten metal and ferrotungsten, valued at \$222,447."

The properties and uses of tungsten are discussed in some detail in this chapter.

**Radium, Uranium, and Vanadium.** FRANK L. HESS. Separate 25, from Mineral Resources of the United States, 1914, Part I, pp. 943-6. Published February 26, 1916. "The year 1914 was an eventful one in the industry of mining ores of radium, uranium, and vanadium, and showed by far the largest annual output yet made, amounting to 4,294 short tons of dry ore carrying 87.2 tons of uranium oxide,  $U_3O_8$ , and 22.3 grams of metallic radium. The ore was valued at about \$441,300. The ore produced in 1913 contained 41 tons of uranium oxide and 10.5 grams of radium, and that produced in 1912 contained 26 tons of uranium oxide and 6.7 grams of radium. About nine-tenths of the radium is thought to be recoverable under improved processes.

"The radium-uranium ores mined were all of the oxidized type and nearly all were carnotite ores. The only other uranium ore mined was that containing uranite.

"No vanadinite or similar ores are known to have been sold for vanadium during the year, but a number of mines in New

Mexico and Arizona shipped and sold such ores for their content of lead and silver. No radium or vanadium salts are known to have been imported during the year, though some ferrovanadium may have been imported. Oxide and salts of uranium valued at \$1,176 were imported during the year."

Tests for uranium-radium minerals and tests for vanadium are described and data are given as to the best information available regarding various constants of the three elements.

**Antimony.** FRANK L. HESS. Separate 26, from Mineral Resources of the United States, 1914, Part I, pp. 947-52. Published February 26, 1916. "During the early part of 1914 the prices of antimony were low, and when in the latter half of the year the demands caused by the European war raised them they were so unsteady that they offered little inducement to miners and prospectors to produce the ore, and none is known to have been mined and sold in the United States during the year.

"Antimony ores cannot be worked profitably at the usual prices under the high cost of labor in the mining regions of the United States unless the deposits are very large and advantageously situated, and no deposits have been found that fulfill these conditions. As a result, practically all of the antimony metal used here is imported from European, Chinese, and Japanese smelters. Most of the ores for these smelters come from China, Mexico, and France, though smaller quantities are obtained from Japan, Austria, and other countries.

"For several years the production of antimony in the United States from domestic ores has been confined to that contained in antimonial lead and the small quantities recovered in the electrolytic refining of copper and lead. A small quantity of antimony, determinable only by estimate, is produced from foreign ores."

**Arsenic.** FRANK L. HESS. Separate 26, from Mineral Resources of the United States, 1914, Part I, pp. 953-64. Published February 26, 1916. In 1914 the output in the United States of arsenious oxide amounted to 4,670 short tons (of 2,000 lbs.), valued at \$313,147. The production exceeded the largest previous annual output by nearly 49 per cent. "No white arsenic from minerals treated primarily for their content of arsenic has been directly produced in this country for several years, because the arsenic saved at the smelters as a by-product and the imported material have been so plentiful and so cheap that direct production would have been unprofitable."

A discussion of the following subjects is included in this chapter: Characteristics of arsenic, arsenic minerals, occurrence of arsenic minerals, other resources, foreign production, uses, and field tests for arsenic.

**Bismuth.** FRANK L. HESS. Separate 26, from Mineral Resources of the United States, 1914, Part I, pp. 965-8. Published February 16, 1916. "So far as is reported to the Geological Survey, bismuth ores were produced and sold as such during 1914 from only one mine in the United States."

**Selenium.** FRANK L. HESS. Separate 26, from Mineral Resources of the United States, 1914, Part I, pp. 969-74. Published February 26, 1916. "The commercial supply of selenium is furnished by the electrolytic copper refineries. Nearly all, if not all, blister copper sent to the electrolytic refineries contains some selenium, and, while the anodes are wasting away, the selenium, with tellurium, gold, silver, and other impurities, drops to the bottom of the tanks, forming the anode slimes or muds."

The selenium contained in blister coppers is shown to range from 13.7 to 170 lbs. per 100 tons, varying greatly with the source of the blister copper. The occurrence, uses and field tests for this element are described.

**Tellurium.** FRANK L. HESS. Separate 26, from Mineral Resources of the United States, 1914, Part I, pp. 975-7. Published February 26, 1916. "The tellurium of commerce is all



obtained as a by product from copper ores in which the form of the tellurium is unknown. It cannot be stated positively which mineral is the most plentiful."

It is interesting to note that combined with the gold produced in Cripple Creek since the opening of that camp in 1901, there would have been about 600 tons of tellurium made available if it had been completely recovered, assuming the ratio now known to have held good throughout the full period.

Electrolytic refining of copper can furnish, however, much greater quantities of tellurium than the gold ores.

**Mineral Production of the United States in 1914. A Summary.** H. D. McCaskey. Separate A, from Mineral Resources of the United States, 1914, Part I, 64 pp. Published February 10, 1916. This gives a brief statement for each of the minerals discussed in the full report and presents statistical summaries of the mineral production during the period. Excellent tabulated data are given for general information. Those desiring to secure a general idea of mineral statistics will find this report more valuable than the several detailed reports issued separately.

#### HYGIENIC LABORATORY

**Standardization of Disinfectants.** Bulletin 82. Paper, 10 cents. This publication gives methods for standardization of disinfectants both with and without organic matter and describes a method for the determination of the phenol coefficient of some commercial disinfectants. It is available only by purchase from the Superintendent of Documents.

#### BUREAU OF STANDARDS

**Determination of Oil and Resin in Varnish.** E. W. Bough-ton. Technologic Paper 65, issued February 19, 1916. 32 pp. Paper, 10 cents. "The proposed method for the determination of oil and resin, involving esterification by the Twitchell or Wolff methods, the use of either as solvent after esterification and correction of the figures by appropriate factors, gave results which were sufficiently accurate for practical purposes, and appears to be the best method so far devised for general use."

**Preparation of Pure Iron and Iron-Carbon Alloys.** J. R. Cain, E. Schramm and H. E. Cleaves. Scientific Paper 266, issued February 29, 1916. 25 pp. Paper, 10 cents. [See *This Journal*, 8 (1916), 217.]

**Colorimetric Determination of Acetylene and Its Application to the Determination of Water.** E. R. Weaver. Scientific Paper 267, issued February 29, 1916, 65 pp. Paper, 15 cents. "A colorimetric method for the detection of small amounts of acetylene has been developed in the course of an investigation upon the determination of small amounts of water by the use of calcium carbide. The results upon the quantitative determination of water have not been satisfactory, but a simple and very sensitive qualitative test for water is easily made."

"The method for the determination of acetylene has been worked out successfully. The determination is made by conducting the gas to be investigated into an ammoniacal solution of cuprous chloride containing gelatine and alcohol, and comparing the red colloidal solution so obtained with a suitable standard, which may be either a solution of red dye or a piece of ruby glass."

#### HOUSE OF REPRESENTATIVES PUBLIC LANDS COMMITTEE

**Exploration for and Disposition of Oil, Gas, Coal, Phosphate, Potassium, and Sodium.** Two committee reports, one favoring and one opposing passage of House Bill 406, on this subject are printed as Parts I and II of House Report 17. The hearing held early in 1914 on a similar bill of the previous Congress is available in the report of this Committee of the 63rd Congress. These documents are available through the Document Rooms of the House of Representatives only.

#### COMMERCE REPORTS—JANUARY, 1916

In a statement on the fertilizer situation in the United States, issued by the Secretary of Agriculture, the prospects of the

production of **potash** from feldspar, alunite, and kelp, are discussed. Even with increased local production of potash there will be a shortage in that available for fertilizers, owing to increased demands for potash in other industries. To remove the present difficulties in the manufacture of **superphosphates** (owing to shortage of sulfuric acid) the use of phosphoric acid, produced in electric furnaces, is urged. This process has, however, a limited application, being feasible only in localities where phosphate rock, coal and cheap water power are available. While the **nitrogen** shortage is not serious, the greater use of fish scrap and garbage tankage is urged. Experiments are also being conducted toward the production of concentrated fertilizers, such as ammonium phosphate, etc. (Pp. 20-4.)

The **flax straw** now mostly wasted in the United States is valuable for **paper stock**. (P. 37.)

In connection with the recent construction of a plant at Perth Amboy for the smelting of Bolivian **tin** ore, and subsequent electrolytic refining, a detailed description of the tin supply of the world is given, including the geology and methods of extraction and trade statistics. (Pp. 49-63.)

American **dyes** thus far imported into South China, have not proven satisfactory. The use of native indigo is increasing. (P. 83.)

The Spanish government is developing the **platinum** deposits near Malaga. (P. 89.)

The principal mineral products of China are **tin, copper, antimony and lead**. Coal and iron deposits are extensive, but not well developed. (P. 91.)

Extensive **coal** deposits in Spitzbergen are now being operated. During most of the year the temperature in the mines is below freezing so that no pumping is required. (P. 93.)

Owing to the great shortage of **bromine** in the United States, wells at Pomeroy, Ohio, and Mason City, West Virginia, which have been idle for years are again in operation. (P. 98.)

The Research Committee of the Chemical Society (of London) have now succeeded in furnishing formulae for the manufacture of all special **glass** required in various industries. (P. 115.)

The embargo on **logwood** and its extract from Jamaica, has been removed. (P. 129.)

A plant is to be erected at Hamilton, Canada, for the production of **vegetable glue**, prepared from tapioca flour, and used in veneering. (P. 135.)

The present production of **nitrate** in Chili shows a marked increase over that of 1914, and some increase over 1913. (P. 163.)

In a report by Dr. T. H. Norton (Special Agents' Series 111) upon the "Dyestuff Situation in the United States, November, 1915," it is stated that the present production of **dyes** in this country is at the rate of 15,000 tons annually as against 3,300 tons before the war. The former imports were 25,000 tons. There are 17 firms making intermediates, and 12 firms making finished dyes. (P. 179.)

Prospects for a **petroleum** industry in New Zealand are promising. (P. 186.)

A new **aluminum** factory is to be erected in Norway, with 20,000 horse-power, and an annual production of 4,000 tons of aluminum, to be made from French **bauxite**. (P. 193.)

Among unusual **fibers** now used in the Austrian textile industry are those of the common nettle, the common broom, the hop plant, and the basket willow. (P. 197.)

Statistics of the imports of **chemicals, drugs and dyes** into the United States in 1915, show a falling off compared with 1914 and 1913, except in the case of **argols and gums** which show an increase. (P. 243.)

Prices of certain **drugs** in England, especially **bromides and coal-tar products** are from 9 to 16 times normal. (P. 254.)

The Guatemala government has assumed control of all **oil lands** which will be leased. (Pp. 259, 337.)

Of the mineral products of Japan, the output of **gold, petroleum, zinc, lead and tungsten** has increased, and that of **coal, iron, and sulfur** has decreased. (P. 264.)

The principal mineral products of India are **coal, gold, petroleum, manganese ore, salt, saltpeter, and tungsten ore**. (P. 350.)

Owing to increased demands for **tanning material**, the mangrove bark industry has been established in Trinidad. (P. 357.)

In order to increase the **fiber** production of Brazil the cultivation of "*Foucroya gigantea*," is being encouraged. The fiber is being used principally for **rope**. (P. 364.)

In connection with detailed comments upon the operation of the British **pottery** regulations, it is shown that there has been a marked decrease in the number of **lead poisoning** cases in recent years. (Pp. 374-9.)

The residue obtained after the extraction of **indican** in India from the indigo plant is being used as **fertilizer** for tobacco. (P. 395.)

The **zinc refining** industry of Japan has so increased that that country will probably be independent of other countries for its supply of zinc. (P. 420.)

A plant for the electrolytic production of **caustic soda and bleach** is to be erected at Osaka, Japan. (P. 420.)

The Japanese Glycerine Company, a subsidized concern, will soon be in business. (P. 420.)

Exports of **anhydrous ammonia** from the United States to South America are increasing. (P. 422.)

SPECIAL SUPPLEMENTS ISSUED IN DECEMBER, 1915	
FRANCE—5f	PANAMA—35b
ITALY—8d	ARGENTINA—38c
SWEDEN—16c	VENEZUELA—48b
SCOTLAND—19o	FRENCH WEST AFRICA—69a
NEWFOUNDLAND—33a	MOROCCO—75a
STATISTICS OF EXPORTS TO THE UNITED STATES	
HONGKONG—88	PIEDMONT, ITALY—Sup. 8d
Chemicals	Asbestos
Earthenware	Glue stock
Metals	Glycerine
Peanut oil	Hides
Aniseed oil	Metal dust
Cassia oil	Reclaimed rubber
Paper	Talc
Sugar	MANTES, FRANCE—Sup. 5f
Tin	Glycerine
MARACAIBO—Sup. 48b	Caseln
Mangrove bark	Cork
Copaiba gum	Animal black
Hides	EDINBURGH—Sup. 19o
NEWFOUNDLAND—Sup. 33a	Fertilizers
Fish oils	Gelatine
Guano	Glue
Iron ore	Linoleum
Flint pebbles	Paper stock

# COMMERCE REPORTS—FEBRUARY, 1916

Experiments are being made in England upon the substitution of "**niter cake**" (sodium acid sulfate) for **sulfuric acid, in wool scouring, refining of grease, etc.** (P. 473.)

The Dutch government has assumed control of the distribution of all **coal** in the Netherlands. (P. 497.)

Efforts are being made to reopen **tin** mines in Austria. (P. 513.)

The **paper-pulp** industry of Japan is increasing. (P. 546.) The output of **rubber** from the Dutch Indian plantations shows a remarkable increase. (P. 564.)

Remarkable results have been obtained in England by the use of "**homogen**," a new bacterized **peat fertilizer**. (P. 594.)

Over twice the normal amount of **indigo** is now being raised in the Madras district of India. (P. 599.)

Two plants are now in operation in Columbia for the production of **tanning extract** from mangrove bark, the product being now entirely shipped to the United States. (P. 604.)

The manufacture of **thymol** in India is urged. (P. 610.)

Improvements in the methods for the production of **flax** in Canada are briefly described. (P. 611.)

Efforts are being made to develop **iron ore** deposits of Finnish Lapland, where there are large deposits of high-grade hematite and magnetite. (P. 612.)

Extension of the **oil pressing** industry of India is urged, including **castor, rape, cottonseed, linseed, poppy and mustard**. Stress is laid upon the retention of the seed cake for cattle food, thus avoiding soil impoverishment. (P. 650.)

A new Cuban **fiber**, useful, *e. g.*, for sugar sacks, is the "*malva blanca (Urena lobata)*," formerly considered a weed, but now being cultivated for fiber. (P. 715.)

The production of **thymol** from a Philippine seed "*carum copticum*" is suggested. (P. 727.)

The development of the large bone deposits of the Pribilof Islands for use as **fertilizers** is urged. (P. 728.)

Efforts are being made to increase the **asbestos** industry of South Africa. (P. 493.)

Two new **oil-bearing nuts** of the Philippines are the "*calumpang*" yielding a light yellow edible oil, and the "*balucanag (Chioschiton cumingianus)*" which yields an oil, "*cato*," useful for soap making, and also as a laxative. (P. 662.)

**Peat powder** is being used successfully for fuel in locomotives in Sweden. (P. 663.)

The **mineral output** of British Columbia shows a marked increase, especially of **copper, silver and zinc**. (P. 739.)

Western Sweden is suffering severely from a shortage of **petroleum**. (P. 742.)

A new Japanese process for **artificial silk** makes use of chrysalis oil and mulberry cellulose. (P. 745.)

A large **tin plate** factory is to be erected in Stavanger, Norway, using American equipment and management. (P. 746.)

At a conference upon the **dyestuff situation** between representatives of the Department of Commerce and representatives of the interested industries, stress was laid upon the need of coöperation between manufacturers and consumers of dyestuffs and textiles. In spite of the increased production, neither the quantity nor variety of desired dyestuffs is being made in this country. (P. 747.)

Exploration for **oil** in British Guiana is being conducted by the Government and by private parties. (P. 751.)

Switzerland is now importing large quantities of **sugar** from the United States. (P. 754.)

Among substitutes for **aniline dyes** now proposed in England are lac dye, a waste product of the **shellac** industry, and certain Indian roots. The greater use of **prussian blue** is also urged. (P. 764.)

Efforts are being made to increase the use of **seaweed** as **fertilizer** in Nova Scotia; especially to find economical methods of drying it for transportation. (P. 772.)

A detailed analysis, by districts, of the **exports from Germany** to the United States, not suitable for abstracting, is given. (Pp. 792-5.)

Arrangements have been made for the erection of a **nickel refinery** in Canada. (P. 823.)

Steps are being taken in Australia for the establishment of a **Government Institute for Research** in science and industry, laying stress on the problems connected with important existing and prospective industries. It is expected that the government will appropriate \$2,500,000 for the initiation of the enterprise. (Pp. 826-9.)

STATISTICS OF EXPORTS TO THE UNITED STATES. (Pp.)	
BRITISH INDIA—Sup. 50a	ALASKA—730
Jute	Antimony ore
Lac	Copper ore
Mica	Fertilizer
Manganese ore	Fish oil
Myrobalan nuts	Gypsum
Vegetable oils	Lead ore
Castor seeds	Tin ore
Saltpeter	Gold
Cutch	Silver
Hides	CEYLON—780
Paraffin	Rubber
CUBA—738	Tea
Copper ore	Graphite
Hides	Cocconut oil
Bones	Citronella oil
Sugar	
Wax	



## BOOK REVIEWS

**The Sampling and Chemical Analysis of Iron and Steel.** By O. BAUER AND E. DEISS, of the Royal Testing Bureau at Gross-Lichterfelde, Germany. Authorized translation from the German, by WILLIAM T. HALL AND ROBERT S. WILLIAMS, Assistant Professors of Analytical Chemistry, Massachusetts Institute of Technology. First Edition,  $5\frac{1}{2} \times 8$ . 135 illustrations. xiv + 373 pp. McGraw-Hill Book Co., Publishers. Price, \$3.00, net.

The book is divided into two parts. Part I is written by Prof. Bauer and translated by Robert S. Williams with very few changes in the text. In a general discussion, in Chapter I, the author particularly emphasizes the importance of proper sampling of iron and steel for chemical analysis. He states that "The value of proper sampling in technical work is not properly recognized or appreciated. Quite often in practice the chemist in charge, who is responsible for the accuracy of the results, has nothing whatever to say about the way in which samples submitted to him for analyses shall be taken.... Judgment based on chemical analysis alone is not always correct as the analytical results are influenced to a marked degree by the method of sampling..... Irregularities in chemical composition of the sample due to local segregation are often far greater than the possible errors of analysis..... Metallography is of the utmost value to the chemist in helping him to detect such local differences..... It is to the interest of the employer and advantage of the chemist that the following conditions be filled:

"1—The Chief Chemist should be trained in metallography.

"2—A metallographic laboratory, even though a small one, should be connected with every steel works laboratory.

"3—In all cases the taking of samples should be directly in charge of the one responsible for the subsequent analysis."

The above statements and recommendations are to the point and are consistent with the best present-day practice in the large iron and steel plants of America.

Chapters II and III, containing ten pages, are devoted to metallography wherein the author gives detailed information in regard to the proper manner of taking, polishing and etching samples preparatory for microscopical examination. In Chapter IV, containing fifteen pages, the author describes the metallographic characteristics of the constituents occurring in iron and steel, showing the different structures by photomicrographs. In Chapters V to XI, the author describes how representative samples of the different kinds of iron and steel may be taken, with special reference to conditions that make the taking of representative samples difficult. Many tables of chemical analyses are given showing segregation phenomena in the different materials. All data are clearly explained and all for the purpose of showing "To what a marked extent analytical results are dependent on the method of sampling."

Part II is written by E. Deiss and translated, with many additions conforming to laboratory practice in the United States, by William T. Hall. The author states in his preface: "In collecting these methods the main object has been to include only those methods which have been found reliable and have undergone the test of years of use at the Royal Testing Bureau. They are suitable for test and umpire analyses. Descriptions of the very rapid "Works Method" are omitted because the processes aim to give quick results rather than values of great accuracy." To this the translator in his preface adds "The work done by a number of chemists in connection with the establishment of standard samples of iron and steel by the Bureau of Standards, Washington, D. C., has shown beyond any doubt that many of the rapid methods give results which are nearly, if not quite, as good as those ob-

tained by much more laborious procedure. The translator therefore has included about twenty-five methods which are not given in the German edition."

Methods are given for the determinations of carbon, silicon, manganese, phosphorus, arsenic, sulfur, copper, nickel, cobalt, chromium, titanium, iron, tungsten, vanadium, molybdenum, oxygen and nitrogen.

The methods given, as a whole are clear and well defined. The detail is excellent, supplemented with many notes and references. To those who desire information relative to the sampling and chemical analysis of iron and steel, this book is most heartily recommended.

WILLIAM BRADY

**A Handbook for Cane-Sugar Manufacturers and Their Chemists.**

By GUILFORD L. SPENCER, D.Sc., Chief Chemist in Charge of Manufacture, The Cuban-American Sugar Company. Fifth Edition, partly rewritten and enlarged. xv + 529 pp.,  $4 \times 6\frac{3}{4}$ . 93 illustrations. John Wiley & Sons. Price, leather, \$3.50, net.

This fifth edition of Spencer's well-known handbook presents the very latest and best that has been accomplished in its special field. The many improvements which have taken place in sugar manufacture during the past decade have led the author to enlarge considerably the previous edition. Newer equipments for the sugar-house are described, fuller details are given regarding matters of factory management and the various processes employed in the manufacture of raw and plantation white sugar are treated. The chemical section of the fourth edition has also been thoroughly revised to meet the growing needs of the large sugar factories which are now being operated in the tropics. Full descriptions and illustrations of the latest apparatus for the sugar laboratory are presented and special attention is devoted to the chemical control of sugar factories and the interpretation of laboratory results. Throughout the entire book Dr. Spencer gives us the best results of his own extensive experience in factory and laboratory, the result being a finely proportioned work in which science and practice are evenly balanced.

A noteworthy addition to the new volume is the well-written chapter upon sugar refining and refinery control by G. P. Meade, Superintendent of the Cardenas Refinery, Cuba. It is by far the best presentation of the subject according to American practice that has yet appeared.

Another interesting feature of this edition is the insertion of Dr. Lippmann's Index of the 622 substances that have been used or proposed for clarifying sugar solutions. This list, so far as known, has never before been published in English.

There are but few points about the new volume which the reviewer would criticize. The typographical errors are few and unimportant. The formula for determining the volume of lead precipitate on page 178 should be corrected in order to conform with the example. It is also to be regretted that the 1915 table of atomic weights was not substituted for the 1905 table, as the later determinations have caused a considerable revision in many of the older values.

The neat compact appearance of the previous edition of the handbook has been retained. Although the number of pages has been increased from 331 to 529, this enlargement has not caused any increase in bulkiness. The new edition actually weighs 20 per cent less than its predecessor and has therefore gained in its convenience as a pocket companion.

The new work is cordially recommended as an indispensable guide to all who are interested in either the manufacture or chemistry of sugar.

C. A. BROWNE

# NEW PUBLICATIONS

By IRRENE DeMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

**Analysis:** *Einführung in der chemischen Analyse.* **LUDWIG MEDICUS.** 16th Ed. 8vo. 186 pp. Price, \$0.75. H. Laupp, Tuebingen.

**Analysis:** *Elektroanalytische Methoden.* **W. D. TREADWELL.** 8vo. 250 pp. Price, \$2.50. Gebrüder Borntraeger, Berlin.

**Assaying:** *A Textbook of Fire Assaying.* **E. E. BUGBE.** 8vo. 150 pp. Price, \$2.00. Ranger Co., Boston.

**Foundryman's Reference Book.** **J. F. BOWE.** 16mo. 92 pp. Price, \$2.50. Eagle Printing & Binding Co., Pittsfield, Mass.

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Aluminum Sulfate, high-grade.....	100 Lbs.	5.00	@	5.25
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Ammonium Chloride, gray.....	Lb.	8 1/2	@	9
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Aqua Ammonium, 16°, drums.....	Lb.	21 1/4	@	21 1/2
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ORGANIC CHEMICALS

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Starch, potato.....	Lb.	6	@	6 1/2
Starch, rice.....	Lb.	8	@	10
Starch, sago.....	Lb.	3 1/2	@	4
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Cottonseed Oil, crude, f. o. b. mill.....	Gal.	72	@	73
Cottonseed Oil, p. s. y.....	Lb.	111 1/4	@	111 1/4
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Fusel Oil, crude.....	Lb.	4.00	@	4.50
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Calcium Nitrate, Norwegian.....	100 Lbs.	—	@	—
Castor Meal.....	Unit	—	@	—
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## SPRING MEETING AMERICAN CHEMICAL SOCIETY

The Fifty-Second Meeting of the American Chemical Society was held at the University of Illinois, Urbana-Champaign, April 17th to 21st. The meeting was the largest to date, the total registration being 728 (570 members and 158 guests).

The Council met on Monday evening at 6 o'clock in the Woman's Building, where they dined as guests of the local Councilors. The dinner was served by the Department of Home Economics and was followed by the regular business meeting, which was held in the library of the new Chemistry Building. Among the various items of routine business transacted and reported directly in the *Journal of the Society*, the following are of especial interest.

Mr. Crane, Editor of *Abstracts*, reported that advance subscriptions to the number of 1,938 had been received for the ten-year index to *Abstracts*. On the basis of this report Mr. Crane was authorized to proceed at once with his plans for getting out the index. Further discussion of the details will be found in a note to be published by Mr. Crane in the next issue of *THIS JOURNAL*.

The Committee on Industrial Diseases reported that they are planning a symposium on industrial diseases for the next general meeting of the Society; the installation of plants for the manufacture of dyes has brought up several points worthy of discussion.

A committee was appointed to consider the possibility of the establishment by the Society of a publicity bureau to aid in the dissemination of correct information of a chemical character to the public through the newspapers and the popular magazines.

At the suggestion of President Herty, the editors of the *Journal of the Society* and of *THIS JOURNAL* were authorized to exchange dates of issue. As soon as the necessary arrangements can be made, *THIS JOURNAL* will appear on the first of the month and the *Journal of the Society* on the sixth of the month.

The regular opening session was held in the University Auditorium Tuesday morning. Professor W. A. Noyes introduced President Edmund James James, who welcomed the Society in the name of the University. President James outlined the history of the University, and pointed out the influence of the people of the State on the growth and development of the university departments, citing the Ceramics department as an example; the Clay Workers' Association of Illinois have been responsible for the increase of the building appropriations for this department from \$1,000 to \$150,000 in a period of eight years.

President Herty responded for the Society and contrasted the meagre appropriations ordinarily allowed by the various States with those obtained for the University of Illinois. President Herty was of the opinion that the great success of the University of Illinois was due to the broadmindedness and efficiency of the various departments and to the sympathetic attitude maintained toward the people of the State.

He emphasized the part that institutions of this sort must play in meeting the chemical problems now before the American people, one of the principal ones being the necessity of making clear to the public that the foundation of the dyestuffs industry is absolutely necessary in order that proper equipment and the trained men essential to the manufacture of explosives in case of war may be available. To meet this need the chemical departments of the various universities must necessarily expand, but the administrative heads are warned against encouraging the students to leave with Bachelor's degrees in order to accept the large salaries that will be offered for control work. For the proper development of the chemical industries and chemical science in the United States it is absolutely necessary that the number of men up for the Doctor's degree must likewise increase, since upon these men will devolve the research upon which all progressive industrial development is based.

The opening addresses were followed by the five general addresses listed in the Society program printed elsewhere in this issue.

The public lectures given complimentary to the people of Urbana-Champaign by Professor Charles L. Parsons and Doctor Curtis F. Burnam on the production of radium and its use in the treatment of cancer were well attended. The lectures were well illustrated by specimens, models and moving pictures.

On Wednesday afternoon the new Chemistry Building of the University of Illinois was dedicated, the exercises being held in the auditorium.

### ORDER OF EXERCISES

HONORABLE EDWARD F. DUNNE, GOVERNOR OF ILLINOIS, Presiding  
SCRIPTURE READING AND PRAYER, REV. GEORGE P. HOSTER, D.D., Rector  
of Emmanuel Episcopal Church, Champaign

MUSIC....."Illinois"

ADDRESS.....PRESIDENT EDMUND JAMES JAMES

ADDRESS, "THE TRAINING OF CHEMISTS," ALEXANDER SMITH, Professor of  
Chemistry, Columbia University

ADDRESS, "RESEARCH AS A NATIONAL DUTY," WILLIS RODNEY WHITNEY,  
Member of the U. S. Naval Board, Director of the Research  
Laboratory of the General Electric Company

MUSIC....."America"

The addresses by President James, Professor Smith and Doctor Whitney, with an illustrated description of the new building, will appear in the next issue of *THIS JOURNAL*. After the regular program the audience adjourned for an inspection of the Chemistry Building, and for a reception at which Mrs. W. A. Noyes, Mrs. E. W. Washburn and Mrs. Arthur W. Palmer were hostesses.

The meetings of the Divisions were held in the various lecture rooms of the Chemistry Building. All the Divisions were unusually well attended, and offered programs of exceptional interest. The programs are printed elsewhere in this issue, and a large number of the papers will appear in full in the *Journals of the Society*. Some notable features were the special program on Home Economics held by the Division of Biological Chemistry; the Symposium on the Activated-Sludge Method of Sewage Purification, offered by the Division of Water, Sewage and



SCENE AT BANQUET HALL ON WEDNESDAY NIGHT, WHEN 402 MEMBERS, DELEGATES AND WOMEN GUESTS GATHERED IN LARGE DINING ROOM IN TEMPLE

Sanitation; and the Symposium on "The Chemist and Food Control" by the Division of Agricultural and Food Chemistry.

The University of Illinois has the only brigade of college students in America, and the largest number of cadets, 2,100 men being enrolled. On Tuesday afternoon a review of the University Brigade was held on the drill grounds, and was witnessed by a large audience. The University Military Band is claimed to be the best college band in America; the complete assembly of two bands, with a trumpet and drum corps, offers a monster band of 160 to 170 pieces. The First Regiment Band of 75 pieces, which is the concert band of this organization, gave a concert in the University Auditorium at 7.30 P.M. on Tuesday. This was much enjoyed by the large audience present. It was followed by the "Get-Together Smoker" in the gymnasium. Here refreshments were served as a measure of preparedness for the rest of the evening. The entertainment consisted of novel experiments illustrating various principles such as are usually treated in the courses on physical, inorganic, analytical, organic, pharmaceutical, physiological and agricultural chemistry. The audience was invited to join in the songs and limericks, copy of which was furnished in the program. The various stereopticon views shown furnished considerable amusement.

The regular banquet was held on Wednesday evening at the Masonic Temple. The room was lavishly decorated with pink roses and pink and white carnations furnished by the greenhouses of the University.

Four hundred and two guests sat down to an elegant eight-course repast, after which President Herty proposed a toast to the University of Illinois, rendered in the single word "Pep." He then introduced as toastmaster Professor Bogert, of Columbia University, who, with his well-known humor, presented the following speakers:

GEORGE B. FRANKFORTER, Dean of the School of Chemistry, University of Minnesota.  
 LOUIS KARLENBERG, Professor of Chemistry, University of Wisconsin.  
 WILDER D. BANCROFT, Professor of Physical Chemistry, Cornell University.  
 WILLIAM B. MCKINLEY, Congressman from the Nineteenth District of Illinois.  
 HENRY P. TALBOT, Professor of Chemistry in Charge of Department, Massachusetts Institute of Technology.

The central idea of the speeches was the willingness of the American chemist to coöperate in defense of our country and the necessity for extensive application of scientific knowledge to the multitude of industrial problems now before the American people. The management of the Beardsley Hotel Company is to be especially complimented for the efficient and rapid manner in which they handled the serving of the banquet to such a large number of people.

Delicious luncheons were provided in the Gymnasium Annex on Tuesday, Wednesday and Thursday, by the Department of Home Economics. The convenience of this arrangement was greatly appreciated and the department deserves much praise for serving so many people with excellent food.

The regular Abstractors' dinner was held in the Y. M. C. A. building on Tuesday evening at 6 o'clock, the dinner being served by the management of the



Y. M. C. A. Cafeteria. Brief talks were made by Editor Crane, former Editor J. J. Miller and Dr. Bigelow.

Tuesday and Thursday afternoons from 1.30 to 4.30, and Wednesday afternoon after the dedication were given over to excursions about the buildings and grounds of the University. The visitors were divided into small groups furnished with special guides. The 16-page itinerary of excursions containing statistical data and much information concerning the various buildings and departments was found exceedingly useful and the thoughtfulness of the Illinois Section in providing them was greatly appreciated.

The College of Agriculture was an especially popular place; it runs an especially modern and efficient creamery, which contains the only dry hardening room operated by a dairy department in this country, and owns the only commercial sized condensing pan operated by any school dairy department in this country. In the Animal Nutrition and Dairy Husbandry Laboratory, charts, photographs and exhibits illustrated the cutting of beeves, the composition of feedingstuffs, the study of rations of different protein contents upon the growth and development of pigs, and the influence of different proportions of concentrates and roughages and of varying amounts of feeds upon the digestibility of cattle rations. Especial interest was shown in the exhibits of plant breeding in the crop production laboratories and pot-culture department. The experimental plots started by Professor Morrow in 1879 are the oldest in the United States. The greenhouses have a floor space of 28,000 square feet under glass, and twenty-four professional students are busy carrying out experiments, mainly on commercial fertilizers and plant diseases. In the Genetics Building are 400 cages, containing 2500 mice and rats; a total of about 10,000 mice have been raised; 33 generations consisting of 55,000 individuals of the fruit fly, *Drosophila*, have been grown; twelve experiments are being carried on relating to the different phases of heredity and variation. In the Stock Pavilion the visitors inspected representatives of the University herd, flocks, and studs, which include about 500 pure-bred beef cattle, sheep, swine and horses; several hundred fowls, ducks and turkeys; and 100 pure-bred and 80 grade cattle.

Among the other buildings visited the following deserve special mention: The Locomotive Testing Laboratory, fireproof building, 117 ft. by 42 ft., connected by a spur with the Illinois Traction System's tracks; the Ceramics Engineering Building, built of texture brick and polychrome terra-cotta, and intended to present modern achievement in the use of ceramic structural materials; the Ceramics and Mining Laboratory, containing a large kiln, a large furnace room, a mining engineering laboratory, a chemistry laboratory for the Department of Mining Engineering, and a mine rescue station equipped and arranged for training men in the methods of mine rescue work; the Physics Laboratory; Engineering Hall; the Pumping Station of the University Water Works, containing a masonry reservoir providing for the fire reserve supply and

having the various pumps, tanks and connections arranged to give opportunities for experimental work; the Laboratory of Applied Mechanics; the Electrical Engineering Laboratory; the Botany Annex; the Central Heat and Power Plant; Mechanical Engineering Laboratory; the Vivarium, intended to provide the Departments of Zoology and Entomology and the State Laboratory of Natural History with facilities for experimental work with living animals under controlled conditions; the Metal Shops; the Library Building; and the Law Building erected in 1878 as a chemical laboratory and so used until the building of the larger chemical laboratory in 1902.

In the basement of the Chemistry Building the chemical show described in our previous issue was available for visitors during the entire session of the meeting. The exhibits were as follows:

Abbé Engineering Company, New York. Laboratory ball mill, vacuum pump, model of tube mill.  
American Coal and By-Products Co., Chicago. Coal-tar products  
Armour Ammonia Works, Chicago. Anhydrous ammonia.  
P. Blakiston's Son & Company, Philadelphia. Technical books.  
Braun Corporation, Los Angeles. Analytical electrolytic outfit.  
Celluloid Zapon Co., Chicago. Lacquer materials.  
Central Scientific Co., Chicago. General laboratory apparatus  
Chattanooga Chemical Company, Chattanooga. Coal-tar products.  
Dearborn Chemical Co., Chicago. System of boiler water treatment with typical examples of flue corrosion.  
J. P. Devine Co., Buffalo. Display of photographs of chemical machinery.  
Duriron Castings Co., New York. Duriron.  
Edison Storage Battery Co., Chicago. Edison cells.  
Eimer and Amend, New York. General laboratory apparatus.  
Elyria Enameled Products Co., Elyria, Ohio. Glass enameled apparatus.  
Fairview Fluorspar Lead Co., Golconda, Ill. Fluorspar  
General Electric Co., Schenectady. The Research Laboratory exhibit from the Panama-Pacific Exposition  
Henry Holt & Company, New York City. Technical books.  
Herold China Pottery Co., Golden, Colo. Chemical porcelain.  
Laboratory Supply Co., Columbus. General laboratory apparatus  
Leeds & Northrup Company, Philadelphia. Electrical measuring apparatus.  
Room 165.  
Lenz & Naumann, Inc., New York. Chemical apparatus  
Libby Glass Company, Toledo. Chemical glassware.  
Longmans, Green & Co., New York. Technical books  
Emil E. Lungwitz, New York. Filter press.  
Macbeth-Evans Glass Company, Pittsburgh. Chemical glassware.  
Manhattan Rubber Co., Passaic, N. J. Rubber from crude state to finished products.  
McGraw-Hill Book Company, New York. Technical books.  
McIntosh Stereopticon Co., Chicago. The stereopticons used in the sessions of meeting.  
Metallurgical Chemical Engineering, N. Y.  
Mitchell Lime Company, Mitchell, Indiana. Lime products.  
Mojonnier Bros. Company, Chicago. Milk testing machinery.  
National Carbon Company, Cleveland. Electric cells and carbon specialties.  
National Lead Company, Chicago. Lead products.  
Norton Company, Worcester. Alundum.  
Palo Co., New York. Thermometers.  
The Permutit Company, Chicago. Demonstration of Permutit process.  
Pfauder Company, Rochester. Enameled tanks.  
Sarco Company, Inc., New York. Temperature regulators and steam traps.  
Schaeffer & Budenberg Mfg. Co., Chicago. Gauges and thermometers.  
Schutte & Koerting Company, Philadelphia. Chemical manufacturing machinery.  
Scientific Materials Company, Pittsburgh. Laboratory apparatus.  
Sharples Specialty Company, Chicago. Demonstration of centrifugals.  
Sowers Manufacturing Co., Buffalo. Vacuum pans, kettles, etc.  
Duplicate of exhibit at New York show.  
E. R. Squibb & Sons, New York. Chemicals.  
Standard Calorimeter Company, Moline, Ill. The Parr apparatus.  
Sweetland Filter Press Company, New York. Demonstration of filter press.  
Thermal Syndicate, New York. "Vitrosil."  
Thwing Instrument Company, Philadelphia. Pyrometers.  
Toch Brothers, New York. Paints and enamels.  
U. S. Bottlers Machinery Company, Chicago. Bottling machinery.

U. S. Metals Refining Co., Chrome, N. J. Samples of precious metals.  
 Walrus Mfg. Co., Decatur, Ill. Laboratory desks.  
 John Wiley & Sons, New York. Technical books.

Members and guests to the number of 206 left Urbana-Champaign on Friday morning at 8 o'clock for Danville. A special train was furnished by the Illinois Traction System. Members of the Chemistry Faculty and of the State Geological Department pointed out and explained the geology and the plants of interest as they were passed by the party. The cars stopped first at the Hegeler Zinc Smelter. This plant began operations in August, 1908, with 800 retorts: at the present time there are 5400 retorts in operation with a daily production of 75 tons of spelter. High-grade Joplin blende concentrates are roasted in Hegeler multiple hearth kilns, the sulfur dioxide being utilized in sulfuric acid manufacture by the lead chamber process. The acid systems have a daily capacity of 150 tons of  $\text{H}_2\text{SO}_4$  (60° Bé.). The roasted ore is mixed with anthracite slack coal and carried by belt conveyors to the charge bins in the furnace building. The distillation furnaces are of the Hegeler producer-gas fired type and have 900 retorts each. Boilers are installed upon some of the furnaces to utilize waste heat. During the morning visit all the operations connected with the beginning and end of the 24-hour cycle for each retort were seen, including drawing and casting of the zinc, removing and cleaning the condensers, removing residues from the retorts, recharging the retorts, setting up and closing the ends of the condensers.

The party was entertained in Danville by the Chamber of Commerce, who furnished a most delicious luncheon, cafeteria style, consisting of an enormous variety of cold meats, salads, relishes and sandwiches, with steaming hot coffee.

In the afternoon the parties divided, one section going to a glassworks, which is making window glass, and the other to the Carbon Hill Stripping Mine. In this mine a 5-yard steam shovel with a 90-ft. boom is operating along a face from a quarter to a half mile long, taking out a strip from 28 to 35 feet wide, with an overburden from 8 to 45 feet in thickness. The coal seam averages about six feet in thickness and the product is of good quality. Of unique interest to chemists is the pyrite washery operated at this mine, which runs through 75 tons of material per day, yielding 35 tons of high-grade pyrite. This is sold to acid manufacturers as "coal brasses" on a guarantee of 47 per cent sulfur. The company also

owns the Mission Field Mine, the oldest and most extensive stripping in the district. This was seen from the train on the return trip to Champaign: it has been worked for over 25 years and is now exhausted: underground operations are continued, however, by means of slope and drift mines.

The party then proceeded to the plant of the Western Brick Company, which manufactures a number of different kinds of brick and tile. The shale used is taken from the strata lying above the coal seam in the company's strip mine adjacent to the plant. The company has two other plants in the vicinity of Danville. In all they operate 76 kilns and have an annual production of 100 million brick.

The number of ladies at the meeting was not as large as usual. The ladies of the town and the ladies of the faculty, under the leadership of Miss Isabel Bevier, were especially active in looking after those present. On Tuesday afternoon, Mrs. S. T. Bussey and Mrs. David Kinley were hostesses at a reception in the Woman's Building; afterwards automobiles were available for excursions through the grounds. All the exercises of the regular program were attended by the ladies and their guests. On Wednesday a reception and luncheon at the Champaign County Country Club, with Mrs. B. F. Harris, Mrs. D. P. McIntyre and Mrs. Stanley Boggs as hostesses, was given in honor of the visitors. On Thursday afternoon the Woman's Building was open for inspection, and Mrs. Bartow and Mrs. Green were hostesses. The ladies present expressed themselves as not only well entertained, but considerably educated by their visit, as the Home Economics Department is an exceedingly complete and efficient one, and the Woman's Building, with its wonderfully complete equipment, offered many interesting suggestions to home-makers.

The visiting members were amazed at the efficient manner in which arrangements had been made to carry out smoothly the various features of the program; everywhere one noted the pains that had been expended on the plans to make comfortable in a small town the large number of guests present. The Local Committees, headed by Professor Edward Bartow, and made up almost entirely from the faculty of the Chemistry Department, can be congratulated on having engineered our most successful and largest general meeting and on having furnished another illustration of the executive ability of the American chemist.

## ORIGINAL PAPERS

### THE DEVELOPMENT OF LOW EXPANSION GLASSES<sup>1</sup>

BY E. C. SULLIVAN

Low thermal expansion coefficient in glass is useful mainly because it carries with it the property of withstanding sudden heating and cooling without fracture. The expansion is one of six factors which determine the ability of the glass to resist such treatment.<sup>2</sup>

This coefficient of thermal endurance is proportional directly to the tensile strength and to the square root of the heat conductivity and proportional inversely to the expansion coefficient and to the modulus of elasticity and to the square roots of the specific gravity and of the specific heat. Thanks to the pioneer work of Otto Schott of Jena, Germany, we know that the expansion can be varied over a very wide range. Disregarding quartz glass and speaking only of glasses

<sup>1</sup> Presented before the Society of Chemical Industry on March 24, 1916.

<sup>2</sup> Winkelmann and Schott, *Ann. Phys. Chem.*, **51** (1894), 730.



which can be melted and worked by the usual methods, the expansion of glass now can be varied in the ratio of six or seven or more to one. There is no reason to think that any such range is possible with respect to the other properties mentioned.

Ordinary lead glass has a linear expansion coefficient of 0.0000092 while lime glass is somewhat higher. Glasses are made without difficulty having expansions as high as 0.0000130 or 0.0000140, copper by way of comparison being 0.0000175, iron 0.000013. Going down the scale we find the Jena normal thermometer glass 19''' at 0.0000085, and Jena borosilicate thermometer glass 69''' at 0.0000064. The well-known brands of laboratory ware are made of glass having expansion from 0.0000055 to 0.0000075. A glass recently developed in America which is finding some application for laboratory ware and for culinary utensils, although the bulk of it goes into battery jars and lantern globes for railroad purposes, has expansion of 0.0000032.<sup>1</sup> This expansion is practically the same as that of the best porcelain and the glass makes a satisfactory permanent seal with porcelain. Quartz glass has an expansion of 0.0000006 to 0.0000007.

The glass maker who endeavors to reduce the expansion of his glass soon encounters the serious difficulty that as expansion decreases, fluidity is likely to decrease also. The glass of low expansion tends to become very stiff at the ordinary glass-melting temperature. This is obviated to some extent by the use of boric oxide, but this has its limitations not only because the expansion of the glass passes through a minimum and begins to increase again as the amount of boric oxide is increased, but also because boric oxide, used in large quantities, affects the stability of the glass very injuriously. One successful low expansion glass containing an unusual percentage of boric oxide was slowly but completely soluble in water. Jars of this glass  $\frac{1}{8}$  in. thick went to pieces with water in them in two or three months, while acid ate through them in a few days, and yet the glass was perfectly satisfactory for certain service and hundreds of tons of it were used.

Two glasses of equally low expansion will not, however, in general have precisely equal viscosity and it is by taking advantage of slight differences in viscosity when the expansions are alike that the most favorable relation between expansion and meltability is worked out step by step.

THE EXPANSION is measured by the method of Holborn and Day in a water-jacketed electric furnace consisting of a horizontal porcelain tube wound with resistance wire. Within the tube is supported horizontally a rod of the glass to be measured, about 3 mm. in diameter and 25 cm. long and pointed at each end. Directly beneath the pointed ends of the rod are vertical openings in the bottom of the furnace through which, by means of totally reflecting prisms, small telescopes can be sighted on the points. Cross-hairs and a micrometer screw on each telescope fix the position of the extremities of the rod and so its

length. The temperature cold is determined by means of a thermometer thrust into the end of the porcelain tube and hot by means of platinum-platinum-rhodium thermocouples which extend half the length of the tube. The temperature is carried usually to 350° C. or 400° C. and the expansion coefficient as determined is accurate to a few tenths of one per cent which is adequate for the purpose.

A more direct comparison of coefficients of thermal endurance which requires less time than the expansion measurement, is made by heating eight or ten glass rods in a vertical electric furnace to a definite temperature and then dropping the rods all at once into water by removal of the supporting asbestos slide. The temperature at which 50 per cent of the rods fracture is a figure which for purposes of comparison represents the coefficient of thermal endurance of the glass in question.

THE SOFTENING TEMPERATURE is measured by a method similar to that described by Dr. Schaller of the Jena laboratory.<sup>1</sup> A thread of glass approximately 1 mm. in diameter and 23 cm. long is suspended vertically through a small electric furnace in such a way that the thread is heated through the upper 9 cm. of its length. The temperature is raised and noted at short intervals and as the thread elongates of its own weight the movement of the lower end is read off on a scale and plotted against the time. The moment at which the thread was elongating at the rate of 1 mm. per minute is read from the curve at a glance and the temperature of the upper part of the thread at that moment is taken as the softening point of the glass. This is, of course, an arbitrary point.

This method gives us the viscosity at low temperatures and is useful in determining the sealing qualities of a glass. It does not, however, give us as much information as we should like regarding the viscosity at high temperatures, which goes far toward determining the ease of melting. Behavior when worked in a hot flame gives some indication on this point.

THE WORKABILITY of a glass depends on its freedom from tendency to crystallize, on its viscosity curve, and on its surface tension. The glasses which are most satisfactory in the hands of the glassworker are those which remain pasty through an extended range of temperature. It is this possession of a viscosity curve which is low at comparatively low temperatures and yet does not decrease rapidly as the temperature rises which gives lead glass its advantage in the construction of electric incandescent lamps and other apparatus. The lead glass after being sealed to wire or other glass as it cools remains soft to a low temperature and thus can yield to stresses caused by uneven cooling or unequal expansions and can cool without strain. Lime glass is more like a crystalline substance, which remains rigid until a definite temperature (its melting point) is reached, when it at once becomes very fluid. The viscosity curves of such glasses cross, and the lead glass which is softer, that is, less viscous than the lime glass at low temperatures, is harder or more viscous

<sup>1</sup> Sullivan and Taylor, *THIS JOURNAL*, 7 (1915), 1064.

<sup>1</sup> Abegg, "Handb. d. anorg. Chem." Bd. III, Abt. 2 (1909), 373.

at high temperatures. This is easily shown in the pull-test, which is a simple method used by the glass-worker for comparing the working qualities of glasses. The two glasses in cane or tube of the same diameter are sealed together and heated as nearly alike as possible and are then removed from the flame and slowly pulled out a few inches, the joint being first slightly blown up in the case of tube. The harder glass will have greater diameter at the joint than the softer after pulling out. This is a sensitive and very useful method for checking up the uniformity of different lots of glass. In this test as already indicated the result in the case of glasses which differ widely in composition may depend on the temperature of pulling. A lead glass which appears softer than a lime glass at low temperatures may turn out to be harder than the same lime glass if the test is made quickly when the glasses are very hot.

THE TENDENCY TO CRYSTALLIZE is determined by a method described by Schaller.<sup>1</sup> A number of small crucibles containing the glass under investigation are maintained at a low temperature favorable to crystallization for a definite time, and the proportion of cases in which crystallization begins is taken as a measure of the tendency of the glass to devitrify.

RESISTANCE TO ATTACK BY REAGENTS is most accurately measured by forming beakers of the glass and subjecting them to the solvent action of redistilled water on the steam bath. The temperature thus attained is about 80° and the usual time is 48 hours. The solution is evaporated in a small platinum dish and the residue weighed. Nonvolatile matter in the water used is determined and allowed for. Titration of the alkali dissolved instead of weighing is sometimes permissible but should be employed only for the comparison of similar glasses as the assumption is not always warranted that the alkali found is proportional to the total amount dissolved.

On the other hand, neither the alkali nor the total solids dissolved from the glass will in all cases answer as index to the serviceability for the reason that some glasses leave more opaque residue on dissolving than others do. The glass which is less soluble may become more cloudy when attacked by reagents than that which is more soluble. For comparison in this respect we find a steam digester useful with pressure at about 100 lbs.

A rapid method which has been very satisfactory consists in enclosing a short length of glass rod with 10 cc. distilled water in a steel tube provided with screw cap and maintaining at a temperature of 180° C. for 2 hrs. The alkali in the water is then titrated. Eight or ten of these tubes are run at one time.

An unexpected result when the glass baking dishes were put into service was the fact that baking took place more rapidly in them than in dishes of the ordinary materials.<sup>2</sup> Investigation developed a sufficient reason for the phenomenon but the fact was nevertheless very surprising. Metal reflects according to various authorities from 83 to 99 per cent of the radiant

heat which strikes it while glass reflects only 3 to 14 per cent. That radiation and not convection or conduction is the preponderant factor in baking was established by the following experiment:

The reflectivity of a glass baking dish was changed in part from that of glass to that of metal by silvering in a thin film on the outer surface in alternate quarters. A cake was baked in it in an ordinary kitchen oven heated by a gas flame. Where the cake had been protected by the metal coating, the bottom after baking was light-colored, sticky, and imperfectly baked, while in the other quarters it was brown and well done. As the cake was turned out bottom up the quartering was plainly visible on it.

CORNING GLASS WORKS  
CORNING, N. Y.

## A RAPID METHOD FOR THE DETERMINATION OF SOLUBLE NITROCELLULOSE IN GUNCOTTON

By H. C. MALLINSON

Received December 21, 1915

According to the British Government specifications the determination of soluble nitrocellulose in guncotton is conducted as follows:

"Four grams of dry guncotton are shaken up with 200 cc. of ether alcohol every 15 minutes for about 6 hours and then allowed to settle. When the solution above the guncotton is clear, 75 cc. are transferred to a small weighed flask, the solvent evaporated, and the residue dried until constant in weight, at a temperature not exceeding 65° C."

This method, which may be styled the evaporation method, is, to say the least, extremely tedious; and what is of more importance, it is not at all accurate owing to the occlusion of solvent which cannot be driven off. A step in the right direction is the method used by some analysts in which water is added to the solution before evaporating. This "indirect precipitation" method is as tedious and takes a little longer time than the regular evaporation method, although the results are lower, denoting greater accuracy, for it is obvious that if none of the ether alcohol-soluble matter is lost, the lower the results the greater the accuracy.

It is our practice at the laboratory of the smokeless plant of the American Powder Mills, to determine solubilities by what may be called the "direct precipitation" method, which is not only much quicker but gives more accurate results.

Some comparative data (percentages) on different samples show interesting results:

Sample No.	British Specification Evaporation Method	"Indirect Precipitation"	"Direct Precipitation"
1.....	7.30	7.20	7.00
2.....	9.30	8.56	8.40
3.....	20.00	19.22	18.82
4.....	25.05(a)	24.26	23.82

(a) Obviously the error in the evaporation method increases as the solubility rises. By applying a correction, solubilities may be found by precipitation and made to agree closely with results obtained by evaporation.

The following results show that repeated determinations are fully as satisfactory by the direct precipitation method as by the other methods, the same sample of cotton giving:

Direct Precipitation Method 2b	"Indirect Precipitation"	Evaporation Method
16.84	17.20	18.08
16.84	17.66	18.16
16.88	17.36	18.10

<sup>1</sup> Loc. cit.

<sup>2</sup> Sullivan and Taylor, *Loc. cit.*



The evaporations were all conducted at the same time and under identical conditions. I am of the opinion that if they were evaporated under different conditions of heat and humidity, these results would not check quite so well, while with our method there is no chance for conditions to play a part.

Another sample, treated according to each of the three methods quoted below, gave these results:

Method Number. . . . .	1	2a	2b
Percentages. . . . .	11.36	11.28	11.34

We carry out the direct precipitation method as follows:

A 5-gram sample (or if the solubility is known to be 25 per cent or higher, a 2-gram sample) is treated with 200 cc. of ether alcohol in a 200 cc. graduated cylinder. After settling, 50 cc. of the supernatant liquid are transferred to a porcelain dish of 650 or 700 cc. capacity. About 500 cc. of water at a temperature of 75 or 80° C. are slowly poured down the inside of the dish. This completely precipitates the dissolved cotton and the last traces of solvent are driven off by submerging with a glass rod the floating disk of cotton. The appearance of the precipitated mass determines the next step.

1—*Precipitate consists of one mass or disk (or one disk and a few small particles of cotton which may be added conveniently to the disk with forceps).* The disk is removed and laid as flat as possible on a piece of filter paper which has been marked with the sample number, and rests on a folded towel or some other absorbent material. The sample is now moistened with alcohol to shorten the time necessary for drying, covered with another filter paper, and the towel folded over all. By pressing with the hand the disk is dried to such an extent that drying in the oven occupies but a very short time, about 20 minutes at 160° F. if the sample is not large. The top filter paper is removed before drying, the lower one with the sample being placed in the oven until curling and crispness indicate dryness. The sample is then transferred to the balance and weighed directly. (*Wt. in grams  $\times$  80 = Per cent solution.*)

2—*Precipitate does not hold together and (1) is impractical.* (a) Counterpoise two filter papers of convenient size, fold, and place one within the other, putting both in a funnel. The mixture of water and precipitate is poured onto the filter, any traces adhering to the sides of the dish being freed by a policeman. The dish is then rinsed with alcohol, and the alcohol poured onto the filter so that it washes the cotton down into the apex of the cone. The filters are removed from the funnel, flattened out by pressing between the folds of a clean towel, then removed to the oven. When dry, the sample is weighed by placing the outer filter paper on the weight side of the balance. Thus the weight is found directly.

(b) A quicker and very exact method is to use a tared metal or porcelain Gooch crucible. Ordinarily this will suffice to hold the precipitate without any trouble whatever, and the bulk of the water may be poured through first. But if this seems inadvisable in certain cases, the largest mass may be transferred

to the crucible, carefully covering the perforations; it then acts as an excellent filtering medium, retaining the smaller particles when the remainder is poured through. The filtrate should be caught in a clean beaker and examined to make sure that it is free from precipitate. The mass is moistened with alcohol, the crucible placed on a clean folded towel, and the cotton is pressed first against the side of the crucible with a glass rod, then down on the bottom, somewhat after the manner of making a Munroe crucible. In the case of an isolated sample, or when the cotton has been badly separated, a Munroe crucible may be used to good advantage.

Cotton treated by the direct precipitation method has much greater stability than when evaporated from an ether alcohol solution, and will stand a temperature of 170° F. without loss of weight long after it is dry.

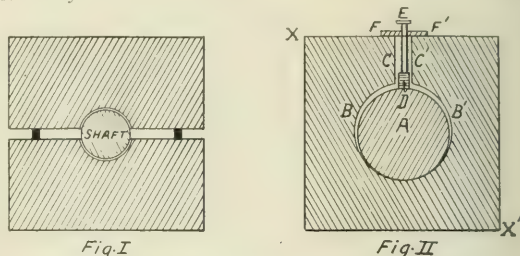


Fig. II: X, X'—Cross-section of bar. A—Cylinder-section in place. B—Hole in the bar through which the cylinder is inserted. C—A 1/2 in. hole at a right angle to B. D—A loose-fitting rubber plunger. E—Screw for forcing plunger against A. F—Metal plate screwed to bar, threaded to fit screw E.

We usually have results in half an hour after drawing off the clear liquid, or in an hour and a half after the dry cotton is put into the cylinder and the solvent added. Complete solution of the soluble matter is effected in less than an hour by placing the flasks in a revolving apparatus, instead of taking 6 hours when shaken 4 times per hour by hand. A revolving shaking apparatus may be obtained from any chemical apparatus dealer (e. g., Eimer & Amend, No. 6148). If the revolutions are 6 per minute, then the flask is inverted 360 times in an hour, more agitation than it would get by hand-shaking in 6 hours.

We obtain the same results by attaching two box-like containers to the shaft of a water-wheel as in Fig. I. The cylinders are held in place with straps, and the wheel revolves five or six times per minute.

An excellent apparatus for the purpose may be made from a 3-in. diameter wooden bar. Holes slightly larger than the diameter of the cylinders are bored along the length of the bar, alternating at right angles to each other; if bearings are provided at the ends one may be furnished with a handle for hand turning, and the other with means for attaching to or connecting with a motor. (small electric or water) arranged to give from five to ten revolutions per minute. Fig. II shows a way by which cylinders may be quickly inserted and held firmly in place. This can be easily made by any mechanic, and is quite as convenient and easy of operation as one obtained at greater expense.

## OXYGEN DEMAND OF SEWAGES

By F. W. BRUCKMILLER  
Received December 6, 1915

During a recent investigation<sup>1</sup> of the sewage disposal plants of the state, the nitrate method for oxygen demand was used in preference to the modified English dilution method, for the following reasons:

- I—It is more easily manipulated.
- II—It lends itself better to field work.
- III—It is not open to any great errors in manipulation.

The modified English dilution method<sup>2</sup> consists in making dilutions of the sewage in question with aerated distilled water, incubating at 20° C. for 10 days, determining the residual oxygen, and, from that dilution in which between 30 to 60 per cent of the oxygen is used up, the oxygen required for the sewage is calculated. Since each sewage is different from every other one, that dilution which will work for one sewage will not always work for another. A preliminary series of dilutions must, therefore, be made in each sewage in order to determine the proper dilution. This requires time and considerable equipment, both of which were lacking in the work under discussion. Furthermore, considerable laboratory apparatus is required to make the dilutions as well as the oxygen determinations, all of which must be made in the field where the sample is collected.

The nitrate method<sup>3</sup> on the other hand adapts itself to field work. No dilutions are necessary which, as has been previously shown, are a great source of error in the English method.<sup>4</sup> In an unknown sewage, Lederer<sup>5</sup> advocates that varying quantities of NaNO<sub>3</sub> equivalent to 100, 130, 160, 190, 210 and 240, P. P. M. (I. O.) be added to a constant quantity of sewage and that the sample which remains sweet and free from sediment be taken as the one containing the proper quantity of oxygen. From the residual nitrate and nitrite present, the oxygen equivalent can be readily calculated. At most, this procedure requires 6 bottles. Instead of adding varying quantities of NaNO<sub>3</sub>, an excess can be added to one bottle and the presence of nitrate be indicated by methylene blue. This was the procedure adopted in our work, after we had satisfied ourselves that the excess NaNO<sub>3</sub> had no effect on the biological action during incubation. The results obtained were quite gratifying. No determinations need be made in the field. After incubation, the samples can be chloroformed and sent to the laboratory for examination. This in itself is a great feature in favor of the nitrate method for oxygen demand in field work.

Because of the manipulations through which the sewage must go in the English method, it is open to many grave errors. In the first place, in making the dilutions, aeration results unless great care is exercised. Oxygen is lost during incubation through leaky stoppers. Gases invariably collect under the glass stoppers and escape when the stopper is removed

to introduce reagents. That oxygen is lost in this way has been shown by a number of investigators.<sup>1</sup> Only when the dilution is such that the same percentage of oxygen is used up in each sample do the results coincide very well. To get this dilution each time is rather difficult and constitutes one of the greatest objections to the dilution method. Lastly, errors in the oxygen determinations are possible. Unless all the organic matters and nitrites are removed, accurate results are not possible.

The simplicity of the nitrate method eliminates any errors due to manipulations. Its great source of error lies in the determination of large quantities of nitrites and nitrates. An error in the determination of the latter is of more concern than in the former, since the former are seldom present in quantities greater than 5 P. P. M. An error of 1 P. P. M. in the nitrite would, therefore, not seriously affect the results, producing, as it were, in oxygen equivalent, an error of only 1.7 P. P. M. of oxygen which is well within limit of error on sewages that demand 300 P. P. M. of oxygen. By making the dilutions carefully with respect to the nitrates and using the phenol-disulfonic acid method for their determination, reasonable accuracy can be assured.

Because of these considerations, the nitrate method was used in all the oxygen demand determinations connected with our sewage investigations.

The sewages with which we worked were all domestic sewages from small towns. Partial analyses of a few typical sewages are given in Table I.

TABLE I. RESULTS EXPRESSED IN PARTS PER MILLION

No.	—SOLIDS—			NITROGEN		Oxygen consumed	Chlorine consumed	Oxygen demand
	Total	Volatile	Suspended	Free NH <sub>3</sub>	Or gaseous			
630	734	446	120	70	80	...	88	142
131	800	458	172	20	30	...	70	220
317	974	344	376	5	35	700	105	297
528	482	304	58	16	50	112	72	63
572	814	546	96	8	25	220	68	75
407	1638	992	476	16	35	650	230	89

A two weeks' stay was made at each town. A portable laboratory permitted the estimation of oxygen consumed, chlorine and oxygen demand, together with a number of engineering observations. Composite samples were sent to the laboratory at Lawrence, where the solids and the nitrogen content were determined. As only one man made the trips it was necessary to simplify the work as much as possible. This factor more than any other led us to use the nitrate method in preference to the dilution method for oxygen demand; not, however, until we convinced ourselves by experiments herewith related and also by those of others that the results from the nitrate method could be depended upon.

For nitrate procedure we filled a 250-cc. bottle through a funnel with settled sewage, overflowing half in order to get rid of all the air in the bottle. The nitrate solution was of such a strength that 2 cc. were equivalent to 500 P. P. M. of oxygen. The samples were incubated at 20° for 10 days. Such a quantity of sewage was taken for estimation of nitrates that a reading of about 30 on the colorimeter was always obtained.

<sup>1</sup> Lederer, *Am. J. Pub. Health*, 6, 355, also Lederer, *This Journal*, 6 (1914), 887.

<sup>2</sup> Under the direction of the State Chemist Research Dept. and Sanitary Engineering Dept., of Kansas.

<sup>3</sup> *This Journal*, 6 (1914), 884.

<sup>4</sup> *J. Infect. Dis.*, 14, 482.

<sup>5</sup> *This Journal*, 6 (1914), 886.

<sup>6</sup> *J. Infect. Dis.*, 14, 485.



In general, we secured consistent results. Once in a while anomalies would occur; that is, we would obtain results which were entirely out of harmony with the other values. These errors were mostly plus in character and were attributed to an ununiform mixing of the sample of sewage. Rarely was a determination lost and then only due to carelessness or technical errors. Some samples went foul the third or fourth day when experience had shown that they contained enough nitrate to keep them sweet at least 10 days. These "freak" results were also attributed to poor mixing of the sample, or the presence of an undue amount of organic matter in suspension. In general, however, the method worked quite smoothly and gave consistent results all through the work.

Before the investigation began, some preliminary work in the laboratory was done, the results of which strengthened the conclusions above noted. In connection with other collaborators of Dr. Lederer on the English method, we endeavored to find the best dilution and also a value at 5 days from which the absolute value of oxygen demand could be calculated. This we found not to be feasible. The results in Table II show no agreement whatsoever in the various dilutions. One would expect the error in a 1 per cent dilution not to be any more than twice as large as the error in a 2 per cent dilution. Our experience, as the table shows, has been contrary to this supposition. A method whose results vary so with each dilution employed requires, in our judgment, some further study in order to determine the reason for the deviations.

TABLE II—EFFECT OF VARYING DILUTIONS OF SEWAGE INCUBATED AT 20° C.

Per cent Sewage in Mixture	Incubation Days	Oxygen Absorbed in Diluted Sewage		Ratio of Oxygen Absorbed in 5 : 10 days	Oxygen Absorbed (Basis of Sewage)	
		P. P. M.	Per cent		P. P. M.	Per cent
0.36	1	0.4	5.55	..	111.1	5.25
	2	0.0	0.00	..	111.1	5.25
	3	0.6	7.90	..	166.6	7.89
	4	0.6	7.90	..	166.6	7.89
	5	1.1	14.42	68 Per cent	305.5	14.47
	6	1.4	18.40	..	511.1	24.20
	7	1.6	21.05	..	584.0	27.66
	8	1.6	21.05	..	584.0	27.66
	9	1.6	21.05	..	584.0	27.66
	10	1.6	21.05	..	584.0	27.66
1.00	1	1.6	21.05	..	222.2	10.54
	2	1.6	21.05	..	222.2	10.54
	3	1.6	21.05	..	222.2	10.54
	4	1.6	21.05	..	222.2	10.54
	5	1.6	21.05	51 Per cent	222.2	10.54
	6	2.2	28.94	..	305.8	14.47
	7	2.2	28.94	..	305.8	14.47
	8	2.6	34.21	..	361.3	17.20
	9	2.6	34.21	..	361.3	17.20
	10	3.1	40.79	..	431.0	20.40
2.00	1	3.8	50.00	..	211.0	10.00
	2	4.6	60.52	..	255.5	12.10
	3	5.1	67.10	..	283.2	13.43
	4	5.4	71.05	..	299.5	14.20
	5	5.6	73.68	93 Per cent	310.3	14.72
	6	5.8	76.31	..	322.2	15.56
	7	5.8	76.31	..	322.2	15.56
	8	5.8	76.34	..	322.2	15.56
	9	6.0	78.94	..	333.5	15.80
	10	6.0	78.94	..	333.5	15.80

Using a known sewage, comparisons of both methods of procedure of the nitrate method were made. The results contained in Table III confirm those published by Lederer.<sup>1</sup> Those in Method A were obtained by adding varying quantities of  $\text{NaNO}_3$  to the sewage, and noting the one which just remained sweet. Those in Method B were obtained by adding an excess of  $\text{NaNO}_3$  and 0.4 cc. methylene blue to just one bottle of sewage. All determinations were made after 10

days' incubation at 20° C. in 250 cc. glass stoppered bottles.

TABLE III—OXYGEN DEMAND (P. P. M.) BY NITRATE METHOD  
A—By adding excess  $\text{NaNO}_3$   
B—By adding 10 cc.  $\text{NaNO}_3$  (26.56 g. per liter)

Trial No.	1	2	3	4	5	6	7	8	9	10
Method A	300	265	250	310	287	326	297	269	307	278
Method B	310	270	248	308	290	320	300	265	310	275

The agreement in Table III shows that the excess of  $\text{NaNO}_3$  does not affect the biologic process upon which the loss of oxygen depends. From this we decided that the addition of excess  $\text{NaNO}_3$  to the sewage would give us as reliable results as the use of varying concentrations would.

In order to see whether the two methods, the excess nitrate and the dilution method, gave results of close agreement, the two were tried on a known sewage. For the dilutions, aerated distilled water with a temperature of 20° C. was used; 250 cc. bottles were filled to overflowing and 3 cc. of sewage added near the bottom of the bottle. After mixing they were incubated for 10 days at 20° C. The Rideal and Stewart<sup>1</sup> procedure was used. Thirty-five per cent of the oxygen was absorbed at the end of 10 days.

TABLE IV—COMPARISON OF OXYGEN DEMAND (P. P. M.) BY THE NITRATE AND THE DILUTION METHODS, INCUBATING AT 20° C.

Trial No.	Dilution Method	Nitrate Method	Trial No.	Dilution Method	Nitrate Method
1	305	301	11	293	298
2	298	285	12	298	296
3	301	299	13	307	303
4	310	312	14	290	285
5	302	304	15	310	306
6	285	283	16	288	293
7	297	294	17	296	300
8	289	285	18	298	293
9	300	298	19	302	299
10	294	291	20	289	294

Aside from the fact that the nitrate results are consistently lower than the dilution results, the two determinations agree fairly well. In fact, they agree well enough for all practical purposes, and strengthened us in our decision that the nitrate method would give satisfactory results in the field; also they are in strict accord with those obtained by Lederer.<sup>2</sup> Furthermore, our experience has confirmed this decision, and after a year's trial, we conclude that the nitrate method is far better adapted to field work than the modified English dilution method.

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## A COMPARISON OF THE PERMANGANATE METHODS FOR THE DETERMINATION OF REQUIRED OXYGEN

By JOHN H. SACHS

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As the determination of required oxygen is of very great importance in the examination of waters, it was thought that it would be well to look into the methods in use for the same and to choose from among them the one that seemed to give the best results. It was realized at the start that the method is not quantitative, and that the results obtained are only comparative. On the other hand, were a large number of waters examined in exactly the same way, the

<sup>1</sup> Analyst, 26 (1901), 141.

<sup>2</sup> Loc. cit.

<sup>3</sup> Fleck, Z. angew. Chem., 1889, 580.

results would surely show the relative quantities of oxidizable matter present.

As early as 1851, Forschammer<sup>1</sup> began using a dilute solution of potassium permanganate for the oxidation. He proceeded by simply adding this to one liter of the water under examination until a faint pink color persisted for one-half hour. From this method has sprung the many methods now in use. These methods may be divided into two classes: (1) *Oxidation in acid solution*; (2) *Oxidation in alkaline solution*. These methods have been further modified according to the time taken for the oxidation, the temperature at which the oxidation is carried out and the amount of permanganate used for the oxidation.

#### OXIDATION IN ACID SOLUTION

The KUBEL<sup>2</sup> method is as follows: To 200 cc. of the water to be examined there are added 10 cc. of dilute  $H_2SO_4$  (1 : 3). To this, when heated to boiling, there is added from a burette a standard dilute solution of the permanganate until a decided color remains. The boiling is continued ten minutes with the addition of more permanganate if the color tends to fade out. Standard oxalic acid solution is then added until the pink color has completely disappeared. The excess of oxalic acid is then titrated with the standard permanganate solution. The difference between the total amount of permanganate used and the permanganate equivalent to the oxalic acid added, gives the amount of permanganate reduced. Correction must be made for ferrous salts, nitrites or hydrogen sulfide, if they be present.

KOBRIKH<sup>3</sup> recommends that the permanganate solution be made by dissolving 0.5 g. of the salt in one liter of water; after the addition of 150 cc. pure concentrated  $H_2SO_4$ , the whole is heated at 90° for 3 hrs. in a flask with a long neck. The solution is then standardized with oxalic acid. 100 cc. of the water to be tested are then mixed with 50 cc. of the permanganate solution and 15 cc.  $H_2SO_4$ . This is heated in the same kind of flask as was used above at 90° for 3 hrs. He points out that chlorides must be removed and corrections made for nitrites present.

TIDY'S<sup>4</sup> process differs from the rest in that the oxidation is carried out at ordinary temperatures. He recommends the use of 250 cc. of the water; to this is added 10 cc.  $H_2SO_4$  and 10 cc.  $KMnO_4$ . After standing in a stoppered bottle for 3 hrs. at ordinary room temperature an excess of KI solution is added, and the iodine liberated titrated with thiosulfate. A blank experiment in which recently distilled water is used is also made.

THRESH'S<sup>5</sup> METHOD—250 cc. of the water to be examined are placed in a flask fitted with a stopper. To this are added 10 cc.  $H_2SO_4$  and 10 cc. of a permanganate solution, of such strength that 1 cc. = 0.1 mg. available oxygen. The stopper is then inserted and the flask with its contents incubated for 3 hrs. at 37°. If the pink color tends to fade out, more of the permanganate solution is added. After 3 hrs. the flask is cooled, 1 cc. of a 5 per cent KI solution added and the iodine liberated titrated with thiosulfate. While the water to be tested is incubating, a blank test is run. The ferrous salts, nitrites, etc., are at first determined by finding how much oxygen is consumed in 5 min. at 37°.

#### OXIDATION IN ALKALINE SOLUTION

SCHULZE'S<sup>6</sup> PROCESS—100 cc. of the water are placed in a

flask of 300 cc. capacity. One-half cc. NaOH solution (2 : 1) is added and from a burette 10 cc. of standard permanganate. After boiling 10 min. the contents of the flask are cooled to 50–60°. 50 cc.  $H_2SO_4$  (1 : 3) are then added and from a burette 10 cc. of a standard solution of oxalic acid. The procedure from this point is similar to that of the Kubel method.

#### EXPERIMENTAL

To choose from among these methods the following series of determinations were carried out, using water solutions of certain organic compounds. The solution of permanganate used was of such a strength that 1 cc. = 0.1 mg. available oxygen.

ACID SOLUTION—100 cc. water + 15 cc.  $KMnO_4$  + 10 cc.  $H_2SO_4$  (1 : 3)  
ALKALINE SOLUTION—100 cc. water + 15 cc.  $KMnO_4$  + 1 cc. NaOH (1 : 1)

Acid	TREATMENTS	Alkaline
I	Boiled in Erlenmeyer beaker 10 minutes (Kubel).....	V
II	Heated in Erlenmeyer beaker 85° for 1 hour.....	VI
III	Incubated in closed flask 37° for 3 hours (Thresh).....	VII
IV	Allowed to stand in closed flask at ordinary temperature for 3 hours (Tidy).....	VIII

After treating as above, the flasks were quickly cooled to 10–15°. The alkaline solutions were acidified with  $H_2SO_4$ . An excess of KI was added and the iodine liberated titrated with thiosulfate. Both the thiosulfate and the permanganate solutions were frequently standardized. The results, expressed in mg., of oxygen consumed by 100 cc. of the water are given in Table I.

TABLE I  
Results in Mg. Oxygen Consumed per 100 cc. Water

Treatment:	ACID SOLUTIONS				ALKALINE SOLUTIONS			
	I	II	III	IV	V	VI	VII	VIII
1 Lactose.....	0.547	0.592	0.110	0.033	0.505	0.473	0.309	0.272
1 Glucose.....	0.641	0.652	0.054	0.027	0.587	0.641	0.543	0.415
1 Sucrose.....	0.783	0.739	0.096	0.020	0.620	0.636	0.488	0.317
1 Urea.....	0.086	0.092	0.023	0.017	0.081	0.083	0.038	0.040
1 Dried Egg Alb.....	0.400	0.483	0.156	0.173	0.415	0.461	0.254	0.161
1 Starch.....	0.571	0.334	0.027	0.016	0.415	0.312	0.178	0.108
1 Agar.....	0.613	0.505	0.046	0.035	0.397	0.402	0.161	0.127
1 Gelatine.....	0.119	0.178	0.037	0.033	0.359	0.312	0.175	0.119
1 Dried Milk.....	0.690	0.837	0.072	0.028	0.524	0.520	0.236	0.212
5 Dried Egg Alb.....	0.908	1.100	0.377	0.484	0.923	0.953	0.496	0.358
5 Gelatine.....	0.242	0.552	0.100	0.077	0.808	0.729	0.407	0.422
5 Lactose.....	1.500	1.500	0.138	0.033	1.183	1.131	1.050	0.888

It is at once seen that at the high temperatures the most oxygen is consumed. It will also be noticed that there is little difference in the results at 85° and 100°. At the lower temperatures, especially in the acid solutions, the consumption of oxygen is much smaller. In almost every case the oxygen consumed at ordinary temperatures is less than that consumed at 37°. In Methods VII and VIII the solution usually took on a green color, due to the formation of  $K_2MnO_4$ . These methods were, therefore, discarded. In Methods V and VI there was usually a larger quantity of the  $MnO_2$  separated than in any other method. This<sup>1</sup> acts catalytically to reduce more  $KMnO_4$ . Grünhut<sup>2</sup> has shown that the presence of Mn in water introduces quite an error by these methods. For these reasons the alkaline methods were discarded.

Another set of experiments was then arranged in which the oxidation of 100 cc. of water was carried out in Erlenmeyer flasks two ways: (1) heating for 1 hr. at 85°, and (2) incubating for 3 hrs. at 37°. Here the amount of  $KMnO_4$  was varied. The results of these experiments are shown in Table II.

From these results, it can be seen that at the higher temperatures the more  $KMnO_4$  used for the oxidation, the more oxygen is consumed. At 37° there is little

<sup>1</sup> Fresenius, *Z. anal. Chem.*, **2** (1863), 425.

<sup>2</sup> Braun, *Ibid.*, **6** (1867), 253.

<sup>3</sup> Kobrich, *Chem.-Ztg.*, **11**, 4.

<sup>4</sup> Tidy, *J. Chem. Soc.*, **35** (1879), 66.

<sup>5</sup> Thresh, "Examination of Water and Water Supplies," **1913**, 309.

<sup>6</sup> Trommsdorff, *Z. anal. Chem.*, **8** (1869), 350.

<sup>1</sup> Noll, *Z. anorg. Chem.*, **24** 1911, 1809.

<sup>2</sup> Grünhut, *Z. anal. Chem.*, **52** 1913, 36.



TABLE II  
 Results in Mgr. Oxygen Consumed per 100 cc. Water

1 Hour—88	15 cc	20 cc	25 cc	30 cc	40 cc
KMnO <sub>4</sub> Solution					
5 Gelatine.....	0.552	0.697	0.821	0.872	0.952
5 Dried Egg Alb.....	1.100	1.293	1.425	1.526	1.790
5 Dried Milk.....	1.500	1.850	2.142	2.336	2.706
Sewage No. 1.....	1.352	1.452	1.588	1.786	2.094
Sewage No. 2.....	1.228	1.415	1.530	1.655	1.730
Sewage No. 3.....	1.082	1.280	1.422	1.605	1.675
City tap water.....	0.372	0.440	0.461	0.482	0.527
3 Hours—37°					
5 Gelatine.....	0.100	0.103	0.108	0.123	0.140
5 Dried Egg Alb.....	0.549	0.539	0.565	0.618	0.670
5 Dried Milk.....	0.460	0.475	0.490	0.494	0.477
Sewage No. 1.....	0.426	0.452	0.444	0.459	0.431
Sewage No. 2.....	0.435	0.460	0.440	0.473	0.455
Sewage No. 3.....	0.455	0.633	0.490	0.482	0.473
City tap water.....	0.155	0.160	0.162	0.178	0.182

difference in this respect. This makes it quite clear that in comparing results of oxygen consumed at high temperatures, only those results can be compared that are obtained by a method in which the same amount of permanganate is used for the oxidation. This is a very important point. However, at 37°, the amount of KMnO<sub>4</sub> used for the oxidation plays no large part and hence such results can be compared no matter whether or not the same amount of permanganate is used.

Although the presence of chlorides interferes with the determination of oxygen required in acid solution, the 37° acid solution method of Thresh seems best. The chlorides can be readily removed by Ag<sub>2</sub>O and hence offer no great difficulty.

CITY HEALTH DEPARTMENT, BALTIMORE

## ESTER GUMS OR ARTIFICIAL RESIN ESTERS

By CHARLETON ELLIS AND LOUIS RABINOVITZ

Received February 2, 1916

The neutralization of acid resins for use in varnishes where the acid character of the resin is detrimental to the quality of the varnish is a problem that has engaged the varnish chemist for a long time. The tendency of acid resin varnishes to "liver" or thicken is a phenomenon that frequently occurs in the case of the so-called enamels or varnishes containing metallic oxides and is one of the greatest difficulties encountered by varnish chemists in the preparation of colors ground in a varnish vehicle. In order to obviate this difficulty it has been the practice among the manufacturers of varnishes to use gums relatively low in free acid such as Kauri and others, which, however, cannot be employed in the cheaper enamels and other similar coating compositions, owing to the comparatively high cost of these gums.

The hard varnish gums for years past have been growing scarcer and more expensive, and the only really abundant source of resin is common rosin. The latter is too soft for use in high-grade varnishes, while in grinding varnishes the acid of the rosin combines with the pigment and makes the product thick or even solid after it has stood a considerable time. Grinding varnishes constitute one-fourth to one-third of the total volume of business of many varnish houses; hence the preparation of a varnish which is stable to basic pigments is an important matter.

**LIME TREATMENT**—One method of treating rosin is to heat it with lime which neutralizes some of the acidity and has a hardening effect. It is not feasible

to use enough lime to make a neutral product as the material would be insoluble in oil and turpentine. Highly limed varnishes do not stand outside exposure satisfactorily.

This condition of the resin market has led to the careful scrutiny of the products known as rosin esters or ester gums which are prepared by esterifying ordinary rosin or similar resin with glycerine and th like. These rosin esters are soluble in oil and turpentine and have been found fairly free from the objection of "livering" or thickening with basic pigments. For a time the consumption of such esters was small but as their value came to be appreciated by the varnish manufacturer the demand increased and has now grown to very substantial proportions. Up to the present time in this country rosin esters have not been made for general sale but a few varnish manufacturers for some time past have been preparing esters for their own consumption. A considerable quantity of ester gum made in Germany and England has been imported. These products vary considerably in quality and the acid numbers range from 10 or 12 to about 50.

At the present time, owing to the lack of consumption abroad of copal and other hard gum, a great reduction in the price of this raw material has been made and in consequence the making of medium-priced grinding varnishes with hard gums is more feasible than it was a few years ago. On the other hand, glycerine, which enters into the manufacture of ester gums, is now extraordinarily high in price and these conditions may tend to diminish temporarily the consumption of rosin esters. Such a condition is, however, only temporary, for at the close of the present European war a large demand will spring up for hard varnish gums, and rosin esters will be again restored to the place which they attained in the resin market prior to the opening of the war.

Before reviewing the previous work on the neutralization of resins it will be rather instructive to present the views held by various investigators regarding the cause of the phenomenon of "livering" or thickening.

Rosicki<sup>1</sup> holds that the thickening of the varnish is due to the formation of salts difficultly soluble in the varnish formed by the reaction of the free resin acids and the metallic oxide present. In support of this theory he cites the fact that copals like Congo and Manila when melted in the normal way do not yield varnishes which stand the addition of basic pigments; they do so, however, when melted or "run" with a loss of 30–35 per cent. This result he claims is due to the large drop in the acid number of the copal during the melting process. In some cases the acid number falls from 150 to about 25. The tendency of varnishes towards thickening decreases proportionately with the decrease in acid number.

Muehle<sup>2</sup> is of the opinion that the thickening phenomenon is due to the coagulation of the high molecular copal particles rather than to the formation of in-

<sup>1</sup> *Farben-Ztg.*, 1913, 1194.

<sup>2</sup> *Ibid.*, 1913, 1119, 1944, 2058, 2178.

soluble salts. Through extensive experiments which he carried out he claims to have found that neither neutralization of the copal acid by basic substances, such as lime and magnesia, nor their esterification, nor any other method tending towards the saturation of the free acids were of use in preventing the agglutination of the varnish. Muehle<sup>1</sup> states that either he nor his associate, Hammelmann, succeeded, through combining the carboxyl group of resin acids by all possible methods (esterification, acetylation, forming anhydrides, etc.), in producing varnishes from Congo and Manila copals, which would stand the addition of pigments. They were able to bring the acid number down to a very low figure, but the danger of thickening was by no means eliminated.

Megerle,<sup>2</sup> commenting on the controversy between Rosicki and Muehle, states that according to his observations during his experience extending over a period of more than twenty years, he is of the opinion that the gelatinizing of varnishes in the presence of zinc or lead basic pigments is due to not one but to both the reactions claimed by Rosicki and Muehle.

#### NEUTRALIZATION OF ROSIN WITH METALLIC OXIDES

The hardening of resins by treatment with lime has long been known. In 1884 Kissel observed that the melting point of natural acid resin could be increased considerably by neutralizing it with lime, magnesia, zinc oxide, and that the hardness increased proportionately with the amount of material introduced to the resin.<sup>3</sup> Later<sup>4</sup> he improved his method by removing the last traces of the free rosin acid that invariably occurred in the hardened rosin by washing the powdered compound with ammonia water. In this way he claims to have obtained a neutral product.

Melvin<sup>5</sup> describes a method of preparation of zinc resins according to which zinc oxide is added to rosin at 230° F., in the proportion of 2½ to 25 parts zinc oxide to 100 parts of rosin. The preparation of the resins of calcium, magnesium and zinc is described by Prager.<sup>6</sup> Zinc resinate is stated to be less affected by water than the corresponding compound of calcium.

Pirschl<sup>7</sup> claims an improvement in the method of preparing metallic resins by introducing a flux containing a greater percentage of the metallic oxide to combine with the acid resin. The flux that he generally employed was rosin oil. According to him the temperature should differ with the metallic oxide employed. The hydroxides he claims are to be preferred to the oxides as more complete neutralization can be effected with the former. He found that rosin is capable of taking up 16 per cent of manganese dioxide, 10 per cent of barium oxide, 40 per cent of lead oxide and 8 per cent of calcium oxide.<sup>8</sup>

The practice of liming rosin and other acid resins has been in vogue in most varnish works for a great many years and the cheaper grade of varnishes containing largely rosin as the resinous stock almost invariably carries a considerable percentage of lime or other base for hardening purposes. The acidity, however, can be only partly neutralized as the use of a sufficient amount of base to furnish a neutral product would yield a resinous body insoluble or very difficultly soluble in the usual varnish thinners. Thus it is not feasible to rely upon liming to prepare a grinding varnish sufficiently neutral to be free from tendency of livering.

According to Prager<sup>1</sup> rosin may be hardened by the addition of 5-10 per cent of sulfur at 140-150° C. The cooled product is dark green in color, possesses a sulfur-like odor, and is quite resistant to the action of weather and chemical reagents.

#### NEUTRALIZATION OF RESINS WITH ORGANIC SUBSTANCES

In order to prepare ordinary esters of soft resins, such as rosin, the softer constituents of the raw resin are removed by distillation in a vacuum in the presence of superheated steam or a current of indifferent gas up to 300-350° C., or sometimes by extracting the raw resin by means of solvents such as dilute alcohol. The residue is then heated with equivalent proportions of glycerine, phenol, naphthol, or carbohydrate at a high temperature with or without the addition of the dehydrating agents and with or without pressure. For example, rosin is heated in a vacuum at 350° C. to remove the volatile materials, the residue is treated with resorcin in the proportion of 100 parts of rosin to 17 parts of resorcin and the vapors which are formed are allowed to escape by opening a valve of the autoclave. The operation of blowing off the generated steam is continued until esterification is substantially complete. This can be roughly determined by shaking an ether or benzene solution of the ester with a dilute aqueous solution of caustic soda and noting the degree of action of the alkali.

Glycerine esters which can be immediately employed in the varnish industry are prepared according to Bottler<sup>2</sup> by heating abietic acid to 180-210° and adding to it 10 to 16 parts of glycerine under constant stirring while subjecting to a vacuum of 10 cm. After the addition of the glycerine the temperature is gradually raised to 280° C., while the vacuum is maintained constant. The operation is continued until the esterification is complete. In order to impart to the ester a greater degree of hardness, the softer portions are distilled off under reduced pressure or in an atmosphere of an indifferent gas at ordinary pressure. If the product becomes very thick toward the end of the operation some linseed oil may be added. Finally, the residue is treated with ½ to 2 per cent of manganese peroxide or red lead and the heating is continued until the solution is complete. The varnish stock thus obtained is of a light color and is readily soluble in benzene and turpentine.

<sup>1</sup> For details of a controversy between Rosicki and Muehle see Stevens and Armitage's "Treatise on the Technology of Wood Oil."

<sup>2</sup> *Farben-Ztg.*, 1913, 2230.

<sup>3</sup> See D. R. P. 30,000, March 5, 1884; U. S. Patent Reissue No. 10,714, April 20, 1886; U. S. Patent No. 303,436, August 12, 1884.

<sup>4</sup> U. S. Patent No. 414,366, Nov. 25, 1890.

<sup>5</sup> U. S. Patent No. 370,640, Sept. 27, 1887.

<sup>6</sup> *Seifen-Ztg.*, 1915, 705.

<sup>7</sup> U. S. Patent No. 521,270, June 12, 1894.

<sup>8</sup> See also Gentzsch, U. S. Patent No. 657,696, Sept. 11, 1900.

<sup>1</sup> *Seifen-Ztg.*, 1915, 706.

<sup>2</sup> "Harze und Harzeindustrie," Hanover, 1907.



Suter<sup>1</sup> claims that he was able to bring about combination between dehydrated molasses and rosin in the presence of asphalt oil dissolved in a vehicle such as alcohol or turpentine. For example, 30 lbs. of copal and 20 lbs. of rosin are supposedly combined with 25 lbs. of molasses and 5 lbs. of asphalt distillate.

Schaal<sup>2</sup> has described various methods of producing resin esters and for separating the soft and hard constituents. He observes that resin acids combine freely with carbohydrates as well as the lower and higher alcohols, phenols, naphthols and similar aromatic hydroxy bodies to form resin acid esters. These products are partly soft and partly very hard resinous substances. The esters may be made (1) by heating equivalent proportions of the materials to a high temperature with or without pressure and with or without the addition of substances capable of absorbing water such as acids or acid salts; (2) by passing through the mixture heated neutral gases so as to expel the water thus formed; (3) by heating the metallic salts of the resin acids with haloid or sulfo combinations of the phenols and their homologues. In an example given by Schaal, colophony is distilled in vacuum at a temperature up to 350° C. in order to remove volatile constituents and the residue, which consists chiefly of a hard resinous substance, is mixed with 10 per cent by weight of dehydrated glycerine. The mixture is heated with agitation and under a pressure of several atmospheres to 250° C. After some time the pressure rises, due to the formation of steam, and the latter is blown off from time to time. When the formation of water ceases the resin esters which have been formed are subjected to distillation for the purpose of separating the softer from the harder portions.

By the foregoing process it will be noted that the reaction of the resin acid with the hydroxy body takes place under a pressure of several atmospheres, while in the method described below Schaal maintains a vacuum in the chamber in which the resin acid and hydroxy body are heated.

The formation of mixed esters of Manila copal and rosin is described by Schaal.<sup>3</sup> According to a procedure given by him, 50 lbs. of Manila copal are melted and an equal amount of rosin added. The temperature is raised to about 180–210° C. and a mixture of 6 lbs. each of fruit sugar and glycerine is gradually added. The mixture is constantly agitated and the temperature is slowly raised to 280° C.; at the same time a vacuum of about 100 mm. is maintained in order to remove the aqueous vapors which are formed. While the temperature is being raised to 280° C., such portion of the hydroxy body as distills off is replaced by fresh material until the formation of the ester is completed. In place of the mixture of fruit sugar and glycerine a mixture of 16 lbs. of phenol with 4 lbs. of cane sugar or mannite and 4 to 5 lbs. of glycerine may be used. The addition of boric acid is regarded as favoring the reaction.

<sup>1</sup> U. S. Patent No. 905,384, Dec. 1, 1908.

<sup>2</sup> U. S. Patent No. 335,385, Feb. 2, 1886, *Ressue* No. 10,823, March 29, 1887.

<sup>3</sup> U. S. Patent No. 501,446, July 11, 1893.

An apparatus used by Schaal in the manufacture of rosin esters is shown in Fig. 1. The kettle *A* is equipped with a charging funnel and stirring device and a gooseneck connects this vessel to a receiver, *B*. The outlet pipe *d* is connected with an air pump so that a partial vacuum can be maintained in the apparatus. The rosin acids are placed in the kettle *A* and heated to 180–240° C. when the glycerine or other hydroxy body is added under constant agitation. A vacuum of 100 mm. is maintained in the apparatus. The temperature is then gradually raised to about 280° C. while the agitation is continued and the heating operation progresses until a portion taken from the kettle *A* and dissolved in benzine, or ether, or ground fine in water, does not give up any soluble matter when mixed with an aqueous solution of sodium carbonate.

A further suggestion by Schaal<sup>1</sup> is that of oxidizing the resinous product before esterification. For example, the rosin is reduced to a fine powder and is subjected to the action of oxygen, which is stated to have the effect of raising the melting point of the rosin to a point where it approaches that of the copals. This product may then be esterified with glycerine, glucose, levulose or cane sugar.

Terrisse<sup>2</sup> has esterified a variety of varnish gums

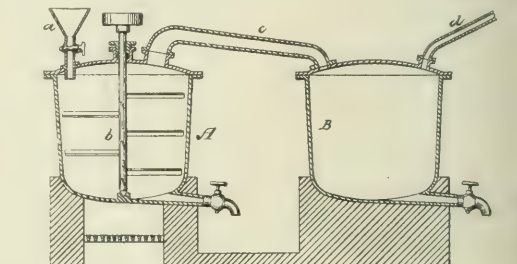


FIG. 1

with glycerine. Fossil resins (including Congo copal, Zanzibar and Madagascar anime, kauri, Benguela copal, pontianak, Manila and others) are "solubilised"<sup>3</sup> by heating them, preferably under pressure in an autoclave at a suitable temperature (240–360° C.), with or without the addition of naphthalene or phenol. The naphthalene or phenol is removed by distillation or otherwise, the acid value of the fused resin is determined, and an excess of high-boiling alcohol, such as glycerine is added. The mixture is then heated until the uncombined alcohol is distilled off, the product consisting substantially of a neutral resin acid ester, readily soluble in linseed oil. For example: (1) 100 g. of ground Zanzibar gum are heated with 350 g. of naphthalene at 280° C. and 4 atmospheres for 4 hrs., or until a test portion is soluble in linseed oil. The acid value is determined, and some excess above the calculated amount of glycerine is added. The mass is then heated in a still or open vessel at 280–320° C. until a test on glass remains transparent on cooling. (2) 100 kilos of Congo copal are fused by the

<sup>1</sup> U. S. Patent No. 698,741, April 29, 1902.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1916, 57; British Patent No. 23,055, Nov. 25, 1914.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1904, 552; 1908, 457.

open-kettle method; its acid value is then determined and the calculated amount of glycerine is added. 5 kilos of copal oil, redistilled under reduced pressure to the state of a greenish yellow viscous liquid, are added, and the mixture is heated in a still, or open vessel, to 280° C.; 5 to 6 kilos of glycerine are then added and heating continued until a test gives a clear bead.

# EXPERIMENTAL

Investigations were carried out with the object of finding a simple and at the same time an efficient method for producing substantially neutral rosin or other resinous compounds that would resist the action of basic pigments, such as white lead and zinc oxide. To be of commercial value the products are required to possess not only a low acid number but good color and hardness as well. This offers difficulties as it is not easy, for instance, to obtain an ester possessing both a low acid number and a good color. Either one or the other property has to be sacrificed in a measure unless special and expensive precautions are taken. To some extent the same is true of color and hardness.

Partial esterification of rosin by means of glycerine readily took place by bubbling gases through a mixture of rosin and glycerine in slight excess, at 280–300° C. Hydrochloric acid gas, carbon dioxide, hydrogen, air and oxygen were successively tested. In no case, however, was an ester obtained of sufficiently low acid number to warrant their use except, possibly, in special cases. A difficulty encountered in the use of these gases was the considerable loss of glycerine carried over by the gaseous current. A rosin ester obtained by the use of hydrochloric acid gas was of almost a semifluid consistency, while the esters prepared by the use of air or oxygen were generally dark in color. This method gave esters having acid numbers of 30 to 40. The use of bodies expected to aid the reaction by catalytic or dehydrating effect, such as sulfuric acid, zinc chloride, sodium acid sulfate and others in the presence of gas, did not materially assist the ester formation. With the exception of hydrochloric acid gas the action of the gases in bringing about partial esterification of the rosin is probably largely a mechanical one. On bubbling through the melted rosin and glycerine the gas brings these two substances into intimate contact with one another. On the other hand, as already stated, the passing gas also causes considerable loss of glycerine. This accounts for the fact that only partial esterification takes place when using approximately equivalent amounts of rosin and glycerine under these conditions.

A considerable improvement in the preparation of rosin esters was made by the introduction of a mechanical stirring device. This afforded the agitating effect of the gases without the drawback of excessive volatilization of glycerine. To reduce further the loss of glycerine a reflux condenser was used. Products were obtained in some of the tests having an acid number as low as 6 or 7. It may be stated, however, that the products having such a low acid number are generally darker in color.

In each of the following runs 60 parts by weight of rosin and 8 parts of glycerine were employed. The yield in each case was about 60 parts of ester. The acid number of the rosin employed was 156.

EXPERIMENT I					EXPERIMENT II				
Time		Temp.		Acid No.	Time		Temp.		Acid No.
Hrs.	Min.	° F.	° C.		Hrs.	Min.	° F.	° C.	
	10	240	118			0	240	116	
	20	250	121			20	365	185	
	30	300	149			30	400	204	
	60	400	204			45	415	213	
1	15	425	218			50	450	232	
1	30	460	238		1	5	465	241	
1	45	475	246		1	25	490	254	
2	10	500	260				500	260	
2	35	500	260	45.0	2	30	500	260	32.0
3	30	500	260		2	55	500	260	
3	30	525	274	36.0	3	15	520	271	20.2
4	5	520	271		3	30	520	271	
4	15	520	271	13.5	3	45	520	271	12.9

## EXPERIMENTAL RESULTS

Wt. of Rosin (C <sub>20</sub> H <sub>30</sub> O <sub>2</sub> )(a)...	60.0	CALCULATED	60.0
Wt. of Glycerine.....	8.0		6.1
Wt. of Ester.....	60.0		62.5

(a) W. Fahrion, Bischoff and Nastvogel. See Allen's "Commercial Organic Analysis," Vol. II, Part 3 (1907), p. 159.

It was found that under ordinary conditions ethyl alcohol, phenol, cresol, aniline and alpha and beta naphthylamine, sugar, starch and glucose did not react with the rosin to form neutral products. Experiments carried out with sugar, glycerine and starch under pressure in the presence of a water-absorbing adjacent layer of unslaked lime similarly gave negative results. For example, 100 parts of rosin and 15 parts of crystallized dextrose reduced to a fine powder and intimately mixed were placed in an open container surrounded by unslaked lime and heated in an autoclave at 253° C., for 3 hrs. The pressure did not rise above 3 atmospheres. The final product consisted of unchanged rosin, the acid number of which was 145.6, while the dextrose was completely converted into a carbonaceous mass. Aniline and alpha and beta naphthylamine when heated with rosin under pressure likewise gave negative results.

According to Hibbert<sup>1</sup> the condensation of polyhydric alcohols is facilitated by the presence of iodine. Tests carried out on the rate of formation of rosin ester of glycerine in the presence of small quantities of iodine did not disclose any beneficial result.

**COLOR OF THE ESTER**—The production of rosin esters meeting the requirements of varnish manufacture as regards lightness of color is a matter of some difficulty, as the resin discolors rather rapidly when exposed to air or oxygen at the high temperature required for esterification. In consequence it is desirable to maintain an atmosphere of an inert gas over the esterifying material during the progress of the reaction and while cooling. Once an ester has become discolored by oxidation it is extremely difficult to better the color by bleaching operations. Small scale experiments carried out to determine the effect of various bleaching agents such as bone-black, fuller's earth and sulfur dioxide showed the coloring matter of the ester to be practically unaffected by these agents.

In some of our experimental work we used apparatus as shown in Fig. II. This consisted of a kettle fitted with a tight cover and stirrer mounted on a varnish kettle truck carrying a countershaft. The

<sup>1</sup> J. Am. Chem. Soc., 1915, 1748; U. S. Patent No. 1,129,467, Jan. 26, 1915.



stirring device was operated by a motor. The kettle could be readily moved on and off the fire without affecting the operation of the stirrer. This apparatus proved very convenient to handle.

**DETERMINATION OF THE ACID NUMBER OF ROSIN ESTERS**—One gram of the ester is dissolved in 25 cc. of benzol or ether and the solution is titrated with *N*/10 alcoholic caustic potash, using phenolphthalein as an indicator.

**ROSIN ANHYDRIDES**—What appears to be the anhydride of rosin acids is readily obtained by passing an inert gas through the rosin at 300° C. The anhydride is soluble in organic solvents such as alcohol, ether, benzol, but it differs from ordinary rosin in its behavior towards aqueous alkali. Rosin dissolved in benzol or ether shaken with a cold aqueous solution of caustic alkali readily reacts with the latter with a formation of rosin soap. The anhydride of rosin under the same conditions remains unaffected or but slowly affected. This gives a simple rough method for the determination of the "anhydride content" of rosin. The procedure consists in dissolving a definite quantity of the materials in benzol or ether and titrating the solution with aqueous caustic potash or soda solution, stirring the mixture vigorously after each addition of alkali and using phenolphthalein as an

the anhydride to be capable of combination with such pigments causing thickening of the mixtures.

**PROPERTIES OF ESTER GUM**—An ester gum made from a good grade of rosin and glycerine when properly prepared should have a light amber color or pale straw color, should be bright and clear, with freedom from tackiness. It should not contain an excess of glycerine, and should dissolve readily in benzene or turpentine. A solution of equal parts of the latter and the ester gum should remain clear on standing. Rosin ester is practically insoluble in 80 per cent alcohol and should be substantially unaffected by a 10 per cent solution of sodium carbonate. Even boiling aqueous solutions of sodium carbonate should have little or no immediate effect. The ester gum should be free from burnt or tarry odor.

**DAMMAR GUM**—A mixture of 50 parts dammar gum and 5 parts of glycerine was heated for one-half hour under agitation at 250° C. The acid number of the gum dammar fell from 39 to 12.5. The final product was dark in color.

**COPAL GUMS**—The esterification of the copals is a far more difficult problem than that involved in producing the esters of rosin. The copals normally are insoluble in the ordinary solvents of the varnish industry and require to be cracked by protracted heating at high temperatures until they become soluble. It is possible to esterify the raw resin or to crack it and esterify the cracked product. It is commonly thought by varnish makers that after an ester of glycerine has been formed it should not be subjected to protracted heating because of the tendency of decomposition with loss of glycerine. Our observations have shown that a number of the esters are very stable at high temperatures, and contrary to the prevailing idea that glycerine is not lost by heating in this manner. The esterification of copal gum with glycerine and subsequent treatment at a cracking heat is, however, sometimes prejudicial to the color of the preformed ester and usually it is desirable to crack the product first and then esterify the soluble resin so formed. Great care, however, has to be taken in esterifying this product to regulate the temperature properly, as infusible products may be formed. For example, Congo gum was run at 327° C. (620° F.) until soluble in turpentine, and was then treated with glycerine. Reaction took place readily, yielding a spongy product which could not be fused even on heating to over 360° C. (700° F.). On cooling, a porous resinous mass was obtained.

**PONTIANAK COPAL**—92 parts by weight of fused gum and 8 parts of glycerine were heated for 5 hrs. at 260–280° C. under constant agitation. The acid number fell from 74 to 34.

**CONGO GUM**—100 parts of fused or cracked Congo gum and 5 parts of glycerine were heated for 4 hrs. at 250–260° C. with stirring. The acid number fell from 72 to 16.

#### SUMMARY

1—The method of preparing rosin esters was reduced to simplest terms. Esters were prepared from

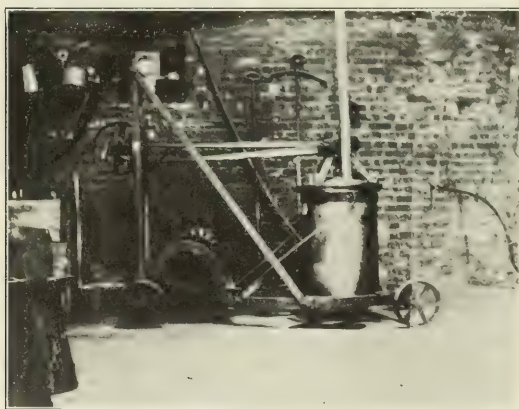


FIG. 11

indicator. Toward caustic potash dissolved in alcohol, rosin and the anhydride of rosin behave alike.

#### EFFECT OF TEMPERATURE ON THE ACID NUMBER OF THE ANHYDRIDE DETERMINED BY AQUEOUS ALKALI

Time Hrs.	1	2	3	4	5	6	7
Temp. (° C.)	155	200	245	290	320	340	357
Acid No.	44	34	30	20	19	18	18.5

Common rosin of normal acid number was heated at about 300° C. until its acid number, determined by titration with *aqueous caustic potash* solution, was found to be reduced to approximately 20. However, on titration with *alcoholic potash* solution the acid number was found to be but slightly reduced. As the anhydride thus appears to have a greater degree of resistance to alkalies than the original resin acids, a series of "livering" tests were carried out with a considerable number of basic pigments. The results showed

rosin and glycerine having an acid number as low as 5 or 7, which were as a rule darker in color than the rosin employed. Esters were prepared whose acid numbers lay between 13 and 13.5 which were good in color.

2—Ethyl alcohol, phenol, cresol, aniline, alpha and beta naphthylamine, sugar, starch and dextrose did not combine with the rosin to form neutral substances under ordinary conditions. Aromatic amino compounds did not combine with the rosin in presence of dehydrating agents even under considerable pressure.

3—Bone-black, fuller's earth and sulfur dioxide had no beneficial effect on the color of rosin esters.

4—A qualitative and quantitative method for determining rosin anhydrides in the presence of rosin acids and rosin esters was studied.

5—Congo gum, pontianak gum and dammar gum were esterified with glycerine to a greater or lesser degree. Copal gums which had been cracked and rendered soluble in varnish makers' solvents were found to esterify readily.

MONTCLAIR, NEW JERSEY

## CEANOTHUS VELUTINUS (SNOW BRUSH) AS A SOURCE OF WAX AND TANNIN

By CHAS. C. SCALIONE AND HERBERT S. BLAKEMORE

Received November 4, 1915

The study of this shrub was undertaken with the hope of being able to utilize a material that at present is both a fire menace and a nuisance in California forests. This study, though not complete, will show that this plant contains easily available products of high commercial value.

### BOTANICAL

*Ceanothus velutinus* (Douglas),<sup>1</sup> commonly known as "Snow Brush," is a widely branching shrub, two to six feet, and sometimes more, in height. The leaves are alternately petioled, roundish or broadly ovate, about three inches in length and have polished resinous upper surfaces, but are somewhat pubescent beneath.

The area inhabited by this plant is bounded roughly by the Coast Range of California on the west, the Columbia river on the north, Colorado on the east, and San Francisco Bay on the south. It is especially plentiful in the Shasta National Forest in the neighborhood of Sisson, California, where it has been estimated<sup>2</sup> that 30,000 tons could be gathered within 5 miles of the railroad and three times this amount could be gathered within 15 miles.

We are indebted to the United States Forest Service for 500 lbs. of leaves and twig ends used in this investigation. This material was gathered at Sisson, California, and shipped to Berkeley.

### EXAMINATION FOR ESSENTIAL OILS

An attempt was made to distill about 50 lbs. of leaves and twigs for essential oils. The distillate was slightly opalescent and by redistillation and extrac-

tion of the distillate a minute quantity of a pungent-smelling oil was isolated. This quantity was not sufficient for examination. Probably if the leaves had been distilled as soon as cut, sufficient oil would have been isolated to study, but the yield would not be of commercial importance.

### EXTRACTION OF WAX

The remainder of the twig ends, after drying on a steam radiator, were separated from the leaves by threshing. The leaves were ground in a coffee mill and sifted through a twenty-mesh screen. They were next thoroughly extracted with dry 86° Bé. gasoline in a specially designed Soxhlet extractor of 10 lb. capacity. The average yield of wax was 7.3 per cent of the weight of leaves.

The wax had a greenish appearance, due to a little chlorophyll. At first it was of pasty-like consistency,



FIG. 1

but on standing on the steam bath and driving off more solvent it became brittle, breaking with a conchoidal fracture. The crude wax had the following constants:

Free acid.....	20.3	Reichert-Meissl No. ....	7.5
Saponification number.....	93.4	Sp. gr. at 15°.....	0.988
Iodine value.....	19.5	Melting point.....	78-79° C.

### CHEMICAL EXAMINATION OF WAX

In order to separate the wax into some of its components, a well-dried portion was extracted with alcohol in a Soxhlet extractor. The material remaining in the cartridge when dried was a dark brown paraffin-like mass. When boiled with alcoholic potash a portion saponified. The unsaponified material was separated from the soap liquors. On examination, this portion proved to be a hydrocarbon. It could not

<sup>1</sup> Parson's "Wild Flowers of California."

<sup>2</sup> Personal communication from Acting Forester of Fifth District



be obtained in a purified state and appeared to be composed of a number or homologous hydrocarbons, having a melting point between 50–57° C. Upon cooling, the potash soap became a mucilaginous mass. On acidifying, filtering and recrystallizing from alcohol solution, an acid crystallizing in straight needles, having a melting point of 76–76.5°, was isolated. Creotic acid melts at 77.8°. When titrated in an alcoholic solution with caustic potash its acid number was 140.5. The acid number of creotic acid ranges from 130–140.<sup>1</sup>

On cooling, crystals separated out of the original alcoholic extract. Water was added to this alcoholic extract and the fats separating out were filtered. They were washed entirely free of chlorophyll with dilute alcohol solution. The fats were saponified in fairly concentrated potash solution, the solution diluted and the unsaponified portion filtered off. The soap liquids were evaporated to a small volume on the steam bath and acidified. The fatty acids separating out were filtered, washed and dried. They melted at 65–67°.

A fractional crystallization was made of these fatty acids with magnesium acetate in hot alcohol.<sup>2</sup> This fractionation was repeated three times and two acids of fair purity were isolated. One melted at 61–62°, the other at 68–69°. The silver salt of the former when ignited yielded 28.85 per cent of silver, the latter 27.56 per cent of silver. Palmitic acid melts at 62° and combines with 29.55 per cent silver. Stearic acid melts at 71–72° and combines with 27.43 per cent silver. The alcohols liberated in the saponifica-

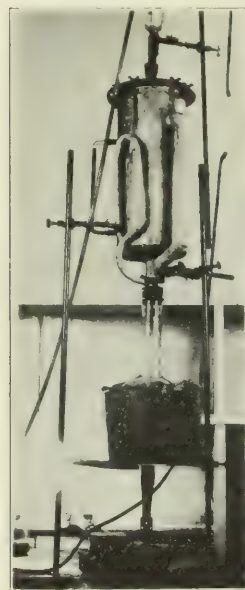


FIG. 11

tion of the palmitic and stearic acids were washed with dilute ethyl alcohol and dried. The melting point was between 78 and 80°. When heated with soda lime<sup>3</sup> and the resulting acids separated, an acid showing the properties of creotic acid as previously described was isolated. This would indicate ceryl alcohol. A higher acid with properties corresponding to melissic acid was isolated, indicating myricyl alcohol. Some traces of a lower acid were present but not sufficient to identify it. The original wax is probably composed of creotic acid in the free condition, a hydrocarbon, and palmitic and stearic acids in combination with ceryl and myricyl alcohols. A faint acrolein test seemed to point to the presence of a small quantity of glycerides.

<sup>1</sup> Lewkowitsch's "Oils, Fats and Waxes," 1898, 51.

<sup>2</sup> Leathe's "Monograph on Fats," p. 79.

<sup>3</sup> Lewkowitsch's "Oils, Fats and Waxes," p. 74.

#### EXAMINATION OF LEAVES

**TANNING.**—The extract from these leaves responded to the following qualitative tests for tannins: hydrogen ion gave a brown precipitate; salt gelatine solution, a heavy white precipitate; iron alum, a green coloration; and bromine water, an immediate precipitation. These tests would indicate the presence of catechol tannins.

An examination for mixed tannins was made as directed by Procter.<sup>1</sup> [The separation of the catechol from the other tannins by this method depending on the insolubility of the catecholic tannin compound with formaldehyde in the presence of hydrochloric acid.] In this case it was found that the tannins were exclusively of the catecholic variety, for on filtering the precipitate and testing the filtrate with salt-gelatine solution, no more tannins were detected.

A portion of the tannin that had been separated by adding dilute acid<sup>2</sup> was thoroughly dried, and distilled in a retort. The distillate recrystallized from alcohol had a melting point of 110°, was soluble in water and ether and with iron alum gave a deep green coloration. An empirical formula calculated from combustion and molecular weight data could be represented as  $C_6H_4(OH)_2$ . This corresponds to catechol.<sup>3</sup>

Glucose was identified partially free but to a greater extent combined, as a glucoside. A water extract of the leaves was taken and divided into two samples. The first sample was treated with lead subacetate and polarized. The second sample was treated with dilute hydrochloric acid, clarified and polarized. The polarization was dextro in both cases, but in the second sample was greatly increased. The presence of glucose was confirmed by preparing the glucosazone and microscopically studying the crystal form and determining the melting point.

A weighed sample of leaves was extracted with a Procter sand filter. The extract analyzed by the official method of the American Leather Chemists' Association<sup>4</sup> showed 17.3 per cent tannins.<sup>5</sup>

**INORGANIC ELEMENTS.**—In order to determine whether or not these leaves contained inorganic salts that in any way would injure hides in tanning, an ash determination was made with the following results:

	Per cent
Moisture in leaves	11.2
Total ash	5.33
SiO <sub>2</sub>	0.65
CaO	1.30
FeO	0.15

#### TANNERY TESTS

Through the courtesy of Mr. David Bloom, of Samuel Bloom & Sons, tanners in San Francisco, a practical test of ceanothus leaves was conducted on hides under tannery conditions.

Samples of hides from the "lime," "pickle" and "bate" were treated in water with these leaves ground

<sup>1</sup> Procter's "Leather Chemists' Pocketbook," p. 51.

<sup>2</sup> Trimbell's "Tannins."

<sup>3</sup> Trotman's "Leather Trades Chemistry," p. 98.

<sup>4</sup> Procter's "Leather Chemists' Handbook," pp. 94–96.

<sup>5</sup> This material compares very favorably with other sources of leaf tans. According to Trotman pistacia contains 14–16 per cent tannins; tannari, 9–10 per cent; quebracho, 17–20 per cent; oak bark, 12 per cent; sumac (crude), 19 per cent.

to pass a twenty-mesh screen. The hides tanned quickly, the grain being completely struck through in a short time. It was found that this material did not plump the hides properly. The hides were in all three cases completely tanned without harmful discoloration. A side of hide that had been prepared for the one-bath chrome, one-bath vegetable tan, was submitted to these leaves for the vegetable tan. Here, too, the hide was well tanned but not properly plumped. Another objection raised was the bulkiness of the leaf residue in the tanning vats. To do away with this nuisance it would be necessary to make this material up into an extract. To this extract suitable plumping organic acids could be added.

The preliminary data above described would indicate that these leaves are an extremely satisfactory source of tannin for tannery purposes. Work along this line is progressing in the tannery.

#### SUMMARY

*Ceanothus velutinus*, a widely distributed plant, has been found to contain 7.3 per cent and 17.3 per cent tannins. The wax was composed of free hydrocarbons, free creotic acid and in a great part of palmitic and stearic acids in combination with ceryl and myricyl alcohols. A trace of glycerides appeared to be present. The tannin was found to be of the catecholic variety. Experiments in the tannery have led the authors to believe that a suitable extract for tanning purposes could be made from these leaves. From the quantity of this shrub available, its objectionable presence in the forests and the value of the products obtainable from this material should become of considerable economic importance.

In concluding, we would wish to thank Mr. Carl J. Kupper and Mr. C. S. Smith, of the United States Forest Service, for obtaining the material for the investigation and for the survey of its occurrence; Professors W. C. Blasdale and H. C. Biddle, of the Chemistry Department of the University of California, for valuable suggestions given during the progress of the work; and Mr. David Bloom, for permitting the experimental work in the tannery.

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#### SOME QUALITATIVE TESTS FOR GUM ARABIC AND ITS QUANTITATIVE DETERMINATION<sup>1</sup>

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#### INTRODUCTION

The group of polysaccharides includes such diverse substances as the starches, cellulose, the dextrins, the true gums and the plant mucilages. They possess in common the property of being decomposable hydrolytically into one or more sugars, usually pentoses and hexoses. By oxidation the acids corresponding to these sugars are formed, but the first step toward this reaction appears to be hydrolysis.

The true gums, of which gum arabic is typical, dissolve in cold water, yielding clear solutions which,

<sup>1</sup> Published by permission of the Director of the Bureau of Standards. Copies of the complete paper, from which this is abridged, can be obtained on application to the Director, Bureau of Standards, Washington, D. C.

though viscous and adhesive, can be filtered. The closely related and quite similar mucilages, such as gum tragacanth and cherry-tree gum, simply swell up and form more or less homogeneous suspensions that cannot be filtered. Perhaps most of the so-called gums are mixtures of one or more representatives of the above classes.

As might be expected from their chemical nature, the gums do not readily lend themselves to reactions of a definite qualitative or quantitative value. One of us learned how unsatisfactory some of the qualitative tests are when samples of mucilage first came to the Bureau of Standards for examination. This led to an extended study of the literature and of the various qualitative reactions that have been published, and finally to a comparatively accurate quantitative method. In the last part of this work the two of us joined forces, hoping to carry on a much more extended investigation than was found later to be possible.

The object of this paper is to discuss briefly some of the more important qualitative and quantitative methods and give references showing, as far as possible, what other methods have been published.

#### QUALITATIVE TESTS

In nearly all cases a 2 per cent solution of gum arabic was used. Similar solutions of dextrin and of gum ghatti, a substitute for arabic, were subjected to the same tests.

(1) FERRIC CHLORIDE AND ALCOHOL—A mixture of 2.5 volumes of 50 per cent alcohol and 1 volume of neutral ferric chloride solution containing 25 g. of the salt in 100 cc., precipitates gum arabic, though often only on long standing.<sup>1</sup> Gum ghatti gives no precipitate, and dextrin a very slight one.

(2) POTASSIUM HYDROXIDE—According to Liebermann,<sup>2</sup> solutions of gum arabic and of dextrin become amber-yellow when warmed with potassium hydroxide, while the closely related gum senegal gives at most a faint yellow color. Sollman<sup>3</sup> stated that dextrin when so treated turns more or less brown, while some sugars and gums other than arabic, behave similarly. Rideal and Youle<sup>4</sup> came to the conclusion that this test is of no value. Two samples of gum arabic, among a number tested by them, gave a green color; a solution of ghatti turned pink, and dextrin a very dark red or almost black. Nevertheless this test is among those recommended in the latest edition of "Lunge."<sup>5</sup> Our own experiments amply confirm the statements that this test is of no value.

(3) COLOR REACTIONS WITH PHENOLS—Reiche<sup>6</sup> found that gum arabic gives a flocculent blue precipitate when boiled with orcinol and concentrated hydrochloric acid. Other carbohydrates gave yellow or brown colors. Other investigators obtained reactions

<sup>1</sup> Roussin, *J. Pharm. Chim.*, [4] **7** (1868), 251. See also Allen's "Com. Org. Anal.," 4th Ed., Vol. III, p. 443.

<sup>2</sup> *Chem.-Ztg.*, **14** (1890), 665.

<sup>3</sup> *Am. J. Pharm.*, **83**, 176; *Chem. Zentr.*, **82**, I (1911), 1560.

<sup>4</sup> *J. Soc. Chem. Ind.*, **10** (1891), 610.

<sup>5</sup> "Chem.-Tech. Untersuchungs-meth.," 6th Ed., Vol. III (1911), pp. 167-8.

<sup>6</sup> *Ber. Ges. Förder. Chem. Ind.*, **1879**, 74; *Chem.-Ztg.*, **4** (1880), 191.



with other phenols.<sup>1</sup> In our work, nine different phenolic compounds were used in alcoholic hydrochloric acid solution. Quite a wide range of colors was obtained, but the test was found to be unreliable for the carbohydrates which were studied.

(4) BASIC LEAD ACETATE. An aqueous solution of neutral lead acetate precipitates neither dextrin nor gums arabic and ghatti. An alcoholic solution of the salt does, however, slowly precipitate gum arabic.<sup>2</sup>

As might be expected from its employment in clarifying sugar solutions before polarization, basic lead acetate is an excellent precipitant for many gums. The solution may be made basic by adding ammonia<sup>3</sup> or by boiling with litharge. The precipitate formed when gum arabic solution is added, is of a peculiar curdy consistency, and of such characteristic appearance that it is hardly necessary to make any confirmatory tests. Allen<sup>4</sup> speaks of this precipitate as a "white jelly." Dextrin solutions are, at most, made slightly cloudy by the reagent, while gum ghatti yields a very small amount of precipitate, most of which remains suspended in the liquid.

The basic acetate solution used in this work was made by long continued boiling of 40 g. of crystallized

(6) MISCELLANEOUS QUALITATIVE TESTS. Many other reagents for gum arabic have been suggested, but they need only be referred to as follows:

(a) Oxidase reaction for distinguishing between gums arabic and tragacanth.<sup>1</sup>

(b) Warming with hydrofluoric acid as a test for gum arabic, glue and dextrin.<sup>2</sup>

(c) Color reaction with alkali and diazobenzene-sulfonic acid.<sup>3</sup>

(d) Reaction with acidified egg albumen as a test for gum arabic and dextrin.<sup>4</sup>

(e) Nessler's reagent to detect gelatin in gum arabic solutions.<sup>5</sup>

(f) Reduction of mercuric acetate in the presence of sodium chloride.<sup>6</sup>

(g) Reduction of molybdic acid.<sup>7</sup>

(h) Color reaction with cobalt nitrate and alkali.<sup>8</sup>

(i) Color reaction with colloidal gold solution.<sup>9</sup>

Other reagents for gum arabic, such as sodium or potassium silicate, borax or ammonium oxalate,<sup>10</sup> would seem to depend largely upon the natural calcium content of the gum, though some of the reagents are said to cause gelatinization. In our work numerous other reagents were tried, but even such promising

TABLE I—CHIEF QUALITATIVE TESTS FOR GUMS AND DEXTRIN

REAGENT	GUM ARABIC	GUM GHATTI	GUM GEDDA	DEXTRIN
Ferric chloride and alcohol	Precipitate	Nearly clear	Slight precipitate	Slightly cloudy
Basic lead acetate	Dense precipitate	Cloudy	Less precipitate than arabic	Slightly cloudy
Copper sulfate and sodium hydroxide, cold	Blue precipitate, colorless solution	Dark blue solution, often cloudy	Light blue precipitate, dark blue solution	Dark blue solution
Copper sulfate and sodium hydroxide, boiled	Precipitate darker, pale blue solution	Slight reduction	Precipitate darker	Complete reduction
Iodine solution	No characteristic color reactions			Reddish purple solution

lead acetate, dissolved in 250 cc. of water, with an excess of litharge. It was filtered, after which it remained clear for a long time.

Basic lead acetate has been recommended probably more frequently than any other reagent as a qualitative test for gum arabic, as well as for removing this and other gums from wines, liqueurs, etc., in which other constituents are to be determined.<sup>5</sup>

(5) COPPER SULFATE AND SODIUM HYDROXIDE—Jettel<sup>6</sup> does not mention the basic lead acetate test, but relies chiefly upon the behavior of dextrin, gum arabic, etc., towards copper sulfate and sodium hydroxide. The test was devised by Liebermann<sup>7</sup> for detecting dextrin and gum senegal in the presence of gum arabic. The details are given quite fully by Jettel. We need only say that gum arabic gives a blue precipitate, the supernatant liquid being colorless. Ghatti gives a dark blue solution which is sometimes turbid, but which clears up on warming gently; there is a little reduction on boiling. Dextrin gives a precipitate which dissolves on warming; at the same time there is considerable reduction to cuprous oxide.

ones as basic zinc salts and sodium zincate were found to be useless.

In Table I is given a comparison of the more reliable reactions for the identification of dextrin, gums ghatti and gedda, and for gum arabic from different sources. Some of these samples were obtained after most of the work described above had been completed, and only the tests tabulated were applied. All samples of gum arabic behaved alike.

#### QUANTITATIVE METHODS

Since the chemical nature of the gums is such as to render most of the qualitative tests of at least doubtful value, it is not surprising that there are difficulties involved in their quantitative separation and determination. Some of the methods that have been proposed will be mentioned below, after which our own procedure will be described.

(1) FERRIC CHLORIDE AND CALCIUM CARBONATE—The details of this method, which was proposed by Roussin,<sup>11</sup> are given by Allen.<sup>11</sup>

<sup>1</sup> Ihl, *Chem.-Ztg.*, **9** (1885), 231; Clermont and Chautard, *Compt. rend.*, **94**, 1254; *Jahresber.*, **1882**, 684.

<sup>2</sup> Chauvin, *Mon. Sci.*, [5] **1** (1911), 317-8; *Chem. Zentr.*, **82**, I (1911), 1656.

<sup>3</sup> v. Lippmann, "Chemie der Zuckerarten," 3rd Ed., p. 1616.

<sup>4</sup> *Op. cit.*, p. 441.

<sup>5</sup> Rideal and Youle, *J. Soc. Chem. Ind.*, **10** (1891), 610; Fromm, *Z. anal. Chem.*, **40** (1901), 143; Papasogli, *L'Orosi*, **21** (1898), 263-5; Scheibler, *Z. Ver. Zuckerind.*, **23**, 288; Battut, *Sucr. Indig. et Colon.*, **32**, 285; v. Lippmann, "Chemie der Zuckerarten," p. 1616.

<sup>6</sup> "Zundwaren" in Lunge's "Chem. Tech. Untersuchungsmeth.," 6th Ed., Vol. III, pp. 167-8.

<sup>7</sup> *Chem.-Ztg.*, **14** (1890), 635.

<sup>1</sup> Payet, *Apoth.-Ztg.*, **25**, 116; *Z. anal. Chem.*, **44** (1905), 453.

<sup>2</sup> Bornträger, *Chem.-Ztg.*, **3**, 1888; *Z. anal. Chem.*, **40** (1901), 131.

<sup>3</sup> Petri, *Z. physiol. Chem.*, **8**, 291; *Jahresber.*, **1884**, 1328.

<sup>4</sup> Gunsberg, *J. prakt. Chem.*, **88**, 239; *Z. anal. Chem.*, **2** (1863), 218.

<sup>5</sup> Vamvakas, *Ann. chim. anal. appl.*, **12** (1907), 12, 139; *Analyst*, **32** (1907), 193, 226.

<sup>6</sup> Hager, *Pharm. Centr.*, **18**, 313; *Z. anal. Chem.*, **17** (1878), 380.

<sup>7</sup> Hager, "Commentar zur ersten deutschen Pharmakopée," Vol. II, p. 116; cf. Stohmann in "Muspratt," 4th Ed., Vol. III (1891), p. 1917.

<sup>8</sup> Papasogli, *L'Orosi*, **21** (1898), 263-5.

<sup>9</sup> Zsigmondy, *Z. anal. Chem.*, **40** (1901), 697.

<sup>10</sup> Allen, *Op. cit.*, p. 441.

<sup>11</sup> *Op. cit.*; also, August. *Ann. Fals.*, **2**, 136-8; *Chem. Abs.*, **5** (1911), 538.

(2) FERRIC CHLORIDE AND SODIUM CARBONATE—This method was employed by Landwehr<sup>1</sup> for the determination of glycogen and, incidentally, of gum arabic. In connection with this he determined the percentages of water held by ferric hydroxide when dried to constant weight at different temperatures.

(3) LEAD ACETATE—The use of this salt, dissolved in alcohol, was proposed by Chauvin<sup>2</sup> and recommended by Rocques and Sellier.<sup>3</sup> As far as we know, the basic salt has not been used quantitatively. Various formulas have been ascribed to the precipitate, and it is not unlikely that it varies in composition.<sup>4</sup>

(4) ALCOHOL—Chauvin employed alcohol acidified with hydrochloric acid to precipitate gum. The acid is unnecessary, for strong alcohol has often been used to precipitate gum from plant extracts, wines, etc.<sup>6</sup>

(5) MISCELLANEOUS METHODS—Methods depending upon hydrolysis,<sup>7</sup> followed by estimation of hexoses or pentoses, and those by which the gum is oxidized to mucic acid,<sup>8</sup> are of no value because samples of gum from different sources yield different percentages of the products. Wide variations in the iodine absorption, acidity, and the amount of alkali taken up from alcoholic potash, are also found.<sup>9</sup>

(6) COPPER SULFATE AND ALKALI—Madsen<sup>5</sup> estimated the gum in licorice juice (*Succus liquiritiae*) by throwing it out with strong alcohol, dissolving in water, and precipitating with copper sulfate and sodium carbonate. The gum is not identical with gum arabic, but for botanical reasons may well be quite similar to it.

During the course of our work, while still unaware of the work of Madsen, it was attempted to use the same reagents, together with alcohol, to precipitate gum arabic quantitatively. The filtrates were always cloudy. Slightly better, but still far too low, results were obtained when sodium hydroxide instead of carbonate was used, and having the combined solutions contain 60 per cent of alcohol. Since any excess of copper over the gum present would be thrown down as hydroxide, thus increasing the difficulty of washing and drying the precipitate, some modifications of Fehling's solution were next tried. The best results were obtained with a reagent made up with copper acetate, sodium potassium tartrate and sodium hydroxide. When this was added to a solution containing about 0.25 g. of gum arabic in 40 cc. of water, there was no precipitation, or at most a slight turbidity. An amount of 95 per cent alcohol equal to the volume of the mixed solutions was then added, with vigorous stirring. This resulted in the formation of a fine-grained precipitate that could be filtered off and washed

with comparative ease. It was dried, weighed, ignited and the ash weighed. The results by this method varied a few per cent below and above 100.

Copper acetate was chosen for making up the reagent because no sodium sulfate or other salt insoluble in alcohol of the strength used could be formed. Even this reagent is not ideal, and the final step taken is described below.

(7) METHOD FINALLY ADOPTED—Copper acetate dissolved in ammonia possesses certain advantages over all the other solutions employed. In order to ascertain the best conditions for precipitation, a few preliminary tests were made. One-quarter gram of gum arabic was dissolved in 50 cc. of water, 25 cc. of ammoniacal copper acetate solution (see below) added, and then enough alcohol to give the required percentage of the total volume of the mixture. Thirty per cent of alcohol gave no precipitate. With 40 per cent there was a faint precipitate, so finely divided that it was practically impossible to filter. With 50, 60, and 70 per cent of alcohol, respectively, dense and easily filtered precipitates were formed. The addition of more alcohol to the filtrates from these three caused no further precipitation. These precipitates gave on ignition the following amounts of ash, practically all cupric oxide:

Percentage of Alcohol Employed:	50	60	70
Ash, gram.....	0.0412	0.0436	0.0544
	0.0402	0.0446	0.0564
	0.0398	0.0452	0.0548
Averages.....	0.0404	0.0445	0.0552

From this it will be seen that in the presence of 50 per cent of alcohol, the gum is precipitated quantitatively and carries down with it less occluded matter than when the mixture contains more alcohol.

The following procedure was finally adopted for the determination of gum arabic: Fifty grams of copper acetate were dissolved in water, an excess of ammonia added, and the solution diluted to 1000 cc., using water and alcohol in such proportions that the final solution contained 50 per cent of alcohol. For each determination a 50-cc. portion of a gum arabic solution, representing 0.25 g. of gum, was pipetted into a 250-cc. beaker, an equal volume of alcohol added, and then 25 cc. of the copper reagent, with constant stirring. The precipitate was allowed to settle, was filtered on a tared paper, washed with 50 per cent alcohol containing ammonia, then with 75 per cent, and finally with 95 per cent alcohol. It was dried to constant weight at 105°, ignited in a porcelain crucible and the ash weighed. The amount of ash was deducted from the weight of the original precipitate and the difference called "net gum arabic." The amount of moisture in the gum originally taken for analysis must be allowed for. This is determined by drying in a current of hydrogen at 105°. No allowance is made for the potassium and calcium which form an integral part of the gum. These may be to some extent retained in the precipitate and, therefore, be included in the ash. Any error that may be introduced by neglecting this is small and very much less than the error inherent in the method.

In some of the preliminary work the gum-copper

<sup>1</sup> Z. physiol. Chem., **9** (1884), 164

<sup>2</sup> See footnote 9; also Ann. Fals., **5**, 27-30; Chem. Zentr., **83**, I (1912), 56.

<sup>3</sup> Ann. chim. anal. appl., **16** (1911), 218-20; Chem. Zentr., **82**, II (1911), 94.

<sup>4</sup> Riegel, Arch. Pharm., [2] **54**, 155; Jahresber., **1** (1847-8), 795; Battut, Sacchar. Indig. et Colon., **32**, 285; Scheibler, Z. Ver. d. Zuckerind., **23**, 288.

<sup>5</sup> Loc. cit.

<sup>6</sup> Diehl, Pharm. Rundschau, **1**, 31; Z. anal. Chem., **22** (1883), 622; Madsen, Pharm. Centr., **20**, 144; Z. anal. Chem., **22** (1883), 134.

<sup>7</sup> v. Lippmann, Loc. cit.

<sup>8</sup> Kiliani, Ber., **15** (1882), 34-7.

<sup>9</sup> Williams, Chem. News, **58**, 224; Z. anal. Chem., **28** (1889), 732.



precipitate was dried at 95° and then at 105°. The additional loss in weight at the higher temperature was usually about 3 or 4 mg., or 1.5 per cent. The following results were obtained with 0.25-g. portions of gum.

RESULTS OBTAINED BY THE AMMONIA-COPPER SULFATE METHOD				
SERIES	A	B	C	D
Percentage of gum found.....	96.6	100.1	100.4	101.6
	98.0	99.0	101.2	102.8
	96.9	98.3	99.1	103.3
	98.4	99.3	99.7	
	96.7	100.7	98.8	
Averages.....	97.3	99.5	99.9	102.6
General average.....	99.5			

It is evident from an inspection of the figures that the method as finally modified is capable of giving results as accurate as could be expected. It is realized, however, that much work could yet be done upon mixtures of gum arabic with ghatti, dextrin, etc., as well as upon mucilages of known composition. A few preliminary determinations, made while Fehling's solution was still being experimented with, indicate that dextrin and ghatti tend to be carried down with gum arabic. At the same time a sample of mucilage was prepared according to the formula in the U. S. Pharmacopoeia; from this the gum was precipitated with strong alcohol, dried and analyzed. The net gum found in four determinations was about 91 per cent. This low result may be due to a fault of the method or to partial hydrolysis of the gum.

The publication of the results so far obtained has been so long delayed, and the opportunity to complete the work seems so remote, that it has been decided to present this paper without further postponement.

#### SUMMARY

The most characteristic qualitative test for gum arabic is the precipitate formed with basic lead acetate. Mixtures of copper sulfate and sodium hydroxide, and of neutral ferric chloride and alcohol are of value as confirmatory tests. A summary of the more important methods that have been proposed for the estimation of gum arabic is followed by a description of the steps that led the authors to the use of alcoholic copper acetate-ammonia solution for this determination.

BUREAU OF STANDARDS, WASHINGTON

### THE OCCURRENCE OF AZELAIC ACID AS A PRODUCT OF THE SPONTANEOUS OXIDATION OF FATS

By BEN H. NICOLET and LEONARD M. LIDDLE

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It is very well known that azelaic acid,  $\text{COOH}(\text{CH}_2)_7\text{COOH}$ , is a normal product of the artificial oxidation of various unsaturated fatty acids. All of the common eighteen-carbon unsaturated fatty acids (oleic, linolic, linolenic) very probably have a double bond located between the ninth and tenth carbons, that is, in the center of the carbon chain. It is further pretty well established that neither linolic nor linolenic acid has a double bond between this position and the carboxyl group. Consequently it was to be expected, and it has been found, that azelaic acid results from the oxidation of these acids with alkaline permanganate, from the decomposition of their ozonides, and from the breaking down of their nitrogen peroxide addition products.

It seemed probable to us that the difference between artificial and natural oxidation would be one of degree, or perhaps only one of time, rather than a complete difference in kind. In this case azelaic acid should be a product, and perhaps an important product, in the development of rancidity, and particularly in its more advanced stages.

Groger<sup>1</sup> exposed some oils to air on filter paper and examined them after four years. One of the products isolated was an impure azelaic acid, supposed to be mixed with some suberic acid.

Sead<sup>2</sup> isolated from rancid material a number of fatty acids ranging from formic to pelargonic, and also most of the corresponding aldehydes. He obtained one fraction of nonvolatile, water-soluble acids, which yielded crystals that he suspected of being azelaic acid.

Here apparently the matter rests to-day. It is the purpose of the present note to call attention to the occurrence in very highly rancid cottonseed oils of amounts as high as 10 per cent of azelaic acid or a glyceride of this acid. The glyceride, whose presence is indicated, would belong to a type heretofore unknown.

Certain grades of fuller's earth are largely used in the bleaching of refined cottonseed oil. The oil remaining absorbed in the earth after filtering and pressing, is in an ideal condition for oxidation by air. In fact the oil-soaked clay, in large scale work, frequently becomes heated to the ignition point by simply standing in contact with air. The oil from a specimen of earth that had been used to bleach cottonseed oil, and had since been kept for a year and a half without any effort to protect it from the air, was extracted for examination.

From 100 g. of clay, low-boiling petroleum ether extracted only 4 g. of oil. Hot alcohol extracted 25 g. The characteristics of the oils from these two extracts are given below.

EXTRACT	Ether	Alcohol
Amount of Extract (grams).....	4.0	25.0
Acid No. (mg. KOH per g. oil).....	145.4	144.8
Saponification No. (mg. KOH per g. oil saponified).....	282.0	260.0
Volatile Acids (mg. KOH to titrate steam-volatile acids from 1 g.).....	46.0	35.0
Azelaic Acid (after saponification).....	3%	10%

In spite of its high acid number, the fraction extracted by alcohol gave very little azelaic acid when extracted with hot water. It was accordingly saponified, and the liberated fatty acids extracted with hot water. The water solution thus obtained was concentrated and gave in various fractions crystals of crude azelaic acid amounting to about 10 per cent of the fat saponified. This crude acid, after two or three recrystallizations from water, showed the constants of pure azelaic acid.

	Found	Pure azelaic acid
Melting point.....	105°	106°
Equivalent weight (by titration).....	95.9	94.0

Another sample of clay was extracted wholly with alcohol, and azelaic acid determined in the hot water extract both from the original material and from the acids obtained on saponification.

<sup>1</sup> Z. angew. Chem., 1889, 62; J. Soc. Chem. Ind., 1889, 202.

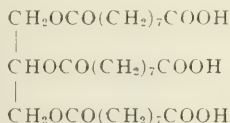
<sup>2</sup> Stas. sper. agr. ital., 30 (1897), 613; Gazz. chim. ital., 38, I (1908), 307; abstract Chem. Zentr., 1908, I, 2085.

AZELAIC ACID FOUND		TOTAL
Before saponification	After saponification	
0.6 per cent	9.8 per cent	10.4 per cent

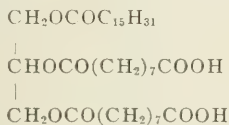
The crude acid had an equivalent weight of 112 (calc. 94).

A "shredded" (laundry) soap, which had developed 2 per cent of free acid on storage, was also worked up for azelaic acid. About 0.5 per cent was found.

The most remarkable thing about the oxidized cottonseed oil described is, however, not so much its abnormally high content of azelaic acid, as the form in which it was evidently present. Only about one-eighteenth of the total amount was present as free acid. The rest was in a form that was insoluble in hot water, and became soluble only after saponification. The simplest assumption to explain this behavior is that the oxidation proceeded practically independently of hydrolysis, and thus gave rise to the formation of glycerides of a hitherto unknown type, the semiglycerides of dibasic acids. The simplest one that might be present here may be called trisemiazelain.



The formation of mixed glycerides is of course not excluded. For instance,  $\alpha$ -palmito diolein might be expected to give  $\alpha$ -palmito disemiazelain,



These results tend also to justify the modern tendency to regard rancidity of fats and oils as due not simply to hydrolysis of the glycerides present, but at least equally to oxidation phenomena which are not necessarily dependent on such hydrolysis. In the case described, it is evident that the oxidation and hydrolysis were entirely independent processes.

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### JELLY INVESTIGATIONS

By W. V. CRUICK AND J. B. MCNAIR

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A great deal of work has been done upon the chemistry of pectin and related bodies from both the purely scientific and practical standpoints. One of the best pieces of work has been done by Th. von Fellenberg,<sup>1</sup> who seems to have obtained more definite information upon the derivation of pectin from more complex compounds and upon its composition and chemical behavior than any of the other investigators. Bigelow and Gore in *Bull. 94* of the U. S. Dept. of Agric., Bureau of Chemistry, gave a very good summary of the literature at that date. Miss N. E. Goldthwaite<sup>2</sup> studied jelly making largely from the practical side and dealt with such factors as effect of acid concen-

tration, character of acid, sugar concentration, character of sugar, temperature, pectin concentration and source of pectin, on quality of jelly.

The experiments discussed in the following paper were undertaken to throw light upon some of the practical phases of jelly making, rather than to add anything to the knowledge of the chemical composition of pectin. The main points investigated were: (1) Suitability of various fruits and vegetables for jelly making; (2) yields of jelly from various fruits; (3) clarification of jelly stock;<sup>1</sup> (4) loss of fresh fruit flavor in jelly making by hydrolysis and evaporation and production of jellies without application of heat; and (5) effect of sugar and acid concentrations on jelly. These topics will be discussed in the order given.

#### SUITABILITY OF VARIOUS FRUITS AND VEGETABLES FOR JELLY MAKING

To produce a jelly of the proper consistency when the liquid, obtained from the fruit by cooking with or without addition of water, is mixed with sugar in the proper proportion and cooked, the fruit must contain a good supply of both pectin and acid, or if not a large supply of pectin, a large amount of compounds that break down into pectin at the temperature of boiling water. Some fruits were found to contain sufficient acid and pectin while others lacked one or the other of these necessary constituents. Where the fruits were low in acid, attempts were made to produce jelly without addition of acid and also with addition of citric acid or lemon juice. In most cases the pectin was extracted in the usual way by cutting the fruit into small pieces, adding water to cover, boiling slowly until tender and expressing the hot juice by pressing in a small fruit press or by straining through a coarse cloth with gentle pressure.

The solution so obtained was analyzed for Balling or Brix degree (per cent dissolved solids) and acidity, and if much more dilute than the juice of the fresh fruit itself, was concentrated before being made into jelly. In making jelly, sugar was added in most cases at the rate of 1 1/4 volumes of sugar to 1 of solution. The mixture was then heated to boiling and boiled down to a boiling point of 104–105° C. or to a concentration of 65–70 per cent dissolved solids. At these concentrations, a jelly will form if the fruit is suited to the purpose.

The tests enumerated in Table I show that cull blackberries, loganberries, Isabella grapes, Tokay grapes, oranges, lemons, and pomelos can be used as jelly stock without addition of acid. These fruits are produced in from moderate to very large quantities in California. The culls resulting during picking and packing are in many instances a total loss. Of those noted, only the loganberry is used to any great extent as jelly stock. Commercially, this fruit is boiled with a small amount of water, pressed and the juice is sterilized in 5-gal. cans. It is stored in these cans until needed. The liquid settles in the cans so that when

<sup>1</sup> By "jelly stock" is meant the pectin-containing solution obtained from fruit or vegetables by heating the material with or without addition of water, and pressing or straining to separate liquid from pulp.

<sup>1</sup> Th. von Fellenberg, *Mitt. Lebensm. Hyg.*, **1914**, 226–256.

<sup>2</sup> N. E. Goldthwaite, *This Journal*, **1** (1909) 333; **2** (1910), 457.



the can is opened and the juice is decanted from the sediment, only a small amount of the total need be filtered. The other fruits noted above can be treated similarly with good results, as small scale tests have shown. Oranges do not always contain sufficient acid for jelly making, while lemons are too high in acid to make a palatable jelly. A mixture of the two fruits in the ratio of two oranges to one lemon gives more uniform and satisfactory results. Tokay grapes give a jelly of neutral flavor and should, therefore, be mixed with highly flavored grapes such as Muscat, Isabella or Concord. Muscat and Tokay culls are obtainable in great quantities in California for \$3 to \$10 per ton.

Cull apples, apple cores, and peels, are, of course, used in large quantities for jelly stock, both for apple jelly and blended jellies. By one of the most common methods, the waste apples are dried, baled, and sold to bakeries and jelly manufacturers. The manufacturer then boils the dried fruit with water as the

extracts were kept separate and tested individually for their jelly making properties. They were also combined in various amounts to ascertain maximum amounts of pectin solutions from the last extractions that could be blended with the first two extracts and still give a jelly. Oranges and lemons mixed in the ratio of two oranges to one lemon gave a maximum yield of 1585 cc. jelly per 1000 g. of fruit, or approximately 392 gals. of jelly per ton of fruit, or 8363 6-oz. glasses of jelly per ton. Yields of 300 gals. of jelly from the mixed fruits have been obtained often in the laboratory. Red loganberries gave a maximum yield of 1890 cc. jelly per 1000 g. fruit or approximately 467 gals., or 9962 6-oz. glasses per ton. Similarly, Mammoth blackberries gave 290 gals. jelly per ton. With addition of acid, these yields were considerably increased so that the yields were limited rather by lack of acid than lack of pectin.

CLARIFICATION—A jelly to be most attractive should be clear. Two methods of clarification are in general

TABLE I—COMPOSITION OF JELLY STOCKS FROM VARIOUS FRUITS, AND SUITABILITY OF VARIOUS FRUITS FOR JELLY MAKING

FRUIT OR VEGETABLE	PECTIN SOLUTION Balling (a)	Acidity (b)	Citric Acid Added	Final Acidity	CHARACTER OF RESULTING JELLY
Apple, Yellow Newtown, Smith Cider, Gravenstein Winesap	....	....	....	....	Good jelly in all cases except where fruit was overripe
Apricot	....	....	0	....	Good jelly in some cases. Does not always jelly
Cherry Black Tartarian	23.2	0.55	0.30	0.80	Very soft jelly. Not satisfactory
Citron Melon	7.1	0.32	0	0.32	Did not jelly
Citron Melon	7.1	0.32	0.68	1.00	Soft jelly, but fairly satisfactory
Citron Melon	7.1	0.32	2.68	3.00	Stiff jelly
Cranberry	....	....	....	....	Stiff jelly
Curant	7.0	1.86	0	1.86	Good jelly
Curant (2nd boiling of pulp)	1.3	0.28	1.22	1.50	Good jelly
Blackberry, Mammoth Variety	7.6	1.18	0	1.18	Good jelly
Blackberry, Himalaya Variety	....	....	....	....	Good jelly
Fig, Mission Variety	13.1	0.2 (app.)	0.3 (app.)	0.5	Good jelly
Fig, Mission Variety	13.1	0.2 (app.)	0	0.2 (app.)	Did not jelly
Grape, Isabella	20.0	0.8	0	0.8	Good jelly
Grape, Tokay	20.0	0.7	0	0.7	Good jelly
Huckleberries	....	....	....	....	Did not jelly
Lemons	4.0 (app.)	3.0	0	3.0	Good jelly (this represents dilution of one-half)
Loganberry	13.5	1.85	0	1.85	Very good jelly
Loganberry (2nd boiling)	7.0	0.96	0	0.96	Fair jelly, a little soft
Loganberry (3rd boiling)	3.0	0.40	0	0.40	Did not jelly
Orange, Navel	8.0	0.65	0	0.65	Good jelly
Orange (2nd boiling)	2.0	0.27	0.5	0.77	Good jelly
Orange (3rd boiling)	1.0	0.10	0.5	0.65	Did not jelly
Orange Valencia	....	....	0.64	0.64	Good jelly
Peach, Muir	....	....	....	....	Did not jelly
Pear, Bartlett	....	....	....	....	Did not jelly
Pomegranate	6.3	0.61	0	0.61	Did not jelly
Pomegranate	12.6	1.60	0	1.60	Did not jelly
Pomelo	....	....	....	....	Good jelly
Pomelo plus Lemons in ratio 6 : 1 by wt.	8.0	0.65	0	0.65	Good jelly
Strawberry	5.8	0.76	0	0.76	Did not jelly

(a) Balling degree equals per cent dissolved solids, principally sugars.

(b) Acidity as citric or malic.

fruit is needed for jelly making. Loganberries and citrus fruits have been treated similarly in this laboratory with good results.

Citron melons were found to be high in pectin, but low in acid. They could possibly be mixed with acid fruits when used for jelly.

The suitability of cranberries and currants for jelly is so well known that they need not be dwelt upon.

Peaches, pears, pomegranates and strawberries were found to be too low in pectin for jelly.

Mission figs contain sufficient pectin, but are too low in acid to make jelly. The localities that produce figs often produce lemons; thus the two fruits could be mixed to advantage.

YIELDS—The amount of jelly obtainable from any fruit without addition of acid will depend on the pectin and acid content of that fruit. Maximum yields from several fruits were obtained by making from four to six successive extractions of pectin by boiling the fruit with water and pressing. The several

commercial use. The most common practice is to filter the hot pectin solution. Often the boiled fruit and liquid are thrown together into some form of cloth or felt bag filter. This process is slow and troublesome and does not ordinarily give a brilliantly clear filtrate.

The second method consists in sterilizing the hot juice from the press in 5-gal. cans. These are stored until the sediment deposits. This will ordinarily be a period of several months. The settled juice is then decanted or siphoned off from the sediment directly into the cooking kettles. The process is often modified to the extent of giving the hot juice a bag filtration before canning.

Laboratory tests were made to ascertain the effect of Spanish clay and infusorial earth on the rate of filtration. These substances were added in powdered form to the hot juice and the rates of filtration and clearness of filtrates compared with those of the untreated juice. The Spanish clay, when added dry,

gave an "earthy" taste and did not appreciably hasten filtration. Infusorial earth, when added at the rate of 5 g. per 100 cc., greatly increased the rate of filtration and gave a clearer filtrate with one filtration than could be obtained without the addition of this substance. It was also found that the filtration through short fiber asbestos pulp in the Seitz type of filter was very much more rapid and resulted in a clearer filtrate than was obtained with the bag filter. A mixture of Seitz asbestos No. 5 and Seitz "Brilliant" asbestos added to and mixed with juice to give a filtering layer about  $\frac{3}{8}$  in. thick gave good results. The flavor of the juice is not impaired. Filtration in all cases is made before any sugar is added to the juice.

Jelly stocks from loganberries, currants, and a mixture of oranges and lemons were prepared by boiling the fruits with a small amount of water until soft and pressing through a coarse cloth. The oranges and lemons were mixed in the ratio of two oranges to one lemon before boiling. The juices were divided into small portions. To these portions were added casein from a 2 per cent solution in dilute  $\text{NH}_4\text{OH}$  at the rate of 20, 40, 60 and 100 g. per hectoliter, respectively. To other portions were added egg albumen in the same amounts as noted for casein. To others were added 250, 500, 1000, 1500 and 2000 g. Spanish clay per hectoliter from a 10 per cent suspension of this substance in water. Untreated checks were also prepared. The various lots were bottled and sterilized one-half an hour at  $100^\circ \text{C}$ . It was found that the lemon-orange jelly stock settled very satisfactorily in 24 hrs. after sterilization without the addition of any clarifying material. The untreated loganberry and currant checks did not settle very satisfactorily in 24 hrs., but after several weeks' storage did settle fairly well. Currant juice prepared by heating the crushed fruit to  $85^\circ \text{C}$ ., pressing and sterilizing at  $85^\circ \text{C}$ ., settled better than the juice from the same fruit heated to  $100^\circ \text{C}$ . The casein and egg-albumen findings gave poor results in all cases and resulted in making the liquids more cloudy than the untreated checks. Spanish clay at 250 g. per hectoliter did not aid in clearing; 500 g. per hectoliter seemed to aid considerably in clearing. In some cases, 1000 g. per hectoliter gave a perfect clarification in 24 hrs.; in other cases, 1500 to 2000 g. of Spanish clay per hectoliter were needed to effect clearing of the juice. This was especially true of loganberry juice. In applying this method in practice, preliminary tests on a few hundred cc. of the material should be made before clarifying any large amount.

The Spanish clay was prepared by soaking it in a small amount of water until soft. It was then worked up with the water into a finely divided, thin "mud" or suspension. This can be made to a definite concentration; *e. g.*, 20 per cent or 10 per cent mixtures were found satisfactory. The flavor of the juice is not impaired by the use of the clay in this form.

Preliminary tests with fire clay indicate that this substance can probably be used in a way similar to that employed with Spanish clay.

#### AROMA AND FLAVOR CHANGES IN JELLY MAKING

Fruit jellies when made in the ordinary way usually have a different aroma and flavor than those of the fresh fruits from which they are made. Ordinarily, jellies are made by extracting the pectin by boiling, followed by addition of sugar and boiling until the mixture boils at about  $220^\circ \text{F}$ ., or until the mixture jells, or until a Balling or Brix degree of  $65^\circ$  (corrected for temperature) is obtained. The high temperatures resulted in marked changes in flavor, giving a so-called "cooked" taste to the resulting jelly.

It was thought that this change in flavor and aroma might be due in part to hydrolysis and in part to loss by volatilization. To throw light on loss by evaporation, attempts were made to make jelly from currants, loganberries, blackberries, and a mixture of orange and lemons, at temperatures of room temperature,  $60^\circ$ ,  $70^\circ$ ,  $80^\circ$ ,  $90^\circ$  and  $100^\circ \text{C}$ . The fruits were crushed and heated in water-jacketed aluminum pots to the temperatures indicated and pressed. Cane sugar was added to increase the Brix degree to  $65^\circ$  and the juices were heated to the temperatures indicated to dissolve the sugar.

To note whether loss of flavor was also due to hydrolysis, a second series at the same temperatures indicated above was carried out in a 500-cc. flask fitted with a long water-cooled reflux condenser.

The jellies made by the two methods were compared shortly after they were made. The jellies made in the open kettle at the lower temperatures were superior to those made at the higher temperatures as regards amount of fresh fruit flavor and aroma retained. The same applied to the jellies made under the reflux condenser. After two to three months' storage, the differences in flavor and aroma were not so pronounced. The orange jelly, after long storage, developed a "turpentine"-like taste, probably due to oxidation of the orange oil.

The jellies made at room temperature were especially close to the flavor of the fresh fruits from which they were made. Loganberry and in one or two cases blackberry and orange jelly were made without application of heat, but strawberries did not yield a jelly in any case. Loganberries very readily give a highly flavored aromatic and firm jelly in this way. So far as known, this method has not been described in the literature before.

The jellies made under the reflux condenser were superior in flavor and aroma to those made at the corresponding temperatures in the open kettle.

The facts that jellies made at high temperatures ( $85$ – $105^\circ \text{C}$ .) were poorer in fresh fruit flavor than those made at room temperature and  $60$ – $75^\circ \text{C}$ ., and that jellies made under the reflux condenser were stronger in fresh fruit aroma and flavor than jellies made at the same temperatures in an open kettle, indicate that loss of flavor and aroma is due both to volatilization and to decomposition of flavoring and aromatic bodies.

#### EXPERIMENTS ON RÔLE OF SUGAR IN JELLY MAKING

The addition of sugar in jelly making is necessary to raise the concentration of dissolved solids sufficiently



to cause setting of the pectin. The amount of sugar necessary to cause setting will depend upon the pectin and acid concentrations, but the amount used normally is controlled by the concentration of sugar necessary to prevent fermentation or molding. Tests with loganberry and orange jellies showed that jellies could be obtained at 60° Brix or lower, but that in such cases molding or fermentation took place unless jellies were sterilized in sealed containers. Jellies with varying amounts of sugar were inoculated with mold and yeast and caps were placed on the glasses. It was found that 65° Brix prevented spoilage but that much below this concentration, mold growth took place. Where the sugar concentration was increased from 72° to 75° Brix crystallization of sugar often took place. This crystallization depends on the amount of cane sugar present. The tendency to crystallize was most noticeable in jellies of low acid content and in which little hydrolysis of the cane sugar had probably taken place. Where glucose is used for jelly making, the concentration may be considerably above 70° Brix without crystallization.

In the ordinary household method of jelly making, equal parts of volume of juice and sugar are used. The mixture is then boiled down until it jells. This results in prolonged boiling at temperatures above 100° C. and consequently in considerable loss in flavor and aroma. Jellies were made by this method and compared with jellies from the same fruits made by adding enough sugar to bring the juice to the proper concentration (65° Brix) at once and only heating enough to dissolve the sugar. The latter method gave jellies of better flavor and aroma than the former.

A simple method for calculating the amount of sugar to add to a juice of a given degree Brix to bring the liquid to 65° Brix is as follows:

Let  $a$  = Brix of juice.  
 $V$  = Volume of juice.  
 $S$  = Grams sugar necessary to bring to 65° Brix.  
 Then  $(65 - a)V/35 = S$ .  
 Example:  
 $V = 250$  cc  $a = 5^\circ$  Brix.  
 $(65 - 5) 250 / 35 = S = 428.5$  g. sugar.

For practical purposes, a little more than 1½ of sugar to one of juice by weight will be found satisfactory.

If this method is used, the fruit juice cannot be so dilute as where a mixture of one of sugar to one of juice is used and where the pectin is concentrated by boiling off excess water. The juice must contain enough pectin to give a jelly without concentration of the juice.

Sugar added to the crushed fruit before pectin extraction seemed to help retain the flavor and the jelly so made appeared to be superior in this respect to jelly made by the usual methods.

A solution of 65° Brix will boil at 103.9° C. or 219.02° F. at sea level. This point can be used to determine the proper density of the boiling jelly if the proper allowance is made for elevation of locality in which the jelly is made. The boiling point of water for any given locality may be determined and then the boiling point of jelly at the proper concentration will be 3.9° C. or 7.02° F. above the boiling point of water.

#### TESTS ON EFFECT OF ACID IN JELLY MAKING

It was found that pectin solutions made by boiling and pressing fruit and containing less than 0.5 per cent acid as citric or tartaric usually did not jelly, but it was also found that if the acid were increased to 0.7 or 0.8 in such cases, it almost invariably gave a jelly. This was noticed especially with citron melon and fig solutions, both naturally deficient in acid, but containing sufficient pectin for jelly making. Tests made with a 1 per cent solution of pure orange pectin in distilled water indicated that a concentration of 0.3 per cent acid in the final jelly was necessary to give a firm jelly. Increase of acid in the final jelly to 1.0 per cent acid resulted in softening of the jelly; 1 per cent acid in the final jelly gave good results and corresponds to about 1.5 acid in a fruit juice before addition of sugar. 0.3 per cent acid in the final jelly would similarly correspond to about 0.5 per cent acid in the fruit juice before addition of sugar. This would indicate a range of 0.5 to 1.5 per cent acid in the original fruit juice for the proper concentration of acid calculated as citric acid. This corresponds very well with results obtained with pectin-containing orange juices made by boiling this fruit and pressing. In this case an acidity of 1.5 per cent in the juice gave a finished jelly that set quickly but which finally softened, while 0.5 per cent gave a fairly good jelly, and less than 0.5 per cent did not give a jelly or resulted in a very soft jelly.

Working with purified pectin and different amounts of pure citric acid, it was found that for the same treatment as regards amounts of sugar added, time of boiling, etc., the color of the resulting jelly was darkened in direct proportion to the amount of acid used. The colors were compared by means of a Dubosq colorimeter. This darkening is probably due to caramelization of the sugar.

#### SUMMARY

I—It was found that of the fruits produced in any great quantity in California, namely, grapes, apples, loganberries, blackberries, lemons and pomelos in all cases contained sufficient acid and pectin to give satisfactory jellies. Oranges always contained enough pectin, but were found to give better results if mixed with lemons to increase the acidity. Apricots and cherries occasionally gave jellies, but in general were not satisfactory because of deficiency in pectin. Pomegranates and strawberries did not have enough pectin to give jellies, although the acidity was sufficient. Peaches, pears, and the huckleberries lacked sufficient pectin and acid. Figs and citron melon gave satisfactory jellies when acidified with citric acid or lemon juice.

II—Maximum yields of 392 gals. jelly per ton of oranges and lemons mixed in ratio of two oranges to

<sup>1</sup> This pectin was prepared by boiling the sliced oranges under a reflux condenser with 95 per cent alcohol three successive times with three different lots of alcohol. This removes most of the sugars, acid, etc. The residual pulp was then heated with distilled water under pressure. The hot liquid was pressed out and filtered. The pectin was precipitated with 95 per cent alcohol and purified by redissolving in water and precipitating with 95 per cent alcohol. This purification was twice repeated. The resulting pectin was white and friable.

one lemon, 467 gals. per ton of loganberries and 290 gals. per ton of blackberries were obtained in this laboratory.

III—Orange jelly stock was found to clear satisfactorily by settling twenty-four hours; other juices required a longer time and did not settle so completely as the orange jelly stock did. All juices tested were clarified satisfactorily by the addition of 1000–2000 g. Spanish clay per hectoliter (from a 10 or 20 per cent suspension of the clay in water), followed by heating to 100° C. and settling.

IV—Changes in and loss of fruit flavors and aromas in jelly making were found to be due to decomposition by heat and to direct loss by volatilization.

V—Jellies with practically all of the aroma and flavor of the fresh fruit were made by crushing fruits high in pectin, pressing out the juice, and adding sufficient sugar to increase the Brix degree to 65°. Loganberries and currants were especially adapted to this procedure

VI—An acidity between 0.5 and 1.5 per cent for fruit juices to be made into jelly seemed to be the optimum range for production of satisfactory jellies.

VII—A Brix degree of 65° was necessary to prevent spoilage by mold and yeasts where jellies were inoculated with these organisms.

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## THE ANALYSIS OF NON-ALCOHOLIC LEMON AND ORANGE EXTRACTS

By E. L. REDFERN

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During the last year there have appeared on the market various flavoring extracts containing no alcohol but made up with gum tragacanth and glycerine in which the essential oils are held in suspension. It is obvious that the amount of oil present cannot be determined by the ordinary methods and an attempt was made to devise some method by which the oils could be determined quantitatively to see if this class of extracts was up to the legal standard. These extracts are quite viscous and unless warmed slightly, pour with difficulty, but, by warming for a few minutes they can be measured in an accurately graduated cylindrical graduate. The use of a pipette for measuring is not satisfactory, as a considerable amount of the mixture adheres to the inside of the pipette and is difficult to remove, while with a graduate it can be removed by letting the graduate drain for a few minutes into the flask to be used in the analysis and then rinsing with a little alcohol. A standard extract containing 5 per cent of lemon oil was made up as follows: 150 cc. gum tragacanth, which had been soaked in water and reduced to the proper consistency, 40 cc. glycerine and 10 cc. pure lemon oil.

First an attempt was made to extract the oil in a separatory funnel with ether but an emulsion was formed which could be only partly broken up by running in the centrifuge. The ether was drawn off through a small dry filter into a tared flask, evaporated off spontaneously and dried for a few hours in a

desiccator. The final weight of oil obtained from 10 cc. of the 5 per cent extract was 0.2664 and 0.2246 g. in duplicate determinations. Ten grams of extract were then mixed with anhydrous  $\text{CuSO}_4$  to apparent dryness and extracted in a Soxhlet extractor with anhydrous ether but only 17 per cent of the oil was recovered. Distillation with steam gave 24 per cent recovery of oil. The fact that gums are precipitated with alcohol suggested a possible solution of the difficulty: 25 cc. of the standard extract were measured out and transferred to a 200-cc. Erlenmeyer flask, 25 cc. of 95 per cent alcohol were added and the flask was then shaken vigorously. The alcohol was filtered on a Gooch crucible and collected in a 100-cc. graduated flask, care being taken to prevent any of the precipitated gum from running into the crucible. The precipitate was washed several times with 95 per cent alcohol and the filtrate made up to 100 cc. The precipitation method using 50 cc. of this solution did not give uniform results, owing to the fact that with this high strength of alcohol a considerable quantity of the oil was held in solution. The method suggested by Howard<sup>1</sup> was then used which gave 4.96 and 5 per cent oil in duplicate tests on the 5 per cent standard.

An orange extract was made up as in the case of lemon, using orange oil, and gave in duplicate tests with Howard's method 4.80 per cent of oil.

Duplicate tests of an unknown extract gave 5.2 and 5.04 per cent. In these tests a Babcock milk bottle graduated to 1 per cent was used to insure more accurate reading as the amount of oil in the dilutions is small. Especially is this true in substandard extracts. If the analysis of an extract shows that it is much below standard, the author has found it advisable to repeat the analysis using a skim milk bottle graduated to 0.01 per cent, which makes it possible to read very small amounts of oil. The supernatant liquid in the skim milk bottle can be easily drawn off by attaching a suction tube to the filling tube on the bottle and decanting off the remaining small amount through the capillary tube as the chloroform carries the oil present and remains on the bottom. The method has been used in this laboratory for several months and has given uniform results.

IOWA DAIRY AND FOOD COMMISSION  
DES MOINES

## THE ANALYSIS OF MAPLE PRODUCTS, VIII

### The Application of the Conductivity and Volumetric Lead Subacetate Tests to Maple Sugar

By J. F. SNELL AND G. J. VAN ZOEREN

Received August 27, 1915

In Papers I<sup>2</sup> and VII<sup>3</sup> of this series a conductivity test and in Paper VI<sup>4</sup> a volumetric lead subacetate test for purity of maple syrup have been described. The question remained how these tests could best be applied to sugars. Two methods of procedure suggested themselves: (1) A quantity of sugar sufficient

<sup>1</sup> *J. Am. Chem. Soc.*, **1908**, 608.

<sup>2</sup> *This Journal*, **5** (1913), 740.

<sup>3</sup> *Ibid.*, **8** (1916), 331.

<sup>4</sup> *Ibid.*, **8** (1916), 241.



for the test could be weighed out and dissolved in a definite quantity of water; (2) a larger quantity of sugar could be dissolved and the solution boiled down to a syrup, which could then be tested as a syrup.

Under the direction of the senior author, Mr. J. M. Scott in 1913 determined the conductivity values of some twenty pure sugars by both of these methods of procedure. For the first, 15 g. of sugar were dissolved in hot water and made up to 50 cc. at 250° C. For the second method a solution of the sugar was boiled until the temperature reached 219° F. The values obtained were seldom identical; in some instances the former method, in other instances the latter method, gave the higher result. This indicated variation in sampling, and as material suitable for a study of the question of sampling was not immediately available the investigation was laid aside. It has now been resumed with reference to the volumetric lead test as well as to the conductivity test.

Ten of the syrups of the season of 1915 used in the work reported in Papers VI and VII were used in these new experiments. About 200 cc. of each were boiled to 243–245° F., poured into moulds, and allowed to stand for a day or two. The sugars thus obtained were redissolved, boiled to 219° F. and filtered through cotton wool. The conductivity values and the volumetric lead numbers were then redetermined on the regained syrups and compared with those found in the original syrups. The results are given in Table I. They show no material difference between the original syrup and that obtained by redissolving the sugar. This method of applying the tests to maple sugar is, therefore, satisfactory.

TABLE I.—COMPARISON OF VALUES IN ORIGINAL AND REGAINED SYRUPS

No.	10	13	14	16	18	19	22	27	29	43	Av.
CONDUCTIVITY VALUE											
Original Syrup.....	107	119	99	106	97	108	112	109	117	125	109.9
Syrup from Sugar.....	106	119	99	106	98	106	112	110	113	125	109.4
VOLUMETRIC LEAD NO.											
Original Syrup.....	5.3	5.3	5.1	5.3	5.8	6.0	5.7	5.1	5.6	5.2	5.44
Syrup from Sugar....	5.4	5.6	5.3	5.4	5.4	6.2	5.6	5.0	5.5	5.8	5.52

The tests have been applied in the same manner to 16 sugars of the season of 1913, which were collected from the makers with the syrups reported in Paper III.<sup>1</sup> 75–100 g. of sugar were dissolved, the solution boiled to 219° F. and filtered through cotton wool.

The conductivity values found vary from 97 to 148 and the volumetric lead numbers from 5.1 to 6.5. These results are all within the limits found in pure maple syrups.<sup>2</sup> The conductivity values obtained by Mr. Scott by this same method (22 pure sugars) are also within the limits found in pure maple syrups.

Three sugars collected from grocers in the western provinces of Canada in 1912, tested in like manner, gave the following results:

No.	Conductivity Value	Volumetric Lead No.
1.....	16	0
2.....	146	5.6
3.....	79	0

Nos. 1 and 3 are condemned by the tests, while No. 2 appears to be a genuine maple sugar.

METHOD—Dissolve a fairly large representative sample (say 100 g.) of the sugar in hot water. Boil

to 210° F. (103.9° C.). Filter through cotton wool. Test the resulting syrup as directed in Papers VI and VII.

#### SUMMARY

Pure maple sugars converted into syrups give conductivity values and volumetric lead numbers within the limits found in genuine maple syrups.

MACDONALD COLLEGE, PROVINCE OF QUEBEC

#### DETERMINATION OF TARTARIC ACID

By B. G. HARTMANN, J. R. EOFF AND M. J. INGLE

Received December 30, 1915

The determination of tartaric acid in numerous soda fountain beverages, grape juices, wines and other food products, has necessitated a modification of the Halenke and Möslinger method, the provisional method of the Association of Official Agricultural Chemists.<sup>1</sup> Since modifications of this method presented as reports of the Associate Referee on Wine of the above Association have not thus far been available to many chemists who may be doing work of this nature, it is considered desirable to review briefly the recent methods for the determination of tartaric acid<sup>2</sup> and to give the results of a successful search for the cause of the discrepancies noted in the determination of this acid. These variations in results, even of the same analyst, were noted especially on wines containing free acid and alcohol.<sup>3</sup>

Most of the earlier methods depended on the precipitation of potassium acid tartrate, the original method being that of Berthelot and Fleuriu<sup>4</sup> published in 1889. This method was modified by Halenke and Möslinger<sup>5</sup> in 1895. Of the numerous methods which have been described for the quantitative determination of total tartaric acid in wines, this method may be considered as deserving first mention as to simplicity of manipulation, accuracy and adaptability to varying conditions. This is the method which the authors have still further modified.

Magnier de la Source<sup>6</sup> was perhaps one of the first to note the fact that when free tartaric acid was present the cream of tartar precipitate did not represent the total tartaric acid content. He, however, suggested the neutralization of one-fifth of the total acidity by adding standard alkali. This procedure did not give satisfactory results on wines containing much free tartaric acid, such as Catawba and Scuppernong. The Goldenberg method<sup>7</sup> for the estimation of the tartaric acid content of argols or crude tartar, consisted in dissolving the argols in hydrochloric acid and, after completely neutralizing with potassium carbonate, adding acetic acid to transform the neutral salt to the insoluble acid tartrate. This procedure, however, was open to criticism, since (as noted by Lampert and by Ordonneau<sup>8</sup>) iron

<sup>1</sup> U. S. Bureau of Chemistry, *Bull.* **107** (1912), 86.

<sup>2</sup> E. P. Haussler, *Schweiz. Apoth. Zeit.*, **52** (1914), 525–7, 537–40, 553–6, 569–72.

<sup>3</sup> B. G. Hartmann, *Proc. A. O. A. C.*, **1914**.

<sup>4</sup> M. Berthelot, *Chimie Végétale et Agricole*, **4** (1889), 423, in collaboration with M. de Fleuriu.

<sup>5</sup> A. Halenke and W. Möslinger, *Z. anal. Chem.*, **34** (1895), 263.

<sup>6</sup> M. L. Magnier de la Source, *Ann. chim. anal.*, **1** (1896), 205–6.

<sup>7</sup> *Zeit. anal. Chem.*, **47** (1908), 57–59 (from *Chemischen Fabrik*).

<sup>8</sup> M. C. Ordonneau, *Bull. soc. chim.*, **7** (1910), 1034–41.

<sup>1</sup> *This Journal*, **6** (1914), 216.

<sup>2</sup> See Papers VI and VII.

and aluminum, commonly present in argols, tend to lower the result. Heczko<sup>1</sup> calls attention to the fact that the freshly precipitated calcium carbonate tends to react with the neutral potassium tartrate. The Marseille method<sup>2</sup> was used as an approximate method for the determination of tartaric acid in argols and depended on the precipitation of neutral calcium tartrate from an ammoniacal solution.

The most recent precipitation method is that developed by A. Kling.<sup>3</sup> This is an extremely satisfactory procedure and, as tried out at the Enological Laboratory of the Bureau of Chemistry, gave the best yield of any method tried. The principle of the method is the formation of the very insoluble calcium racemate under conditions which give a theoretical yield from synthetic solutions. When applied to two authentic wines representing the extremes in ratio between cream of tartar and free tartaric acid, it gave results which were all that could be desired.<sup>4</sup> As the tartaric acid present in the grape and the commercial article derived from it is always the dextro form, the addition of an excess of laevo salt would form the racemate, so that by forming the calcium salt under the favorable conditions prescribed, a most efficient method is developed. This is accomplished by adding calcium acetate and alkaline laevo-tartrate of ammonia in excess, and titrating the calcium racemate precipitate with a standardized potassium permanganate solution.

Iron and aluminum introduce a source of error in this determination which has been corrected by a modification, using an ammonium citrate solution.<sup>5</sup> The presence of esters of tartaric acid is also allowed for by saponification as detailed by Kling and Gelin.<sup>6</sup> The present prohibitive price of laevo-tartrate of ammonia, the instability of a tartrate solution, which requires a preservative, and the need of a microscope, are all factors tending to inhibit a general use of this method in commercial laboratories.

Other investigators have made use of the reducing action of the tartaric acid radical; thus Chapman and Whitteridge<sup>7</sup> oxidize a bismuth tartrate precipitate; Mestrezat<sup>8</sup> and Kling also finally titrate with potassium permanganate. Pozzi-Escot<sup>9</sup> oxidizes barium tartrate, while Ferentzy<sup>10</sup> ignites magnesium tartrate and weighs the resultant MgO, but Gowing-Scopes<sup>11</sup> modifies this method and titrates the magnesium tartrate with permanganate.

Evaporation, with a subsequent addition of alcohol, or alcohol and ether, has been advanced by Pasteur, Reboul, Magnier de la Source, and Malvezin. The addition of potassium bromide brings the free

tartaric acid into the reaction, so that on the addition of the alcohol-ether mixture all the tartaric acid is precipitated as tartar. These methods are not considered satisfactory as the evaporation is productive of losses through volatilization of esters and possible decomposition, and acid malates are titrated as tartrates<sup>1</sup> as are also other acid-reacting substances. This method as given by Malvezin was also tried out in the Enological Laboratory, and gave concordant but uniformly high results.

It has been demonstrated in routine work by the authors that the Halenke and Möslinger method is unreliable when employed on wines and fruit juices containing a considerable amount of free tartaric acid, such as Catawba, Iona, or Scuppernong grape juices or wines. This is due to the failure of the method to precipitate the free tartaric acid quantitatively as potassium acid tartrate and is attributable to the reversibility of the main reaction ( $\text{H}_2\text{T} + \text{KCl} \rightleftharpoons \text{HKT} + \text{HCl}$ ). It has been noted by the authors that the addition of potassium acetate for the purpose of offsetting the disturbing influence of the hydrochloric acid formed ( $\text{KAc} + \text{HCl} \rightleftharpoons \text{KCl} + \text{HAc}$ ) does not altogether correct this fault, one-fifth to one-third of the free tartaric acid being lost.<sup>2</sup> Furthermore, the addition of the potassium acetate to wines not containing free tartaric acid has a tendency to decrease the yield by dissolving the potassium acid tartrate.<sup>3</sup>

Having thus recognized that the value of the Halenke-Möslinger method was in the main dependent upon the elimination of the disturbing influence of the hydrochloric acid liberated, the authors decided that the best preventive for the formation of hydrochloric acid was to completely neutralize the acidity of the wine and to add the molecular equivalent of tartaric acid for the alkali added in order to convert the neutral tartrates into acid tartrates, and from this point on to proceed as prescribed in the Halenke-Möslinger method, omitting the potassium acetate addition altogether. By this procedure no intermediate products which might possibly interfere with or redissolve the potassium acid tartrate were to be expected, thus forming favorable conditions for a quantitative separation of the total tartaric acid as potassium acid tartrate. Trials of the procedure upon various synthetic solutions of tartaric acid and its salts proved its superiority to the older method.

Unfortunately, these experiments are not final since they were for the greater part undertaken on aqueous solutions, but it is quite possible that the behavior of a wine containing various other ingredients, such as phosphates and sulfates, may augment the usefulness of the method.

This modification has the decided advantage over the Halenke-Möslinger method in that, where there is a small amount of tartaric acid present in a wine (as in ports, sherries, and other fortified wines), the

<sup>1</sup> Arnold Heczko, *Z. anal. Chem.*, **50** (1911), 73-82.

<sup>2</sup> M. d'Hector de Rochefontaine, *Ann. chim. anal.*, **1** (1896), 25.

<sup>3</sup> Andre Kling and L. Gobert, *Ann. fals.*, **4** (1911), 185.

<sup>4</sup> *J. Assoc. of Offic. Agr. Chem.*, **1** (1915), 136.

<sup>5</sup> M. Andre Kling and D. Florentin, *Proc. 8th Intern. Cong. Appl. Chem.*, **1** (1912), 237-9.

<sup>6</sup> M. Andre Kling and E. Gelin, *Ibid.*, **1** (1912), 251-6.

<sup>7</sup> Alfred C. Chapman and Percy Whitteridge, *Analyst*, **32** (1907), 163-6.

<sup>8</sup> Note of M. W. Mestrezat presented by M. Müntz, *Compt. rend.*, **143** (1906), 185.

<sup>9</sup> Em Pozzi-Escot, *Ann. chim. anal.*, **13** (1908), 266-9.

<sup>10</sup> Josef V. Ferentzy, *Chem. Zeit.*, **31** (1907), 1118.

<sup>11</sup> L. Gowing-Scopes, *Analyst*, **33** (1908), 315-19.

<sup>1</sup> M. L. Magnier de la Source, *Ann. chim. anal.*, **2** (1897), 281-3.

<sup>2</sup> B. G. Hartman, Bureau of Chemistry, *Bull.* **162** (1913), 71.

<sup>3</sup> *Ann. chim. anal.*, **1** (1896), 205-6.



addition of the tartaric acid insures a precipitation that otherwise might not occur.

#### HARTMANN AND EOFF METHOD

**FOR WINES** Neutralize 100 cc. of wine with normal sodium hydroxide. The amount of alkali necessary for neutralizing may be calculated from the acidity of the wine previously determined. To the neutralized wine add the molecular equivalent in grams, of powdered tartaric acid,<sup>1</sup> corresponding to the amount of alkali required for neutralization. After the tartaric acid has dissolved add 2 cc. glacial acetic acid and 15 g. potassium chloride and after solution add 15 cc. alcohol (95 per cent). Stir until precipitation has started, then allow to stand over night at a temperature not above 15° C. After this interval filter the solution through either a Gooch crucible prepared with filter paper pulp or a Buchner funnel of 7 cm. diameter, into which is fitted exactly

TABLE I DETERMINATIONS OF TARTARIC ACID BY HARTMANN-EOFF METHOD

SUBSTANCE	Results in Grams Tartaric Acid per 100 cc. Liquid		
	Actual Content	Hand Stirred	MECHANICALLY STIRRED 30 min. 15 min.
Tartaric Acid Solution...	0.481	...	0.482
	0.481	...	0.483
	0.241	...	0.238
	0.241	...	0.236
	0.241	...	0.238
	0.120	...	0.110
	0.048	0.042	0.025
	0.048	0.042	0.012(a)
California Hock Wine ..	0.254(b)	0.240	0.255
California Sauterne Wine.	0.221(b)	0.215	0.217
California Zinfandel Wine	0.235(b)	0.211	0.243
California Sherry Wine...	...	0.088	0.099
California Port Wine....	...	0.113	0.120
California Sherry No. 2...	...	0.101	0.100
California Port No. 2....	...	0.120	0.120

(a) Stirred one hour.

(b) Content determined by method given on p. 86 of U. S. Dept. Agr., Bureau of Chemistry, *Bull.* 107 (Rev.).

a strong filter paper; use gentle suction and wash three times with 7 cc. of a solution composed of 100 cc. of water, 15 g. potassium chloride and 20 cc. of 95 per cent alcohol. Transfer the precipitate and paper to the original beaker with 50 cc. hot water, bring to a boil and immediately titrate with *N*/10 sodium hydroxide, using phenolphthalein as indicator. Increase the burette reading by 1.5 cc. as a correction for solubility, multiply by 0.015 and subtract the tartaric acid added. This will give the total tartaric acid in the wine in terms of grams per 100 cc.

#### OTHER MODIFICATIONS

**STIRRING**—It was noted that stirring until a precipitate actually formed was essential to the accuracy of the method. By means of the mechanical stirring of solutions the time factor was lessened and it was found practicable by this expedient to determine correctly the tartaric acid content of a synthetic solution in 15 to 30 minutes.

**HALF-NEUTRALIZATION METHOD.**—An attempt to neutralize one-half of the acidity of wine proceeding according to the Halenke-Möslinger method, omitting

TABLE II—DETERMINATION OF TARTARIC ACID IN WINES IN WHICH THE ACIDITY WAS HALF NEUTRALIZED

Experiment No.	1	2	3	4	5	6	7
Hartmann-Eoff Method.....	0.74	0.54	0.99	0.76	0.72	0.78	0.80
Half-Neutralization Method...	0.68	0.50	0.96	0.71	0.63	0.71	0.77

the potassium acetate addition, gave less accurate results than complete neutralization, from 3 to 9 per cent less acid being found than was present.

<sup>1</sup> The acid used should be pure and well dried.

**TEMPERATURE**—The authors also find that the temperature at which the reaction mixture of the Halenke-Möslinger method is held for 15 hrs. influences the precipitation, there being a decided increase in yield of tartrate at low temperatures.

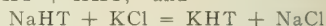
TABLE III EFFECT OF CHILLING ON PRECIPITATION WHEN UNMODIFIED METHOD WAS USED

No.	Temperature C.	GRAM TARTARIC ACID Actual	Found	Per cent Acid Recovered
1	5	0.994	0.774	77.9
2	5	0.994	0.792	79.7
3	5	0.497	0.401	80.7
4	5	0.497	0.405	81.5
5	17	0.994	0.698	70.2
6	17	0.994	0.698	70.2
7	17	0.497	0.354	71.3
8	17	0.497	0.357	71.8

Before entering upon the final description of the methods resulting from these experiments it should be remarked that although other investigators have attempted to avoid the disturbing influence of mineral acids by neutralizing a part of the acidity of the wine, the authors have been unable to find records showing that this has been done with any marked degree of success and that the addition of tartaric acid to the neutralized solution for the purpose of precipitating potassium acid tartrate has evidently not been previously tried.

#### ROCHELLE SALT METHOD

The tartaric acid required may be efficiently added as Rochelle salt. In that case the method is based on the following reactions:



As Rochelle salt contains exactly four molecules of water of crystallization, it may be used without drying. For every cc. of normal alkali required for neutralization, add 0.141 g. of the salt. As only 53.17 per cent of the salt is normally tartaric acid, weighing errors are minimized. If this salt is ground or unduly exposed to the air it may lose some of its water of crystallization. It is, therefore, necessary to obtain the actual acid content at the time used. This may be done by dissolving 1 g. of the salt in 100 cc. of water, adding 2 cc. acetic acid, 15 g. KCl, and 20 cc. of 95 per cent alcohol, stirring until precipitation starts, and allowing to stand in an ice box with a maximum temperature of 15° C. The addition of alkali may, therefore, be dispensed with.

The following results were obtained on five samples of grape juice, using the proposed method and the Rochelle salt method:

TABLE IV

No.	Grams Rochelle Salt Added	Grams Tartaric Acid in Salt	TARTARIC ACID IN JUICE USING Rochelle Salt	Tartaric Acid H.-E. Method
1	0.776	0.031	0.624	0.627
2	1.297	0.720	1.170	1.205
3	0.874	0.485	0.624	0.636
4	1.199	0.665	0.620	0.638
5	0.677	0.372	0.640	0.637
Rochelle Salt	1.000	0.555	...	...

**FOR GRAPE JUICE**—Take 50 cc. of the filtered juice and neutralize with *N* NaOH. After neutralizing make to 100 cc. volume with distilled water. From this point on, the H.-E. procedure as described under wine is followed, using 20 cc. instead of 15 cc. of

95 per cent alcohol. The occlusion of other organic acids with precipitated pectin bodies and cream of tartar makes the use of only 50 cc. of grape juice advisable for the determination.

In case of syrups, fermentation of sugar or a separation of the acid therefrom as the lead salt<sup>1</sup> is advisable. It may be of interest to mention that Halenke and Möslinger advise a double precipitation in the case of grape juices.

**FOR ARTIFICIAL PRODUCTS CONTAINING FREE PHOSPHORIC ACID AND ALCOHOL**—While experimenting with synthetic solutions, containing tartaric acid, free phosphoric acid and alcohol, it was found that neither the Halenke-Möslinger method nor the Hartmann and Eoff method gave satisfactory results. Further, it developed that these two methods became less reliable as the solutions under discussion aged. This condition was found to be brought about by the formation of ethyl esters of tartaric acid, the amount of ester formed increasing with the time allowed for the reaction. This was shown by saponifying the solution with an excess of alkali before determining the tartaric acid, a complete recovery of the theoretical amount of acid being thereby obtained. It was also observed that in cases where much free phosphoric acid was present the Halenke and Möslinger method failed to give any precipitate of potassium acid tartrate whatever, notwithstanding the presence of considerable tartaric acid in the solution. These two points, the loss of tartaric acid through esterification and the failure of the Halenke-Möslinger method to give even approximate results in presence of free phosphoric acid, were made the subject of investigation in 1914 by the Associate Referee on Wines of the Association of Official Agricultural Chemists. The heretofore unpublished work of five collaborators was very satisfactory and fully substantiates the findings recorded above.

The behavior of alcohol and tartaric acid in the presence of other free organic acids (formation of esters) is a well-known phenomenon and was pointed out by Berthelot and Fleurieu in their original paper describing the alcohol-ether method. Esterification in part may explain why very old wines, when employing the customary methods for determining the total tartaric acid, very often show an exceedingly small amount of this constituent.

It is very important to know the extent of esterification in artificial products containing free phosphoric acid, alcohol, and tartaric acid, since the ordinary methods may not reveal the tartaric acid that is present even in amounts as high as 3 g. per 100 cc. of solution.

It was found that by adding 5 cc. *N* NaOH in excess of neutralization to 50 cc. of the solution under examination, bringing to a boil and allowing to stand over night, a complete saponification could be obtained. The addition of the required amount of tartaric acid, dilution to 100 cc. with water and then proceeding as detailed for wines, yielded quantitative results for total tartaric acid.

Solutions indicated in Table V were analyzed by different analysts on different dates with the results given.

TABLE V—(Results in Grams per 100 cc.)

DETERMINATION	HALENKE AND MÖSLINGER METHOD	HARTMANN-EOFF METHOD	
		Half Neutralized	Completely Neutralized
Acidity as Tartaric.....	4.92	2.52	1.96
Total Tartaric Acid.....	2.00	1.80	1.89
Phosphoric Acid.....	1.91	0.48	0.048
Caramel.....	1.20	1.20	1.20
Amaranth.....	0.024	0.024	0.024
Cane Sugar.....	5.00	5.00	5.00
Alcohol.....	5.00	5.00	5.00

Table VI presents results obtained on three synthetic solutions, on the dates indicated.

TABLE VI—RESULTS (G. per 100 cc.) ON THREE SYNTHETIC SOLUTIONS

Solution Number	DATE 1914	HALENKE AND MÖSLINGER	HARTMANN AND EOFF METHOD	
			Neutralization Half Complete	Preliminary Saponification
I.....	7/20	0.74	1.88	1.90
	8/12	0.64	1.69	1.84
	8/24	0.06	1.54	1.76
	8/26	0.63	1.66	1.67
	10/30	0.00	1.61	1.65
II.....	7/20	1.03	1.76	1.76
	8/12	0.90	1.62	1.68
	8/24	0.67	1.51	1.62
	8/26	0.91	1.57	1.58
	10/30	0.65	1.51	1.63
III.....	7/20	1.23	1.87	1.87
	8/12	1.18	1.77	1.77
	8/24	1.00	1.68	1.77
	8/26	1.22	1.72	1.71
	10/30	0.92	1.63	1.67

The low results obtained by the Halenke and Möslinger method show the necessity of starting the precipitation by stirring as illustrated by the results obtained on August 24th, and October 30th. The gradual esterification of the free tartaric acid is shown by the lower results obtained as the solutions aged.

BUREAU OF CHEMISTRY, WASHINGTON

## THE DECOMPOSITION OF THE ORGANIC MATTER OF KELP IN THE SOIL<sup>1</sup>

By A. W. CHRISTIE

Received November 15, 1915

Considerable interest has been evinced of late in the possible use of kelp as a commercial fertilizer. Burd<sup>2</sup> has shown that probably the most practical and profitable way of utilizing kelp would consist in drying at a low temperature and grinding. The resulting product, in addition to the valuable potash (11.45 per cent  $K_2O$  in air-dried kelp (*Macrocystis*)), contains all the nitrogen and organic matter. Stewart<sup>3</sup> has shown that the nitrogen (1.18 per cent N in air-dried kelp (*Macrocystis*)) becomes slowly available in the soil. In connection with the probable use of dried and ground kelp as a commercial fertilizer or as a filler for mixed fertilizers, it becomes of interest to learn the fate of the organic matter and whether any agricultural value may be assigned to it. The extent and rate of decomposition of kelp in soil were compared with the following materials which are common sources of organic matter in the soil, *viz.*, manure, straw and alfalfa.

### PLAN OF EXPERIMENT

In each of 14 glass jars were placed 300 g. of air-dried soil (fine sandy loam from Anaheim, California),

<sup>1</sup> See also work of U. S. Department of Agriculture on Kelp. [EDITOR'S NOTE.]

<sup>2</sup> "Economic Value of Pacific Coast Kelps," *Bull.* 248, California Agricultural Experiment Station.

<sup>3</sup> "Availability of Nitrogen in Pacific Coast Kelps," *J. Agr. Research*, 4, No. 1 (1915), 21.

<sup>1</sup> C. Schmitt and C. Hiepe, *Z. anal. Chem.*, 21 (1882), 534-41.



and to each jar were added 15 g. of the organic material to be tested. The two samples of kelp used were *Macrocystis pyrifera* and *Nereocystis leutkeana*, the varieties of greatest commercial importance on the Pacific Coast. These samples were oven-dried and finely ground and then allowed to come to constant moisture content by exposure to the air at room temperature. The manure, alfalfa and straw were also finely ground and thoroughly air-dried. Jars 11 and 12, in addition to the 15 g. *Macrocystis*, were inoculated with a few cc. of a solution from a jar of decomposing kelp, to ascertain if the partial sterilization due to oven-drying would have any effect on the subsequent decomposition in the soil. All jars were loosely stoppered to prevent excessive evaporation, yet allowing easy access of air, and were kept at an average temperature of 30° C. for 5 mos. The moisture content was maintained at 18 per cent (optimum for the soil) by frequent additions of sterile water, accompanied by cultivation of the soil.

At the end of 5 mos. the contents of each jar were removed, thoroughly air-dried and ground for analysis. A 10-g. portion from each jar was analyzed for humus and humus nitrogen, using the method of Grandeau, as modified by Hilgard.<sup>1</sup> Table I gives the results obtained.

This table shows that dried and ground kelp in this experiment was decomposed to form humus to approxi-

in which these materials were added to the soil are not the same as would obtain in field practice. None of the materials would be finely ground, with the possible exception of the kelp, if it were part of a complete fertilizer. The alfalfa would ordinarily be plowed under green and the manure moist and fresh; these conditions accelerate their decomposition in the soil. The kelp used in this experiment, as has already been pointed out, was heated to a much greater temperature than would be the case in commercial practice and hence was probably less readily decomposed. The conditions in the laboratory may favor the decomposition of one substance more than another.

The per cent of humus is not necessarily a definite index of the value of the organic matter in the soil. Therefore, it is not desired to convey the impression that the organic matter of kelp is proven by this experiment to be as valuable as the other materials used. The experiment does prove, however, that kelp is not an inert substance in the soil and that its organic matter has some fertilizing value. Final judgment upon these points would require data obtained from field experiments.

#### PENTOSAN DECOMPOSITION

Hoagland<sup>1</sup> has shown that kelp contains considerable amounts of pentosans and since the other materials used are also high in pentosans, it is desirable to study the fate of this group in the soil. The materials were

TABLE I—RESULTS OF 5-MONTH TESTS

Jars	MATERIAL ADDED	PER CENT HUMUS IN SOIL			% N in Humus	% ORGANIC MATTER		% Pentosans in Originals	% PENTOSANS RECOVERED		PER CENT ORIGINAL PENTOSANS DECOMPOSED		
		Duplicates	Av.	GAIN		Original	Humified		Duplicates	Av.			
1 & 2	Alfalfa	0.98	1.08	1.03	0.37	10.15	89.00	8.81	12.18	3.17	2.47	2.82	77
3 & 4	Straw	1.14	1.24	1.19	0.53	8.25	96.50	11.49	27.75	4.34	6.88	5.61	80
5 & 6	Manure	1.08	1.11	1.10	0.44	9.54	65.50	13.98	11.57	2.45	2.49	2.47	79
7 & 8	<i>Nereocystis</i>	1.03	1.16	1.10	0.44	10.50	43.60	21.00	6.16	1.46	1.64	1.55	77
9 & 10	<i>Macrocystis</i>	0.96	1.03	1.00	0.34	11.55	39.60	11.85	7.11	1.72	1.81	1.76	75
11 & 12	Mac. (inoc.)	0.98	1.06	1.02	0.36	9.95	59.60	12.65	7.11	1.62	1.64	1.63	77
13 & 14	[Blanks]	0.65	0.66	0.66	...	13.82	...	...	...	...	...	...	...

mately the same degree as the substances ordinarily employed for that purpose. On a basis of equal weights of original material, the *Nereocystis* is surpassed only by straw, is equal to manure and superior to alfalfa. The *Macrocystis* is somewhat inferior but nearly equal to alfalfa. The inoculation of the *Macrocystis* slightly increased its humification but not sufficiently to cause it to surpass any of the other materials. The variations in the percentage of nitrogen in the humus are slight and no great importance is attached to them.

Since the various materials used contain very different amounts of organic matter which might be humified, the percentage of the organic matter humified during the period of incubation is important. The per cent of organic matter in the original materials and the average per cent of this organic matter which humified appear in Table I. On the basis of a unit amount of organic matter, the *Nereocystis* is by far the best humus producer and even the *Macrocystis* is surpassed only by the manure. The conditions under which this experiment was carried out, viz., constant moisture content of 18 per cent and constant temperature of 30° C. for 5 mos., would certainly be equivalent to a considerably longer period under field conditions. Furthermore, the form and manner

analyzed for pentosans according to the Official method,<sup>2</sup> which is empirical and depends upon the production of furfural from whatever source derived; hence, conclusions regarding the decomposition of pentosan materials must be based simply upon comparative data. The samples of soil and organic materials were the same as those previously described. After 5 mos. incubation the soils were analyzed and the percentages of pentosans found calculated to the original weight of materials added to the soil. Tests on untreated soil showed only very small amounts of furfural-yielding substances, and corrections were made for the blanks. The extent of decomposition in each case is given in Table I. It is evident that the pentosans in the different materials are all decomposed to about the same extent, since in all cases between 75 and 80 per cent of the total amount has been decomposed regardless of the original source or amount. Some slight differences which are evident can be reconciled with previously established facts, e. g., it is known that *Nereocystis* is more easily decomposed than *Macrocystis*; inoculation slightly increased the decomposition of *Macrocystis*. These data also indicate that from the standpoint of pentosan decomposition, kelp may be ranked with the other materials tested.

<sup>1</sup> "Organic Constituents of Pacific Coast Kelps," *J. Agr. Res.*, **4**, No. 1 (1915), 39.

<sup>2</sup> Bureau of Chemistry, U. S. Dept. Agr., *Bull.* **107**, 54.

<sup>1</sup> Hilgard, "Soils," p. 132.

## SUMMARY

Dried and ground kelp decomposes in the soil under laboratory conditions, increasing the humus content to an extent comparable with alfalfa, manure and straw. Of the pentosans present, 75 to 80 per cent was decomposed in all the materials.

Acknowledgment is made to Professor D. R. Hoagland, at whose suggestion the above work was performed.

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ESTIMATION OF CARBON DIOXIDE AS BARIUM CARBONATE APPLIED TO THE MARR METHOD FOR DETERMINATION OF CARBONATES IN SOIL

By C. J. SCHOLLENBERGER

Received December 27, 1915

Closely following the publication by Marr<sup>1</sup> of a method for soil carbonates, a modification embodying its essential features, which are evolution of carbon dioxide by boiling with dilute acid under reduced pressure and absorption of the evolved carbon dioxide in a solution of sodium hydroxide, the carbonate therein being subsequently estimated by the well-known double titration method of Brown and Escombe,<sup>2</sup> was extensively studied in this laboratory and a form of apparatus adapted to it subsequently described by E. W. Gaither.<sup>3</sup>

Extended experience with this method, both in every-day use on routine samples and with the special samples furnished by the Referee on Soils for the Association of Official Agricultural Chemists' work in 1914 and 1915, has served to establish the fact that the decomposition of soil at a moderate temperature *in vacuo* by dilute hydrochloric acid is undoubtedly the most accurate of all procedures so far proposed for this determination, as it reduces to a minimum the activity of acid on organic material. When the soil is treated with acid in the cold there will be for some samples, depending on the nature of the carbonates present, an incomplete decomposition of carbonate. If the soil be boiled at atmospheric pressure with acid there will be an excessive action on the organic matter with consequent liberation of carbon dioxide not derived from carbonates, necessitating a blank determination on an extracted sample and the application of a correction for carbon from organic sources which involves considerable uncertainty.

There is, however, a source of error in the Marr method if the double titration procedure is used for determining the evolved carbon dioxide. This is indicated by the fact that the results by the Marr method, although showing excellent agreement with those obtained by boiling with stronger acid, the proper correction being applied and the double titration procedure used in each case, do not show such good agreement when compared with results obtained by boiling at atmospheric pressure and measuring the carbon dioxide gas, the corresponding correction

for action of acid on organic matter being applied. Nor is it usually found possible to recover by the double titration method all the carbon dioxide from samples of pure carbonates.

As the result of work done in this laboratory, and having for its object the improvement of the Marr method and at the same time the retention of its essential feature, which is decomposition of soil carbonates by dilute acid at reduced pressure and temperature, involving the least possible attack upon soil organic matter which is compatible with complete decomposition of carbonates and complete evolution of the gaseous carbon dioxide in the minimum period of time, it has been found possible to do away with the objectionable double titration. This is accomplished by effecting the absorption of the carbon dioxide evolved from the sample in barium hydroxide solution contained in a Meyer bulb tube. The precipitated barium carbonate is filtered off and determined as described by Cain.<sup>1</sup> The method is essentially the same as that recommended for adoption as a tentative method by the Referee on Soils of the Association of Official Agricultural Chemists in 1915.

E. Truog<sup>2</sup> has described a method for the determination of carbon dioxide by absorption in a measured excess of barium hydroxide solution and titration of the excess of barium hydroxide, using phenolphthalein as indicator. A trial was made of this method also, but effecting the absorption in a Meyer bulb tube, which seemed to be better adapted to the purpose in this instance than did the ingenious bead tower described by Truog. The results were satisfactory when the acid used for the titration was standardized by the use of a sample of known carbonate content, as pointed out by Brady.<sup>3</sup> If the theoretical strength of the acid had been employed in making the calculations, a considerable minus error might have been introduced. The method offers important advantages over the double titration procedure, and will probably give better results in the hands of operators not thoroughly familiar with the latter method, but it must not be forgotten that it is subject to the same great source of error, *viz.*, the presence of substances supposedly neutral to phenolphthalein, but through hydrolysis, alkaline to that indicator—sodium bicarbonate in the one case and barium carbonate in the other.

For the reasons enumerated above, it is evident that absorption in barium hydroxide solution and titration of the residual hydroxide offers only a slight advantage over the older scheme of absorption in sodium hydroxide and double titration on the score of accuracy of results, although it does offer some advantages in the points of speed and convenience. By careful standardization of the method, it would doubtless give satisfactory results for routine work. The filtration method proposed by Cain is not subject to the above sources of error, and should give

<sup>1</sup> Jour. Agr. Science, [2] 3, 155.

<sup>2</sup> Phil. Trans. (B), 193 (1900), 289.

<sup>3</sup> THIS JOURNAL, 4 (1912), 611.

<sup>1</sup> Technological Paper 33, Bureau of Standards; also THIS JOURNAL, 6 (1914), 465.

<sup>2</sup> THIS JOURNAL, 7 (1915), 1045.

<sup>3</sup> Ibid., 6 (1914), 843.



very accurate results when properly carried out. While not so speedy as the simple titration, its freedom from the usual sources of error entitle it to the preference for all exact work.

In Table I are presented results obtained by several methods on a series of six soils, identical with those supplied by the Referee on Soils of the Association of Official Agricultural Chemists for cooperative work in 1915. The figures in parenthesis following sample No. 1 serve as an approximate measure of the extent to which organic matter has been attacked by the reagents in each case, and these percentages have been deducted in the cases of the next three samples in order to afford a better comparison between methods. A similar blank for Nos. 5 and 6 was obtained by extracting a sample of No. 5 with cold dilute hydrochloric acid (1 volume concentrated acid diluted to 10, the same as used for those methods requiring boiling at atmospheric pressure), then washing thoroughly with CO<sub>2</sub>-free water. 0.0090 per cent carbon was obtained from the extracted soil by boiling and estimation by double titration, while none whatever was obtained by the Marr method in either of two

TABLE I—PERCENTAGES CARBON BY VARIOUS METHODS

SAMPLES ANALYZED	
1—Silt Loam, deficient in Organic Matter and supposedly free from Carbonates	
2—No. 1 + a small amount of 100 mesh Limestone	
3—No. 1 + 100 mesh Dolomite	
4—No. 1 + 100 mesh Dolomite	
5—Black Clay Loam, containing Carbonates and much Grit (preventing fine grinding)	
6—No. 5 + 100 mesh Dolomite	

No.	RESULTS BY MARR METHOD (MODIFIED)				
	Boiled at Atmospheric Pressure with 1 : 10 HCl	Double Titration	Gasometric (Cain's) BaCO <sub>3</sub> Titrated	Residual Ba(OH) <sub>2</sub> Titrated	(Brown-Escombe) Double Titration
1	(0.0096)	(0.0093)	(0.0015)	(0.0018)	(0.0007)
2	0.0276	0.0276	0.0274	0.0276	0.0291
3	0.0276	0.0280	0.0279	0.0270	0.0289
4	0.2133	0.2220	0.2237	0.2204	0.2194
5	0.1485	0.1508	0.1498	0.1462	0.1454
6	0.2835	0.2880	0.2868	0.2750	0.2759

trials. In this connection it is but fair to state that only one other analyst reported no carbon by the Marr method from No. 5 after extraction, but, on the other hand, only one reported more from No. 5 after extraction than from No. 1, although No. 5 contains by far the larger amount of organic matter. The explanation may be either that No. 1 actually contains a trace of carbon dioxide, or that extraction with cold dilute acid removes or causes the decomposition of the most readily attacked part of the organic matter. It was noted that the acid extract from No. 5 was very dark in color.

In conclusion, the writer wishes to express his obligations to Mr. J. W. Ames, chief of the Department of Chemistry at this Station, for helpful suggestions and permission to publish this article.

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#### SOME NOTES ON SANDALWOOD, ITS ASSAY, YIELD OF OIL, AND CHANGES IN THE OIL DURING DISTILLATION<sup>1</sup>

By C. H. BRIGGS

Received September 13, 1915

The data set forth in this paper have been collected at various times during the last few years, and as

<sup>1</sup> Presented at the 51st Meeting of the American Chemical Society, Seattle, Aug. 31–Sept. 3, 1915.

similar results have not been noted elsewhere in the literature, it was thought it might be of interest to others.

A few years ago twelve samples of various grades of sandalwood were obtained from the Mysore Province, India. These samples consisted of small pieces of the unground wood representing certain types or classes of sandalwood which could be bought from the Mysore government. The samples varied in weight from a few ounces to a pound, and as there was a considerable range of prices, we were naturally much interested in the content of santal oil in the different grades.

A search of the literature failed to reveal any method of assay for the amount of santal oil in sandalwood that could be applied to these small samples. At first it was thought that this problem was hopeless, but after considerable experimentation a method of assay was evolved which proved to be quite satisfactory. It is as follows:

Place 100 g. of the finely powdered drug in a Soxhlet extractor and extract with sulfuric ether for one day or until completely extracted. Transfer the ether extract to a 200-cc. side neck distillation flask and evaporate off the ether on a steam bath with the aid of a stream of air. Add 35 cc. of glycerine and distill in a vacuum until about 25 cc. of the glycerine have distilled over. Add 25 cc. of water to the distillate and extract with chloroform, using three portions of about 25 cc. each. Evaporate the combined chloroform extracts in a tared dish on a water bath with the aid of a stream of air until the chloroform has all been removed, dry in a vacuum desiccator over sulfuric acid and weigh.

Sandalwood contains a large amount of fixed oils as well as the essential oil and both are extracted by ether. The essential oil cannot be separated quantitatively from this extract by distillation in a vacuum unless glycerine is also added to help carry over the last traces of the essential oil. The essential oil can be separated from the glycerine in the distillate by extracting with chloroform. A 5-g. sample of santal oil was dissolved in ether and assayed by the above method as a check; practically all of the oil was recovered.

The twelve samples of sandalwood obtained from the Mysore government and representing as many different grades assayed as follows:

No.	% OIL	No.	% OIL	No.	% OIL
1	3.7	5	3.7	9	3.84
2	7.44	6	6.8	10	3.53
3	5.9	7	4.7	11	3.66
4	8.3	8	4.73	12	3.8

SAMPLE FROM STOCK, 6.0% Oil

It will be noted that these samples varied from 3.7 to 8.3 per cent. It would be of much value to distillers of santal oil if the cost of the wood could be based on the content of oil, but the commercial conditions governing the sale of sandalwood are such that this cannot be carried out successfully. However, the assay is of value in checking the yield of santal oil from the wood when distilled on a large scale.

#### CHANGES IN THE OIL DURING DISTILLATION

During the course of this work, it was noted that oil obtained from sandalwood by this method of assay had an optical rotation of  $-18^\circ$  or above, whereas

the same wood when distilled with steam in an ordinary essential-oil still yielded an oil having an optical rotation of  $-14^\circ$  or less. It was also noted that the oil obtained by the assay method was readily soluble in 5 volumes of 70 per cent alcohol at  $25^\circ\text{C}$ ., whereas the oil obtained by the ordinary steam distillation required more than 5 volumes of 70 per cent alcohol to dissolve it. Thus a sandalwood which was known to contain an oil which would meet the U. S. P. requirements, would yield by ordinary steam distillation an oil which would no longer meet these requirements. There must, therefore, be some decided change in the oil during distillation with steam.

To study this condition, 500 lbs. of sandalwood were distilled with steam and samples of each day's run collected and the physical properties determined. The results were as follows:

Day	Sp. Gr.	Ref. Ind.	Opt. Rot.	Solubility at $25^\circ\text{C}$ . in 5 parts 70% alcohol
1st	0.969	1.5017	$-12^\circ 34'$	O. K. at $40^\circ$ to $50^\circ\text{C}$ .
2nd	0.970	1.5020	$-12^\circ 22'$	O. K. at $25^\circ\text{C}$ .
3rd	0.972	1.5027	$-12^\circ 46'$	O. K. at $25^\circ\text{C}$ .
4th	0.974	1.5030	$-12^\circ 54'$	O. K. at $25^\circ\text{C}$ .
5th	0.976	1.5035	$-13^\circ 10'$	O. K. at $25^\circ\text{C}$ .
6th	0.978	1.5037	$-12^\circ 30'$	O. K. at $25^\circ\text{C}$ .
7th	0.978	1.5045	$-11^\circ 8'$	O. K. at $25^\circ\text{C}$ .
8th	0.9795	1.5046	$-10^\circ 4'$	O. K. at $26.5^\circ\text{C}$ .
9th	0.981	1.5046	$-9^\circ 10'$	O. K. at $29^\circ\text{C}$ .
10th	0.9815	1.5046	$-8^\circ 20'$	O. K. at $32^\circ\text{C}$ .
11th	0.9820	1.5045	$-7^\circ 45'$	O. K. at $35^\circ\text{C}$ .
12th	0.983	1.5045	$-7^\circ 8'$	O. K. at $38^\circ\text{C}$ .
13th	0.982	1.5046	$-6^\circ 34'$	O. K. at $44^\circ\text{C}$ .

It will be noted that there was a gradual increase in specific gravity with each day's run from 0.969 to 0.982. Also that the refractive index steadily increased from 1.5017 to 1.5046. The optical rotation was fairly constant for 5 days at  $-12^\circ$  to  $-13^\circ$  and then steadily decreased to  $-6^\circ 34'$ . With the exception of the first day's run, the oil was soluble in 5 parts of 70 per cent alcohol at  $25^\circ\text{C}$ . for the first 7 days, but the eighth day's run was no longer soluble at  $25^\circ\text{C}$ . and the solubility grew gradually less up to the end of the distillation.

To determine if this change in the optical rotation of santal oil during distillation was due to prolonged exposure of the oil to boiling water, a sample of oil having an optical rotation of  $-20^\circ 40'$  was boiled continuously for several weeks in a glass flask with a reflux condenser. The same experiment was also carried out by boiling with a 10 per cent solution of sodium chloride.

OBSERVATION	EXPERIMENT I		EXPERIMENT II	
	Water	10% NaCl	Water	10% NaCl
At beginning of experiment	$-20^\circ 40'$	$-20^\circ 40'$	$-20^\circ 40'$	$-20^\circ 40'$
After boiling 1 week	$-18^\circ 50'$	$-19^\circ 42'$		
After boiling 2 weeks			$-16^\circ 10'$	$-19^\circ 40'$
After boiling 2 1/2 weeks			$-15^\circ 40'$	$-19^\circ 45'$
After boiling 3 weeks	Flask broke	$-19^\circ 30'$		
After boiling 3 1/2 weeks			$-13^\circ 16'$	$-16^\circ 40'$
After boiling 6 weeks		$-17^\circ 30'$		

It will be noted that there was a very decided change in the optical rotation of the santal oil by boiling with water, the rotation decreasing from  $-20^\circ 40'$  to  $-13^\circ 16'$  in  $3\frac{1}{2}$  weeks. The change by boiling with the 10 per cent salt solution was much less, being reduced to  $-16^\circ 40'$  in the same length of time.

We must conclude then that under certain conditions prolonged contact with boiling water brings about decided changes in the composition of santal oil and greatly reduces the optical rotation. These

same changes take place in the oil to a greater or less extent during the distillation of the oil from the wood with steam and probably accounts for much of the santal oil on the market having a low optical rotation and poor solubility.

The writer wishes to express his thanks to Mr. S. T. McCallum for his assistance during this work.

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## NOTE ON AMERICAN CHARLOCK OIL

By H. S. BAILEY AND L. B. BURNETT

Received December 21, 1915

During the course of an investigation into the "Production, Botanical Composition and Volatile Oil Strength of American Wild Mustard Seed," Winton and Bornmann<sup>1</sup> separated from northwestern wheat screenings several samples of fairly pure charlock (*Brassica arvensis*) seed. These we combined and further purified in the laboratory until our material was 98-99 per cent charlock, the remainder being nearly all brown mustard (*Brassica juncea*).

After taking out a sample for analysis, the seed was ground in a drug mill and pressed cold in a small hydraulic press, the material remaining under pressure over night. The press cake was then reground and divided into two portions, one of which was extracted with petroleum ether (b. p.  $35-60^\circ$ ) and the other with ethyl ether in a Soxhlet apparatus.

The original seed contained 4.1 per cent moisture, as determined in an atmosphere of  $\text{CO}_2$  at  $100^\circ\text{C}$ ., 30.0 per cent ether extract and 29.6 per cent petroleum ether extract. The chemical and physical factors of the expressed and extracted oils together with an analysis by Grimme<sup>2</sup> of oil of charlock, probably the ether extract of *Sinapis arvensis*, are given in the accompanying table.

PHYSICAL AND CHEMICAL FACTORS OF CHARLOCK OILS

	Expressed Oil	Ether Extract	Petroleum Ether Extract	Grimme's Analysis
Specific Gravity, 15/15	0.9221	0.9272	0.9212	0.9228
Refractive Index, $25^\circ$	1.4734	1.4739	1.4729	1.4720(a)
Saponification No.	182.9	183.1	181.0	179.4
Iodine No., Hanus	121.1	119.8	119.3	102.6(b)
Insoluble Acids and Unsaponifiable	95.3	95.4	95.2	94.21
Soluble Acids	0.0	0.0	0.0	
Mean Mol. Wt. of Ins. Acids	339.1	338.1	334.8	312.4
LIQUID ACIDS:				
Per cent	89.3	90.0	90.0	
Iodine No.	126.0	122.3	125.0	
SOLID ACIDS:				
Per cent	3.1	1.6	2.0	
Iodine No.		62.0	61.0	

(a) Calculated to  $25^\circ$  from Grimme's value 1.4738 at  $20^\circ$ .  
(b) Probably not by Hanus' Method.

As has been pointed out by Winton and Bornmann, there are large quantities of so-called "Wild Mustard" which contain varying proportions of charlock and brown mustard separated from American grains. Some of this is already being utilized as an oil material. Whether or not this oil can be sufficiently refined to make it suitable for food purposes remains to be seen, but undoubtedly it can be used in soap making and possibly in cheap paints.

BUREAU OF CHEMISTRY, WASHINGTON

<sup>1</sup> THIS JOURNAL, 7 (1915), 684.

<sup>2</sup> Lewkowitsch's "Chem. Tech. and Anal. of Oils, Fats and Waxes" 3rd Ed., Vol. II, p. 271.



# LABORATORY AND PLANT

## GAUGING OF STORAGE TANKS—METHOD OF ACCURATELY AND RAPIDLY DETERMINING THE VOLUME CONTENT OF MATERIAL IN HORIZONTAL CYLINDRICAL TANKS WITH BUMPED HEADS

By K. B. HOWELL

Received January 19, 1916

Many horizontal cylindrical tanks find employment in industrial operations of the present day. Some of these serve for storage or transportation of liquid materials, others for purposes of distillation, still others for purposes of admixture or agitation of liquid materials. In connection with these tanks, there often arise occasions where it becomes extremely desirable to know the quantity of liquid material which is contained in them. There have been published from time to time various formulas, charts and mathematical tables which aim to calculate the volume of material contained in these tanks from a knowledge of the vertical height of the material in the tank and the dimensions of the tank. These formulas and methods of calculation, however, are prac-

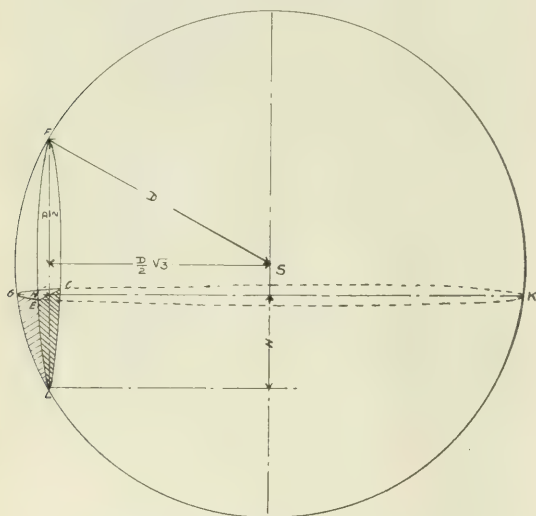
us in many cases to employ methods of measurement which take account of this varying volume content.

Probably the only relatively accurate method is by a direct empirical calibration of the tank filling the same with measured quantities of water. This method is quite slow and laborious.

It has, therefore, seemed to the writer advisable that a method of calculation be worked out for the determination of the volume content of the liquid material contained in a horizontal tank containing bumped heads which shall eliminate the necessity of a laborious calibration of the tank and at the same time permit the calculation to be of a reasonable degree of accuracy. In other words, the method of calculation should possess the following features:

- 1—Simplicity of Calculation
- 2—General Applicability
- 3—Accuracy Commensurate with the Possible Accuracy of Measurement

Expressing the proposition in a somewhat more mathematical form, our problem then resolves itself



tically without exception based on the assumption that the tank is a true cylinder. They, therefore, become applicable with accuracy only to those cases where the tank or still has flat heads. In the majority of cases met with in practice, however, the mechanical advantages to be gained have required that the heads of the tanks be bumped. To such tanks it is impossible to apply the aforementioned method of calculation without the introduction of a considerable error. In the case of the average 8,000-gal. tank car, the volume content of the two bumped heads is about 277 gals., or about 3.5 per cent of the total contents of the car. Since, therefore, the percentage content contained in the heads varies from 0, when the tank is empty, to 3.5 per cent, when it is one-half full, it becomes necessary for

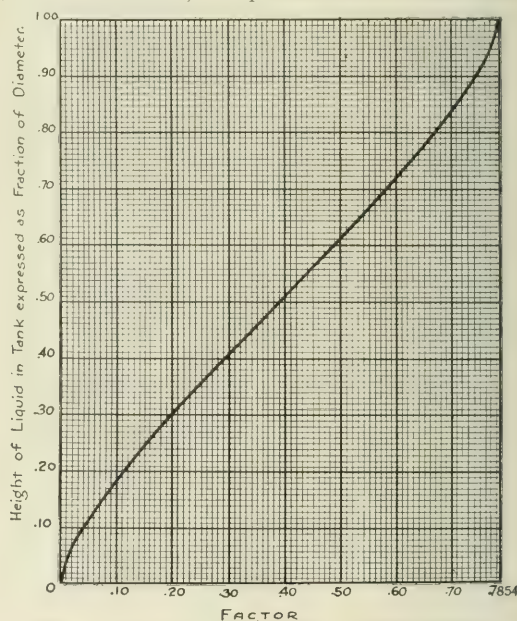


FIG. 1—FOR DETERMINATION OF LIQUID CONTENTS OF BUMPED TANKS IN HORIZONTAL POSITION

Liquid Contents of Tanks (Exclusive of Bumped Heads) is equal to Factor  $\times$  Diameter<sup>2</sup>  $\times$  Length of Tank in ft.

into a determination of a method of calculating the volume of the figure formed by the sides and heads of a "bumped" tank and a horizontal plane at any height,  $H$ , from the bottom of the tank. This volume we have represented by  $V$ . It may be considered as consisting of two parts, the volume  $V_c$  contained in the true cylindrical portion of the tank which is exclusive of the bumps, and the volume  $V_b$  contained in each bumped head. The relationship between these values is expressed by the following equation:

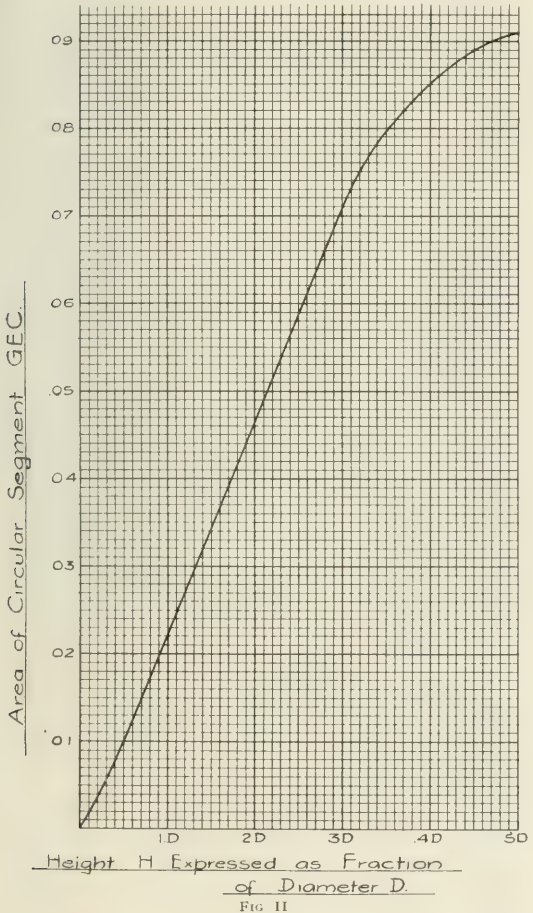
$$V = V_c + 2V_b$$

METHOD OF DETERMINING  $V_c$

This volume is the segment of a true cylinder. Its volume can, therefore, be readily determined by any of the methods, charts or tables recognized in general engineering practice and referred to previously in this article. Fig. I is a graphical adaptation of one of these tables from Kent's "Mechanical Engineers' Handbook," page 121. It is used in connection with the following formula:

$$V_c = 7.48 \times (\text{F. No. 1}) \times D^2 L$$
  
where  $L$  = length of tank in ft.  
 $D$  = diameter of tank in ft.  
7.48 = conversion factor for cu. ft. to gals.  
F. No. 1 = factor obtained from Fig. I

F. No. 1 is obtained as follows: Express the height  $H$  as a fraction of the diameter  $D$ . Locate the resultant value on the vertical axis of the chart. From



this point, move horizontally across the chart until intersection with the curve occurs. From the point of intersection; drop down to the vertical axis. The point of intersection with the latter represents the desired factor F. No. 1.

METHOD OF DETERMINING  $V_b$

This proposition is considerably more complex. It consists essentially in the determination of the volume

of a complex figure formed by the surface of a sphere, a fixed vertical plane and a horizontal plane at varying height,  $H$ , from the lowest point,  $L$ , of intersection of the vertical plane and sphere. This may be otherwise expressed as the volume of a portion of a spherical segment cut off by a plane at vertical height,  $H$ , from the point  $L$ .

The development of any general formula or method of determining this volume is rendered simpler and of somewhat more general application by reason of the very general practice of tank design by which the radius of the bump of the tank head is made equal to the diameter of the tank. While it is quite possible to design and determine upon a method of calculation which applies to a different radius of "bump" yet the

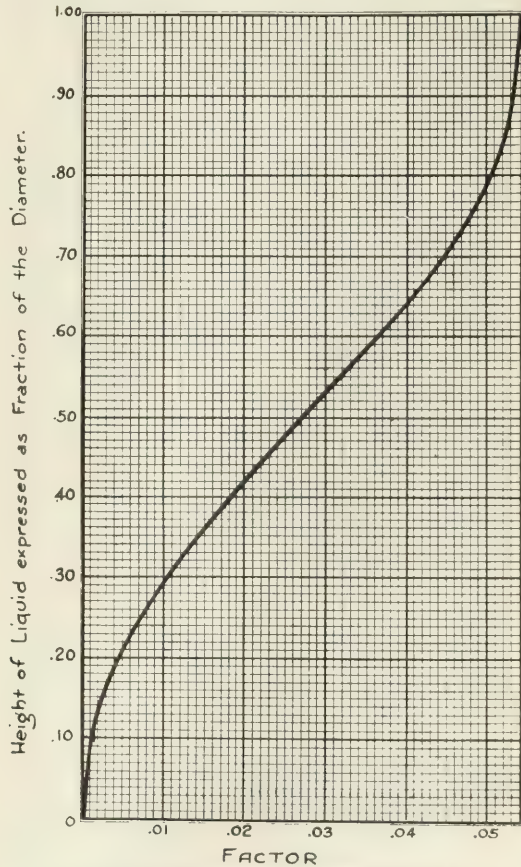


FIG. III—FOR DETERMINATION OF LIQUID CONTENTS OF BUMPED TANKS IN HORIZONTAL POSITION

almost universal acceptance of the above formula has led us to confine our proposition to the above condition. In our subsequent calculations, therefore, we shall take advantage of this condition which results in making the diameter of the base of our segment equal to the radius of our sphere.

Expressed in terms of mathematical symbols, our problem is as follows:



## METHOD OF CALCULATION

Given:

SPHERE S : Diameter =  $2D$ SPHERICAL SEGMENT : Diameter =  $D$ ; Height =  $H$   $D^3 \times \frac{H}{2}$ CIRCULAR AREA LEFC : Diameter =  $D$ CIRCULAR SEGMENT CEF : Base  $CE = B$ ; Height =  $H$ CIRCULAR AREA GECK : Diameter =  $D'$ CIRCULAR SEGMENT GEC : Base =  $CE = B$ ; Height =  $H'$ ; Area =  $A$ 

SECTION OF SPHERICAL SEGMENT GELC

Required:

Volume  $V_b$  of Section GELC

This volume may be expressed by the following expression:

$$V_b = \int_0^H A \, dH$$

To make this expression capable of integration the value must be expressed as a function of  $H$ . The expression for  $A$  in terms of  $H$  contains the inverse sine and is, therefore, difficult of ready mathematical integration. It has, therefore, seemed more advisable to plot this function graphically on Fig. II and perform the integration graphically.

This method of calculation consists essentially of four parts:

(1)—Determination of  $A$  for given values of  $H$ 

(2)—Plotting these values on Fig. II

(3)—Planimetering of Fig. II to determine values of  $V_b$  for given values of  $H$ 

(4)—Plotting these values on Fig. III

(1) DETERMINATION OF  $A$ — $A$  is the area of a segment of height  $H'$  of a circle of diameter  $D'$ . Its value may be determined from the tables of Kent if the value of  $D'$  and  $H'/D'$  are known. These values are obtained as follows:

$$\begin{aligned} \left(\frac{D'}{2}\right)^2 &= D^2 - \left(\frac{D}{2} - H\right)^2 \\ \frac{D'}{2} &= \sqrt{D^2 - \left(\frac{D}{2} - H\right)^2} \\ D' &= 2\sqrt{D^2 - \left(\frac{D}{2} - H\right)^2} \\ H' &= \frac{D'}{2} - \frac{D}{2} \sqrt{3} \\ \frac{H'}{D'} &= \frac{\frac{D}{2} \sqrt{3}}{2\sqrt{D^2 - \left(\frac{D}{2} - H\right)^2}} \end{aligned}$$

Expressing  $H'$  in terms of fractions of  $D'$ , we obtain numerical values for  $H'/D'$ . Employing these values and using the tables in Kent for the determination of the area of a segment, we obtain the values shown in Table I.

TABLE I

$H$	$H'/D'$	Factor No. 1	$A$
0.05 $D$	0.0270	0.00246	0.00782 $D^2$
0.10 $D$	0.0505	0.00603	0.02026 $D^2$
0.15 $D$	0.0707	0.00964	0.03287 $D^2$
0.20 $D$	0.0879	0.01297	0.04721 $D^2$
0.25 $D$	0.1022	0.01583	0.05936 $D^2$
0.30 $D$	0.1138	0.01854	0.07119 $D^2$
0.35 $D$	0.1227	0.02020	0.07898 $D^2$
0.40 $D$	0.1290	0.02156	0.08538 $D^2$
0.45 $D$	0.1327	0.02240	0.08938 $D^2$
0.50 $D$	0.1339	0.02265	0.09060 $D^2$

TABLE II

$H$	$V_b$	Factor No. 3
0.05 $D$	0.00017 $D^3$	0.00017
0.10 $D$	0.00085 $D^3$	0.00085
0.15 $D$	0.00221 $D^3$	0.00221
0.20 $D$	0.00420 $D^3$	0.00420
0.25 $D$	0.00687 $D^3$	0.00687
0.30 $D$	0.01048 $D^3$	0.01048
0.35 $D$	0.01386 $D^3$	0.01386
0.40 $D$	0.01805 $D^3$	0.01805
0.45 $D$	0.02234 $D^3$	0.02234
0.50 $D$	0.02697 $D^3$	0.02697

(2) PREPARATION OF FIG. II—The values of  $A$  are then plotted on Fig. II against the corresponding values of  $H$  expressed as fractions of the diameter. The scale of this chart is as follows:

Vertical—1 in. = 0.02  $D^2$   
Horizontal—1 in. = 0.05  $D$   
1 sq. in. = 0.001  $D^3$

(3) DETERMINATION OF  $V_b$ —The area of the portion of Fig. II beneath the curve and between the origin and any

given height,  $H$ , represents the desired volume  $V_b$  as cut off by the plane at height  $H$ . These areas have been very carefully planimetered, the values of  $V_b$  determined for varying values of  $H$  and the results tabulated in Table II.

(4) PREPARATION OF FIG. III—The values  $V_b$  are expressed as decimal fractions of the cube of the diameter of the tank. The decimal portion of these expressions we have plotted on Fig. III against the values of  $H$  expressed as a fraction of the diameter  $D$ . By reference to this chart, then, we are enabled to obtain for any height,  $H$ , expressed as a fraction of  $D$ , the necessary decimal fraction with which to multiply the cube of the diameter of the tank in order to obtain the volume contained in the bump. This volume can be expressed in terms of gallons as follows:

$$V_b = 7.48 \times (\text{F. No. 3}) \times D^3$$

where  $D$  = diameter of tank in ft.

7.48 = conversion factor (cu. ft. to gals.)

F. No. 3 = factor obtained from Fig. III

in a manner exactly similar to the manner in which F. No. 1 is obtained from Fig. I

## THE GENERAL EXPRESSION

As previously stated, the total volume is expressed by the formula:

$$V = V_c + 2V_b$$

We have then the following formula for the desired partial volume  $V$  of a bumped headed tank:

$$V = 7.48 \times (\text{F. No. 1}) \times D^2 \times L + 2 \times 7.48 \times (\text{F. No. 3}) \times D^3$$

where  $D$  = diameter of the tank in ft. $L$  = length of the tank in ft.

7.48 = conversion factor (cu. ft. to gals.)

F. No. 1 and F. No. 3 are factors obtained from Fig. I and Fig. III as previously described

The use of this formula not only permits the determination of the gallon contents of liquid material contained in bumped tanks from a knowledge of the dimensions of the tanks and the height of the liquid, but also permits the calibration of these tanks by a simple mathematical calculation avoiding the laborious method of filling with known quantities of liquid. At the same time this method affords an accuracy as great as is generally desired in manufacturing operation.

## DISCUSSION OF DEGREE OF ACCURACY

The method of calculation employed is theoretically accurate. The degree of accuracy is limited only by the size scale on which the graphical results are plotted and the number of numerical figures carried in the mathematical calculation.

In so far, however, as the actual mechanical construction of tanks and stills varies necessarily to some extent from the design, it is hardly of any advantage to employ a method of calculation of an accuracy greater than one yielding a maximum error less than 0.1 per cent of the total content of the tank.

To obtain this desired degree of accuracy requires that the maximum possible error in determining  $V_b$  and  $V_c$  should be less than 0.1 per cent of  $V$ . Since  $V_b$  is seldom greater than 5 per cent of  $V$ , this requires that the accuracy of F. No. 3 and the corresponding Figs. II and III shall be such as to permit an error not over 2 per cent. In plotting these charts and in

all calculations, a considerably greater accuracy was maintained.

In the case of  $V_c$ , however, a certain amount of difficulty arises.  $V_c$  represents approximately 95 to 100 per cent of  $V$ . To maintain the desired final accuracy, requires that  $F$ . No. 1 be obtained with an accuracy corresponding to a maximum error of approximately one-tenth of one per cent, and consequently that Fig. 1 be plotted on a scale capable of reading to this degree of accuracy. While such a scale is quite possible, it is quite inconvenient and the writer would recommend in cases where extreme accuracy is desired that the value  $F$ . No. 1 be determined from the table for "Determination of Areas of Circular Segments" given in Kent's "Mechanical Engineering Handbook," page 121. The factor under the heading "Area" represents the desired value  $F$ . No. 1 and is given to very great accuracy. In general, however, the above Fig. 1 plotted on scale 0.1 to the inch is sufficiently accurate for most manufacturing calculations.

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### THE UNIT OF VISCOSITY MEASUREMENT

By PARKER C. McILHINEY

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The scientific world expresses the results of measurement of viscosity in terms of absolute viscosity of which the units are directly related to the fundamental units of mass, length, and time. The practical world speaks of Saybolt seconds, Engler numbers, etc. The absolute C. G. S. unit of viscosity is a relatively large one so that water and similar liquids have absolute viscosities which are inconveniently small numbers, and furthermore, without giving it a name it is impracticable to use such a unit in commercial testing. Many people have the idea that absolute viscosities cannot be determined except when the viscosity is deduced from the absolute dimensions of the instrument and that the practical instruments are not adapted to determine absolute results. The fact is that there are many practical methods by which viscosity may be measured, some of them better than others, all of them subject to disadvantages which differ according to the circumstances of their use, but all of them giving results capable of being translated into the common language of absolute viscosity.

The study of this important physical property of liquids has been seriously hampered by the lack of any kind of uniformity in its measurement. The principal use which is made of viscosity measurements to-day is in the case of lubricating oils, but their use is not more widely extended because workers in different countries with different kinds of instruments think they are unable to obtain anything by their work but results of merely personal interest. Few of them know how to translate the results which they obtain into results comparable with those obtained with another instrument.

This state of affairs would be radically improved if there were some unit of measurement of viscosity which was generally intelligible and in which the results of any determination with any instrument might

be expressed. The absolute unit as already mentioned is inconveniently large and it has no name. The suggestion has been made by Deeley and Parr<sup>1</sup> that the unit of viscosity expressed in C. G. S. units should be called the "poise" in honor of Poiseuille, but the suggestion has not been adopted generally and it is customary to simply speak of the "absolute" viscosity of a liquid. If the "poise" is adopted as the name of the absolute unit, it has been suggested that we might use the decimal multiples and submultiples of this unit, and that then the centipoise—1  $cp = 0.01 p$ —would be almost exactly the viscosity of water at 20° C. or 68° F. Thus for all practical purposes in the lubricating oil business, it would be sufficiently near the truth to say that the viscosity expressed in centipoises is the specific viscosity, that is, the viscosity as compared with water at 20° C. or 68° F. as a standard liquid.

There are, as is well known, a variety of instruments with which the viscosity of liquids generally may be determined. There are three of these instruments which are in commercial use largely for the examination of lubricating oils, namely, the Saybolt Universal, the Engler, and the Redwood. All three of these instruments are capable, as shown by the work done at the Bureau of Standards in Washington,<sup>2</sup> of determining the viscosity of oils with the accuracy usually required in present-day industrial testing. In these instruments, the number of seconds required for a given amount of oil to flow through a small tube or orifice in the instrument is measured.

Tables have been prepared by the use of which the true viscosity may be calculated from the number of seconds required for any one of these three instruments. If these tables could be brought into general use, a determination of the number of seconds required by the Saybolt Universal, Engler, and Redwood instruments would be reported in terms of centipoises. If the centipoise is used as a unit, the figure obtained will be 1.0042 for water and a larger number for all oils, and the number will represent the true relation between the viscosity of the oil examined and that of water with sufficient accuracy for commercial purposes, and also the true or absolute viscosity.

In scientific work, the use either of absolute viscosity expressed in C. G. S. units or of the centipoise for convenience, will enable the workers in all the different fields in which viscosity may be determined, to express their results in a universal language and the result will certainly be that the use of viscosity as a valuable physical property will no longer be confined practically to oils but will be extended to many other lines of work. If, for example, the instrument recently described by MacMichael<sup>3</sup> should prove serviceable in many fields, investigations in viscosity can be carried on with it upon materials for which it is adapted and the results readily compared with those

<sup>1</sup> "The Viscosity of Glacier Ice," *Phil. Mag.*, [6] **26** (1913), 85.

<sup>2</sup> Dr. C. W. Waidner, "Conversion Tables for Saybolt Universal, Engler, and Redwood Viscosimeters," *Proc. Am. Soc. Test. Mat.*, **15** (1915), 284.

<sup>3</sup> R. F. MacMichael, "A New Direct-Reading Viscosimeter," *This Journal*, **7** (1915), 961.



obtained by any other worker using a different form of apparatus.

In order to facilitate such comparisons as well as to assist in the introduction of a uniform method of expressing results throughout the world, it would

bring to the attention of those who are engaged in any kind of viscosity determinations the desirability of expressing all their results in terms of either the centipoise or the poise.

The accompanying tables have been prepared as

Engl. No.	SECONDS				Engl. No.	SECONDS				Engl. No.	SECONDS				Engl. No.	SECONDS			
	Say-bolt	Red-wood	Uncorr. viscosity in centipoises			Say-bolt	Red-wood	Uncorr. viscosity in centipoises			Say-bolt	Red-wood	Uncorr. viscosity in centipoises			Say-bolt	Red-wood	Uncorr. viscosity in centipoises	
2.00	67.8	59.2	11.5		2.31	81	69.4	14.2		2.62	93	79.7	16.8		2.93	106	88.2	19.3	
2.02	69	59.8	11.7		2.33	82	70.3	14.4		2.94	107	90.3	19.5		3.24	119	99.1	21.8	
2.03	70	60.6	11.9		2.34	83	71.1	14.6		3.25	120	100.4	22.0		3.27	120	100.4	22.0	
2.08	71	61.7	12.2		2.36	84	71.9	14.9		3.29	121	101.9	22.4		3.32	122	101.9	22.4	
2.10	72	62.4	12.4		2.38	86	73.6	15.3		3.33	123	102.8	22.6		3.35	123	102.8	22.6	
2.12	73	63.0	12.5		2.41	87	74.3	15.4		3.36	124	103.8	22.9		3.38	124	103.8	22.9	
2.14	74	63.8	12.7		2.44	88	75.2	15.7		3.41	125	104.7	23.1		3.41	125	104.7	23.1	
2.17	75	64.7	13.1		2.46	89	76.1	15.9		3.43	126	105.3	23.4		3.43	126	105.3	23.4	
2.20	76	65.8	13.2		2.49	90	77.0	16.2		3.46	127	106.2	23.6		3.48	128	106.8	23.7	
2.21	77	66.2	13.4		2.51	91	77.6	16.3		3.51	129	108.1	23.7		3.51	129	108.1	23.7	
2.24	78	67.1	13.6		2.56	92	78.5	16.5		3.54	130	109.0	24.0		3.54	130	109.0	24.0	
2.27	79	68.1	13.8		2.59	93	79.7	16.8		3.57	131	110.0	24.3		3.57	131	110.0	24.3	
2.29	80	68.7	14.0		2.62	94	80.9	17.1		3.62	133	111.0	24.7		3.62	133	111.0	24.7	
2.31	81	69.4	14.2		2.66	96	81.5	17.4		3.65	134	112.4	25.0		3.65	134	112.4	25.0	
2.33	82	70.3	14.4		2.69	97	82.1	17.6		3.68	135	113.3	25.2		3.68	135	113.3	25.2	
2.36	83	71.0	14.6		2.70	98	82.9	17.8		3.70	136	114.0	25.3		3.70	136	114.0	25.3	
2.39	84	71.9	14.9		2.76	99	83.9	17.9		3.73	137	114.9	25.6		3.73	137	114.9	25.6	
2.41	85	72.7	15.0		2.78	100	84.5	18.1		3.74	138	115.1	25.8		3.74	138	115.1	25.8	
2.44	86	73.6	15.3		2.80	101	85.1	18.2		3.77	139	116.5	25.8		3.77	139	116.5	25.8	
2.46	87	74.3	15.4		2.82	102	85.7	18.4		3.79	140	117.1	25.9		3.79	140	117.1	25.9	
2.49	88	75.2	15.7		2.85	103	86.6	18.6											
2.51	89	75.9	15.9		2.88	104	87.6	18.9											
2.54	90	76.8	16.1		2.90	105	88.2	19.1											
2.56	91	77.6	16.3		2.93	106	89.2	19.3											
2.59	92	78.5	16.5		2.96	107	90.3	19.5											
2.62	93	79.7	16.8		2.98	108	90.9	19.7											
2.66	95	80.6	17.0		3.01	109	92.1	19.9											
2.69	96	81.5	17.4		3.02	110	93.0	20.2											
2.70	97	81.8	17.6		3.05	112	93.3	20.3											
2.72	98	82.9	17.8		3.08	113	94.2	20.5											
2.76	99	83.9	17.9		3.11	114	95.2	20.7											
2.78	100	84.5	18.1		3.13	115	95.8	20.9											
2.80	101	85.1	18.2		3.16	116	96.7	21.1											
2.82	102	85.7	18.4		3.19	117	97.6	21.4											
2.85	103	86.6	18.6		3.21	118	98.2	21.5											
2.88	104	87.6	18.9		3.24	119	99.1	21.8											
2.90	105	88.2	19.1		3.27	120	100.4	22.0											
2.93	106	89.2	19.3		3.32	122	101.9	22.4											
2.96	107	90.3	19.5		3.35	123	102.8	22.6											
2.98	108	90.9	19.7		3.38	124	103.8	22.9											
3.01	109	92.1	19.9		3.41	125	104.7	23.1											
3.02	110	92.4	20.2		3.43	126	105.3	23.4											
3.05	112	93.3	20.3		3.46	127	106.2	23.6											
3.08	113	94.2	20.5		3.48	128	106.8	23.7											
3.11	114	95.2	20.7		3.51	129	108.1	23.7											
3.13	115	95.8	20.9		3.54	130	109.0	24.0											
3.16	116	96.7	21.1		3.57	131	110.0	24.3											
3.19	117	97.6	21.4		3.62	133	111.0	24.7											
3.21	118	98.2	21.5		3.65	134	112.4	25.0											
3.24	119	99.1	21.8		3.68	135	113.3	25.2											
3.27	120	100.4	22.0		3.70	136	114.0	25.3											
3.29	121	101.9	22.4		3.73	137	114.9	25.6											
3.32	122	101.9	22.4		3.74	138	115.1	25.8											
3.35	123	102.8	22.6		3.77	139	116.5	25.8											
3.38	124	103.8	22.9		3.79	140	117.1	25.9											
3.41	125	104.7	23.1																
3.43	126	105.3	23.4																
3.46	127	106.2	23.6																
3.48	128	106.8	23.7																
3.51	129	108.1	23.7																
3.54	130	109.0	24.0																
3.57	131	110.0	24.3																
3.62	133	111.0	24.7																
3.65	134	112.4	25.0																
3.68	135	113.3	25.2																
3.70	136	114.0	25.3																
3.73	137	114.9	25.6																
3.74	138	115.1	25.8																
3.77	139	116.5	25.8																
3.79	140	117.1	25.9																
6.16	231	192.8	44.1		6.21	233	194.4	44.5		8.61	323	269.5	62.4		10.91	409	341.5	79.3	
6.18	232	193.4	44.2		6.22	234	195.3	44.9		8.62	324	270.4	62.5		10.92	410	342.5	79.5	
6.21	233	194.4	44.5		6.23	235	196.3	44.9		8.63	325	271.4	62.7		10.93	411	343.0	79.7	
6.22	234	195.3	44.9		6.24	236	197.8	45.3		8.64	326	272.0	62.8		10.94	412	344.0	79.9	
6.23	235	196.3	44.9		6.25	237	198.4	45.4		8.65	327	272.9	63.0		10.95	413	344.6	80.0	
6.24	236	197.8	45.3		6.26	238	198.4	45.4		8.66	328	273.9	63.3		10.96	414	345.6	80.3	
6.25	237	198.4	45.4		6.27	239	199.4	45.6		8.67	329	274.5	63.4		10.97	415	346.6	80.6	
6.26	238	198.4	45.4		6.28	240	200.9	46.0		8.68	330	275.4	63.6		10.98	416	347.1	80.6	
6.27	239	199.4	45.6		6.29	241	201.9	46.2		8.69	331	276.4	63.8		10.99	417	348.1	80.8	
6.28	240	200.9	46.0		6.30	242	202.8	46.4		8.70	332	277.0	64.0		11.00	418	349.0	81.0	
6.29	241	201.9	46.2		6.31	243	203.8	46.6		8.71	333	278.0	64.2		11.01	419	349.6	81.2	
6.30	242	202.8	46.4		6.32	244	204.8	46.8		8.72	334	279.0	64.4		11.02	420	350.6	81.4	
6.31	243	203.8	46.6		6.33	245	205.8	47.0		8.73	335	280.0	64.6		11.03	421	351.5	81.6	
6.32	244	204.8	46.8		6.34	246	206.3	47.0		8.74	336	281.4	65.1		11.04	422	352.1	81.8	
6.33	245	205.8	47.0		6.35	247	207.3	47.2		8.75	337	282.0	65.3		11.05	423	353.1	82.0	

the Saybolt Universal, and the Redwood instruments as well as of their reliability.

The accompanying conversion tables do not take into account the varying specific gravity of the liquids examined. For commercial work with oils this is not done at present with the commercial instruments so that no new error or inaccuracy is introduced in such work by comparing the results of different instruments with each other or by converting them into true viscosity on the assumption that they have a uniform gravity of 1.000, but if accuracy is desired, the figure found in the column headed "Uncorrected Viscosity in Centipoises" should be multiplied by the density of the liquid at the temperature of the experiment. The density is the specific gravity of the liquid at the temperature of the test in terms of water at 4° C.

NEW YORK CITY

## A METHOD FOR TESTING THE EFFICIENCY OF BOILER SCALE PREVENTATIVES

By H. K. BENSON AND O. A. HOUGEN

Received March 23, 1916

For the purpose of selecting a commercial boiler compound, the engineers of the University of Washington Power Station submitted samples of scale and of the feed water together with several boiler compounds. After analytical studies of the water, scale, and the boiler compounds were made, a method for determining the relative efficiency of the compounds was devised.

**FEED WATER AND SCALE**—The feed water contained considerable suspended organic matter, fine silt and clay, together with temporary and permanent hardness. The percentage composition of the resulting scale was as follows:

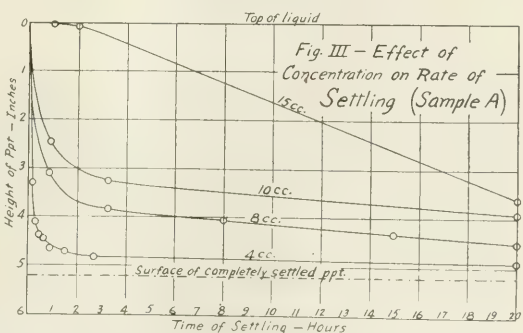
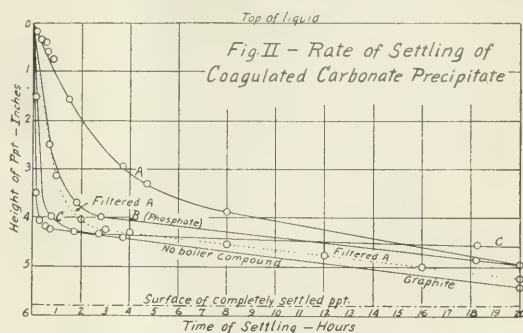
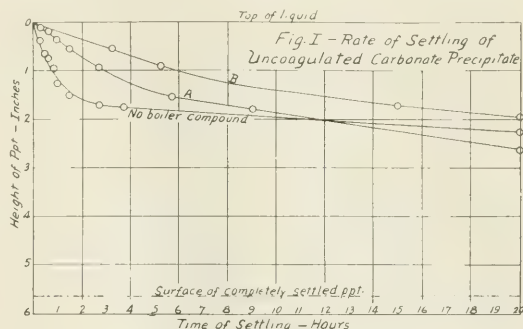
Organic Matter.....	10.93
Silica (SiO <sub>2</sub> ).....	29.70
Iron and Alumina (Fe <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub> ).....	7.42
Lime (CaO).....	38.09
Magnesia (MgO).....	4.90

**BOILER COMPOUNDS**—Sample A was a liquid consisting of water, sodium carbonate, graphite, and an organic solid. Sample B consisted of sodium phosphate (Na<sub>2</sub>PO<sub>4</sub>) in the solid form. Sample C was a commercial liquid compound of undetermined composition.

**EXPERIMENTAL**—900 cc. of feed water were concentrated to about 60 cc. A small quantity of solid matter settled out readily. Upon treating the clear filtrate with filtered solutions of the boiler compounds a large quantity of very finely divided colloidal precipitate was obtained; upon boiling, this coagulated into a flocculent precipitate. Inasmuch as all of the boiler compounds formed such a precipitate it is apparent that some other property than precipitation must determine the relative efficiency of boiler compounds. From the nature of scale deposition it was assumed that the function of boiler compounds is to form precipitates which do not settle out readily but remain suspended in a colloidal or flocculent condition. While the precipitate from concentrated feed water with Sample B settled completely in 2 hrs., that with Sample A was still partly suspended at the end of 5 hrs.

In order to compare the rates of settling, a 2 per cent solution of calcium chloride and magnesium nitrate was prepared. To aliquot portions of this solution equal quantities of Sample B, unfiltered Sample A, filtered Sample A, and graphite, respectively, were added. To a fifth portion no preventative was added. To each of these five solutions 1 g. of sodium carbonate was added to precipitate the carbonates of calcium and magnesium.

The ratio of settling was observed, first from a cold solution, then from one which had been boiled for



several hours at constant volume. The results are shown in Figs. I, II, and III.

### CONCLUSIONS

From the curves on Fig. II it will be observed that the filtered compound has very little effect in upholding suspended water while the unfiltered compound is the most effective. Graphite, likewise, has no effect. While the flocculent phosphate precipitate is effective, the colloidal organic matter seems to be most effective



in holding the precipitate in suspension. While several factors, such as the concentration of the compounds, have not been taken into account, it is believed that the method is of some use in comparing the relative efficiency of the various commercial compounds in the form in which they are offered for actual use.

LABORATORY OF INDUSTRIAL CHEMISTRY  
UNIVERSITY OF WASHINGTON, SEATTLE

### A PRACTICAL DESIGN FOR A TUNGSTEN OR MOLYBDENUM-WOUND FURNACE

By F. A. FAHRENWALD

Received February 21, 1916

The design of furnace herein described is that worked out for use in a series of experiments which required long-time runs at high and constant temperature.

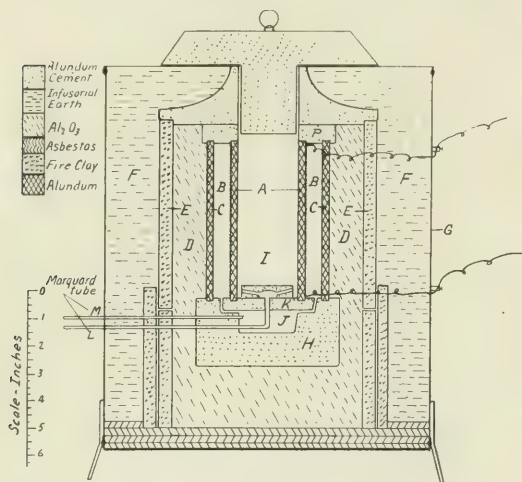


FIG. I

Fig. I is a vertical section showing the wire-wound inner tube A, the annular winding space B, and the second concentric tube C. These tubes were of a very dense alundum, and were quite impervious to gases. The space D was filled with pure, finely ground

The unit H served as a base for the two inner alundum cylinders, and into this were cemented two Marquard tubes, one of which (L) carried the required atmosphere to the melting chamber I; while the other (M) opened through J into the winding chamber B.

Fig. II shows the manner in which this gas distribution was accomplished. The parts here shown were moulded from alundum cement and when dry were carved to proper shape, and then burned. The larger unit H was so constructed that when the disc K was cemented into place over the depression J shown in H a practically gas-tight chamber was formed connecting gas tube M to the openings N, which led to the winding chamber. The tube L connected opening O with the crucible chamber.

Fig. III shows the inner tube A, with winding of spring coiled wire (which was wound more closely near the end of the tube) in position on its alundum base. The winding here shown was of 10.0 mil tungsten wire, but it was found subsequently that there was less danger of fracturing the heating element if several wires were stranded and then wrapped around the tube without coiling. Before placing in the furnace, a heavy coat of alundum cement was added to keep the wire in position. For this work the smooth tubes seem to possess a less tendency to crack than do those made with the spiral groove.

Fig. IV shows the exterior of the completed furnace with gas tubes projecting. These tubes are connected directly by rubber hose to the gas supply. Electrical connection was made by twisting several wires onto the ends of the heating coil and carrying them through the insulating materials to binding posts on the outside (on the far side of the furnace in Fig. IV).

This furnace could be raised to 1500° C. in about 45 min. and held at that point on a wattage of approximately 800; hence, if the drop of potential across the furnace was 100 volts, 8 amperes would be required. The constancy of temperature depended almost entirely upon the regulation of gas flow. The insulation was so efficient that when the heating chamber registered 1500° C. the outer jacket was at about

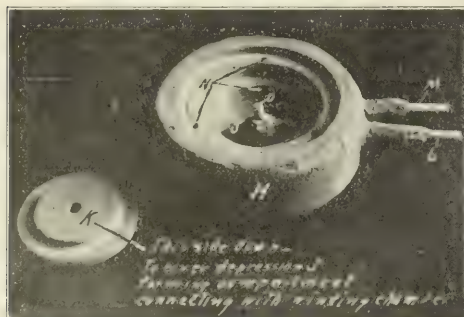


Fig. II



Fig. III

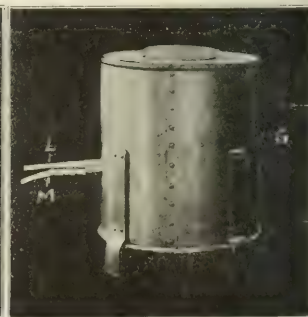


Fig. IV

$\text{Al}_2\text{O}_3$  held in place by the fire-clay cylinder E. The annular space F was filled with infusorial earth, and the whole contained within the sheet iron jacket G. The bottom was protected with several layers of 1/4 in. asbestos board, on which the fire-clay cylinder containing the alumina-packed heating unit was placed.

80° C. This furnace was run up to 1800° C. and in one experiment it was maintained at a temperature of 1500° C. for six days with no variation that could be detected with an optical pyrometer.

CASE SCHOOL OF APPLIED SCIENCE  
CLEVELAND, OHIO

## THE MANUFACTURE OF CHEMICAL APPARATUS IN THE UNITED STATES<sup>1</sup>

By ARTHUR H. THOMAS

I propose to remind you briefly of the facts regarding our sources of supply of a few representative classifications of chemical apparatus as they existed before the European war: to compare with these the conditions as they now exist, and then to consider the possibilities of retaining and extending the manufacture of this same merchandise in the United States.

In this tabulation the term "hollow glassware" is used to designate the product of the glass factory with a furnace—the "hohlglashütte" of Germany—and the term "lamp-blown and volumetric ware" to designate the product of the glass-blowing shop—the "glasbläserei" of Germany—where the finished product is shaped before the lamp from glass tubing, which tubing is, of course, always made in the glass factory or "hütte." In the United States these two industries are mostly conducted separately, while in Europe they are frequently combined in the same establishment.

### I

#### CLASSIFICATION A—HOLLOW GLASSWARE

FLASKS, BEAKERS AND OTHER FACTORY-MADE<sup>2</sup> SHAPES INCLUDING BLANKS FOR SOME VOLUMETRIC WARE. TARIFF 45 PER CENT *ad valorem*

SOURCES BEFORE THE WAR—With the exception of one large factory in the United States which made, in addition to extensive products in other lines, a few flasks and beakers of excellent quality and reasonable price, this ware was purchased exclusively in Europe. The American production was not, in any commercial sense, a factor in the situation.

THE PRESENT SITUATION—Five factories in the United States are now regularly making flasks and beakers in large quantities. The glass used by one of these is superior in several important physical characteristics to that used for similar vessels by the European factory whose flasks and beakers have been heretofore considered the best in the world. The four other makers are using a resistance glass much alike in physical characteristics which, while not quite equal to either the American or European product above referred to, is unquestionably superior to the glass generally used throughout Germany and Austria. There are two other American factories making flasks and beakers, about which I have no definite information from actual tests. The ware turned out in one of them is of excellent appearance and that of the other I have not seen. Neither factory is reported as producing large quantities as yet.

With the present conditions of shortage in almost all of the raw material involved, in the labor situation, and in the exhausted condition of stock in many of the large college and university storerooms, a considerable shortage for some time seems inevitable unless

<sup>1</sup> Address presented before the American Chemical Society, Urbana-Champaign, April 18-21, 1916

<sup>2</sup> While ordinary bottles are, of course, a factory-made product, my remarks are not intended to apply to them.

additional capacity is operated. Under normal conditions the total convenient production of these seven American factories would more than meet our usual consumption.

#### CLASSIFICATION B—LAMP-BLOWN AND VOLUMETRIC WARE

ALL SHAPES MADE OF TUBING BEFORE THE BLAST LAMP INCLUDING THE GRADUATION OF BLANKS MADE IN THE FACTORY IN ADDITION TO THOSE MADE BEFORE THE LAMP TARIFF 45 PER CENT *ad valorem*

SOURCES BEFORE THE WAR—With the exception of a few items not of significance to our discussion, such as hydrometers and thermometers for clinical and industrial use, homeopathic vials and test-tubes, milk bottles and syringes, all staple stock was purchased in Europe. Repair work and the manufacture of a great variety of special items, not in sufficient demand to warrant arrangement for importation in large quantities, was conducted in a few glass-blowing shops operated by some of the larger dealers, in separate small shops in a few of the larger cities, and in the south Jersey district as an important side line in connection with three large glass factories.

THE PRESENT SITUATION—Two of the south Jersey factories referred to have practically given up the making of any regular stock in this classification because of the shortage of labor and the great demand for their own specialties. The other south Jersey factory has greatly increased its capacity for the more staple and easily made shapes and is making a commendable, but as yet totally inadequate, attempt to meet present requirements. This factory, with the few shops just described, constitutes the entire capacity in the United States to make lamp-blown and volumetric chemical apparatus. There are a few additional shops competent to make certain chemical ware, but not so engaged because of obligations in more profitable directions.

The combined output of all these establishments in the great variety of items in this classification is far from sufficient to fill the daily orders for immediate shipment. Commitments at the present time for large educational quantities, as usually undertaken at this time of the year, seem not to be justifiable with definite obligation as to either price or time of delivery.

#### CLASSIFICATION C—PORCELAIN WARE FOR CHEMICAL LABORATORY USE

TARIFF 50 PER CENT *ad valorem*

SOURCES BEFORE THE WAR—These goods were all purchased in Europe. One attempt to manufacture and market American laboratory porcelain ware some seventeen years ago proved unsuccessful because of poor quality of the product.

THE PRESENT SITUATION—Three potteries in the United States are now making crucibles and dishes and some other shapes in fair quantity. Another factory, not yet marketing their ware but conducting extensive experimental work, promises a product superior in quality to those already offered. One Japanese concern is regularly shipping large quantities of very excellent porcelain ware and a second



Japanese factory is sending samples and is reported to have made some shipments. Some Danish ware is being offered and several well-known British factories are advertising laboratory porcelain in the British journals, but it is unlikely that their production is equal to their own demand. The dishes and crucibles made in the United States have not thus far been as serviceable for all purposes as is desirable, but have apparently been acceptable to many users, and in one instance some recent tests show a distinct improvement in quality.

#### CLASSIFICATION D FILTER PAPER

TARIFF 30 PER CENT *ad valorem*

**SOURCES BEFORE THE WAR**—For several years there were two, and sometimes three, paper factories in the United States making qualitative paper of good quality. Both qualitative and quantitative paper were offered by two other American firms, not paper makers, who supposedly purchased their paper stock and subjected it to the usual acid washing and other treatment in their own laboratories. The two brands of filter paper in widest use and for the greatest variety of purpose were purchased entirely in Europe.

**THE PRESENT SITUATION**—The two paper factories referred to are still making filter paper but are unable to contract for large orders because of the great shortage of suitable rags. The two other firms have given up deliveries for the present. Other experienced American paper makers are actively experimenting on quantitative papers. One of the widely used European brands still obtainable is being shipped at infrequent intervals, and prices have been advanced 100 per cent. One new British filter paper has appeared in considerable variety as to purpose and in some quantity, but with deliveries now much behind-hand. Still another new English maker has made a few shipments, and a third is offering qualitative grades only, but has made few, if any, large shipments. The Bureau of Standards at Washington is working on standard methods for the testing of filter papers, which information is urgently needed, as the reports on the same paper from users in actual laboratory work differ widely.

#### CLASSIFICATION E—HARDWARE AND SHEET METAL WARE

BURNERS, CLAMPS, SUPPORTS, WATER BATHS, DRYING OVENS, ETC. TARIFF 20 PER CENT *ad valorem*

**SOURCES BEFORE THE WAR**—Practically all items in sufficient demand to be called staple were made in the United States. A great variety of articles generally listed in dealers' catalogues, but not used in sufficient quantity to justify manufacturing by American methods, were imported.

**THE PRESENT SITUATION**—The above mentioned condition has undergone no significant change. American factories are now making some of the usually imported items in addition to those made heretofore. They would doubtless have undertaken many more such were it not for the general industrial stress now existing.

#### CLASSIFICATION F OPTICAL MEASURING INSTRUMENTS

SPECTROSCOPES AND SPECTROMETERS, POLARIMETERS AND SACCHARIMETERS, REFRACTOMETERS, COLORIMETERS AND MICROSCOPES. TARIFF 35 PER CENT *ad valorem* EXCEPT ON MICROSCOPES, 25 PER CENT

**SOURCES BEFORE THE WAR** The instruments in this classification as used in chemical laboratories were all purchased in Europe with the exception of microscopes, the manufacture of which has, as you all know, been extensively and successfully conducted in America for many years.

**THE PRESENT SITUATION**—There is no new manufacturing in America to be recorded in this line as a result of the war. The explanation is again the enormous pressure being put upon the several factories equipped for such work for deliveries of prism binoculars, range finders, telescopes as used in gunnery, periscope optics, etc. Two British factories have extended their lines to include certain refractometers and saccharimeters not heretofore made in England, but their deliveries are much delayed because of the control of these works by the British government for war requirements. The same situation explains both the inability of certain very excellent French makers of optical instruments to extend their lines, or even—with one exception—to make any deliveries of their regular goods.

#### CLASSIFICATION G—ANALYTICAL AND ASSAY BALANCES AND WEIGHTS

TARIFF 20 PER CENT *ad valorem* ON BRASS WEIGHTS, 50 PER CENT ON GOLD PLATED WEIGHTS

**SOURCES BEFORE THE WAR**—Practically no assay balances have been imported from Europe in recent years, the demand for such balances having been particularly well met by the excellent instruments of two American manufacturers. The business in analytical balances was about equally divided between three standard American makers, and three equally well-known European makers. I include in this statement those imported free of duty for educational use. Analytical weights, although made in the United States of excellent quality, were mostly imported because of price.

**THE PRESENT SITUATION**—The only change to note is that at present all of the American makers are far behind in their deliveries even though one of the foreign makers referred to is still accessible.

## II

Let us now consider the possibilities of the future, mentioning first "Hollow Glassware," particularly flasks and beakers. It seems probable that a fair share of our consumption of flasks and beakers will be made in the United States after the conclusion of the war without any increase in duty or any curtailment of the duty-free privilege. With some restriction of duty-free entry they would, I think, all be made here. This statement is based upon the following facts:

1—The intrinsic excellence of our product. This is certainly the basic economic factor in determining where any merchandise is to be made under normal conditions of competition.

2—The highest priced American flasks and beakers are now

sold at exactly the duty-paid prices prevailing before the war for the best European brand. Furthermore, all other American flasks and beakers are now not only sold at less than these prices, but at prices no higher, generally speaking, than those hitherto prevailing on European goods of inferior quality.

3—There is a sufficient industrial and other duty-paid demand to justify the continuation of a part, at least, of our present war time production even though the large educational business is again placed abroad for duty-free importation. This duty-paid demand is increasingly restricted to flasks and beakers of the highest quality. Those of you engaged in industrial work will agree that in the works laboratory the first consideration is not what the flask or beaker costs but rather that it must not break in use.

4—Flasks and beakers are made in large and well organized glass factories of which we have in the United States several quite competent to undertake such work, and the American glass blower accustomed to the manufacture of incandescent lamp bulbs, thermos bottles, ordinary bottles, and the many shapes of household and other ware, can usually make them with a few weeks' practice.

5—And this is important—There is some possibility as to the application of automatic glass-blowing machines (which have reached a truly remarkable development in the United States as applied to the blowing of bottles and incandescent lamp bulbs) to the manufacture of flasks and beakers if a sufficiently large demand develops. If this should come to pass I think the term "duty-free" would no longer be used in connection with flasks and beakers!

Reasoning in a manner akin to the above seems to justify a similar conclusion—with some qualifications in each instance—for the classifications of "Porcelain Ware," "Filter Paper" and "Optical Measuring Instruments." "Hardware and Sheet Metal Ware" and "Analytical and Assay Balances and Weights" have already shown their ability to take care of themselves.

This disposal of these groups leaves us for further consideration the very important Classification B "Lamp-Blown and Volumetric Ware." It is the shortage in this group which is now causing the greatest inconvenience and it is about the making of such goods that we have much to learn if any significant fraction of our annual consumption is to be regularly manufactured in the United States. As compared with flasks and beakers we here face quite a different array of facts.

1—Our product thus far is, as a general statement, distinctly inferior in workmanship, appearance and (too frequently but not always) in accuracy of graduation.

2—These goods must be sold, on the basis of costs prevailing before the war, at much higher prices than the duty-paid prices on equivalent items of foreign make. Since the war this difference in cost has been still further increased, in many instances to the extent of 100 per cent.

3—The duty-paid demand does not constitute nearly as large a fraction of the total consumption as is the case with flasks and beakers.

4—This ware is mostly made in comparatively small and often poorly organized establishments. This is frequently true even though the shop is operated by a firm which may be fairly designated as "large and well organized" in other directions. The supply of skilled glass blowers competent to handle the great variety of such chemical ware is exceedingly limited. I doubt if there are 250 such workmen in the United States at the present time. These men have mostly come to us from Thüringian factories as skilled and accomplished artisans who

were well paid at home. They naturally demand and get still more here. A good all-round worker now gets from \$45.00 to \$60.00 per week. They do not always lend themselves to the proper subdivisions of labor for economical production. They are quite united in their common interests and naturally not greatly interested in the training and development of apprentices. They frequently are compelled to give up work on general chemical ware because of the high wage they can earn on piece work specialties.

One large concern in south Jersey is here deserving of special mention because of their output in this line which, while as yet confined largely to the simpler and more staple items, is made almost exclusively by young men and women native in the locality under the direction of a few more experienced workers. I recently visited this plant and was favorably impressed with the very encouraging progress these operatives had made in a comparatively few months.

5—And this again is important—There seems to be little possibility as to the application of automatic machines to this line, with the exception of those already developed and in efficient use for homeopathic vials and syringes.

### III

With the important Classification B, "Lamp-Blown and Volumetric Ware," before us, and with flasks and beakers of Classification A still in mind, let us consider for a moment the conditions pertaining to this industry in Europe.

Not a few of you have visited that attractive little section of Thuringia which has, since the beginnings of modern chemistry and before, supplied the world with chemical glassware and with many other interesting things as well. Ilmenau, Stützerbach, Schmiedefeld, Gehlberg, Frauenwald are names familiar to you from catalogues if not from visits. Each of these towns and many others have their one or two "hütten" mostly with a "bläserei," "ätzerei" and "schleiferei" operated by the same firm. There are also many separate lamp-blowing and graduating shops both in the towns and nestled alone among the fir-clad hills, in number quite beyond the reach of a single visit.

Here we still find the formerly wide-spread house-working industry—now decreasing because of the modern organized shop—where certain members of the family too old or unable for other reasons to make full time at the shop, do a great variety of work at home on a piece work basis. They take this finished work to the factory on Saturday night and, securing their supply of tubing for the next week's work, carry it home on their backs.

They also have there the local testing bureaus of the Kaiserlichen Normal-Eichungs-Kommission, such as the Herzoglich Sächsische Eichamt in Gehlberg, from which must radiate a vast influence toward the development of precise standards of workmanship.

There is also their well organized apprentice system and that most important institution, the "Fach-schule." I am not clear enough in the details of either of these to explain them with any authority, but am quite sure that we have in this country no trade or manual training school where a young man can learn the fundamentals of chemical or any other glass blowing, to-



gether with scientific instruction as is required in such work.

Back of all this, and possibly more fundamental than any of it, there is throughout Germany and elsewhere in Europe, a well established association between the chemist in his laboratory and the glass-blowing industry, particularly as regards new apparatus. This association usually begins with the laboratory glass blower and has its first commercial extension through the medium of the small outside glass-blowing shop which is so generally found adjacent to almost every European institution maintaining a laboratory where any original work is done. Such shops are often quite independent of the laboratory but are usually a direct outcome of the work therein, and the world has been largely dependent upon them for the pioneer apparatus in many fields.

This laboratory glass blower and this adjacent outside shop seem to form the connecting link in Europe between the chemist in his laboratory and the more highly organized Thuringian manufacturer who distributes throughout the world his large production of staple articles. The development of the Beckmann thermometer and other apparatus for the determination of molecular weight by the glass blower to The Laboratory of Applied Chemistry, in Leipzig, under Beckmann's own direction; the manufacture and sale in another Leipzig shop of a great variety of apparatus for physical chemistry after Ostwald and Luther; the development and early manufacture in the basement of the Technical High School, in Dresden, of the whole line of gas analysis apparatus after Hempel under his own direction (with its further development by Dennis, of Cornell University), are a few of the many illustrations of this connection.<sup>1</sup>

In the United States we now have some laboratory glass blowers, but should he not be a part of every chemical laboratory conducting original work if we are to develop and manufacture lamp-blown chemical apparatus to any extent? Should we not also encourage the establishment and support of these small outside shops under the wing of our large universities and research institutions where the new and special apparatus which has been developed in their laboratories may be made, still more or less under the watchful eye of the author and sold to those interested until the demand warrants its manufacture in large quantities at the lower prices possible in an organized shop?

Our present great need and our natural aptitude for new enterprise may indeed produce some increase in our capacity for organized manufacturing before the laboratory glass blower and the small outside shop habits become greatly extended. The south Jersey establishment previously mentioned is, in fact, already an instance of this, but it must have for its future profitable existence a fairly constant and

large demand for such recognized staples as can be made in great quantities and with a minimum of highly skilled labor, and should not be burdened with too much special work. You could render great assistance to such effort by eliminating from your regular laboratory practice the many shapes and sizes of lamp-blown ware not in wide use, but the making and selling of which hampers the manufacturer and cumber the shelves of all the larger dealers, and in both places tends to greatly increase the overhead charges and, in turn, the ultimate cost to you of all apparatus you buy.

Let us now consider for a moment, in conclusion, that bugaboo of the whole matter—the tariff! Is a higher tariff fundamentally necessary to the permanent establishment of the manufacture of chemical apparatus in the United States? It certainly is not so far as much of the apparatus we have considered is concerned. Even in our particular Classification *B* of "Lamp-Blown and Volumetric Ware" it seems not so important as a *possible curtailment of duty-free importation*. I am not unmindful that to those of you engaged in teaching, such a suggestion may seem to jeopardize the very existence of educational work in science and to be entirely too high a price to pay for the problematic transplanting of any industry of no great commercial importance.

It might, however, be practicable to discontinue the duty-free entry of at least such glass and porcelain ware as has hitherto been imported in such enormous quantities for routine student work. I mean the flasks, beakers, funnels, burettes, pipettes, evaporating dishes, crucibles, test-tubes and the like which are dispensed from the laboratory storeroom to the students for their individual work and for which the institution is paid by laboratory fees, breakage charges and similar arrangements.

The first result of such a change would certainly be a far keener interest on the part of possible manufacturers in the United States whose first question is always "How much of the consumption is provided for by duty-free importation?" Another outcome might be that the laboratory glass blower or the small outside glass-blowing shop would naturally add the function of dealing to that of glass blowing and would carry in stock for sale to the students the exact apparatus required by the student for his particular course and for which he has always paid in one way or another.

In such event the institution would be relieved of the outlay and expense attendant upon providing and keeping up the present large storeroom stocks and a tendency to extravagance because of the necessity of making up large duty-free orders surely to anticipate the needs for a long period of time might be lessened. The carelessness and indifference of the student, as a result of the apparent abundant supply of apparatus and the direct cash outlay required of him, might also be materially reduced without great, if any, increase in the cost to him of his laboratory courses.

Paragraph 573 of the Tariff Act of October 3, 1913, provides for the duty-free entry of "philosophical and scientific apparatus" by certain societies and in-

<sup>1</sup> Here at the University of Illinois you have a skillful glass blower in connection with the Chemical Laboratories who has rendered valuable assistance in the making of glass parts of the new apparatus for the measurement of the conductivity of electrolytes as developed by Dr. E. W. Washburn, especially the glass cell which will be known in the future as the "Washburn Conductivity Cell!"

stitutions "subject to such regulations as the Secretary of the Treasury shall prescribe." This suggestion as to possible curtailment of duty-free entry might, therefore, be carried out by a comparatively simple change in the present regulations of the Treasury Department, such as might be suggested by a suitable committee of the American Chemical Society! It is conceivable that a reasonable and moderate restriction of this sort submitted to the Secretary of the Treasury by a society composed of both educational and industrial users of apparatus might be more prompt and less disturbing in its effect than an effort on the

part of manufacturers and labor organizations to secure the necessary Congressional action for the withdrawal of the entire duty-free privilege as provided for in paragraph 573!

In the apparatus line as in the dyestuffs we shall do well to remember that the answer to the daily question "Why do we not make it in America?" requires a more profound analysis than is apparent in newspaper editorials and that what is now indicated is an intelligent and, above all, an unselfish coöperation between the manufacturer, dealer and chemist.

WEST WASHINGTON SQUARE, PHILADELPHIA

## INDUSTRY AND THE UNIVERSITY

Addresses before the New York Section of the AMERICAN CHEMICAL SOCIETY, Chemists' Club, April 7, 1916.

### THE INDUSTRIES AND THE UNIVERSITIES

By WILLIAM H. NICHOLS

Chairman of the Board of Directors of the General Chemical Company

In common with you all, I was greatly interested in the program laid down by Dr. Wagner, our Chairman, looking toward a contribution to the question of bringing the universities in closer touch with the industries—an end not only desirable, but vital. Naturally he began with the universities, and you have doubtless read with great pleasure and profit the contributions made by the representatives of two of them on the first two evenings of the discussion, the speakers confining themselves more particularly to the subject of chemistry. I confess my feelings of pleasure were somewhat modified when in Florida, a little while ago, I received notice from Dr. Wagner that I was to be honored with the duty of stating the point of view of the industries, a rather large contract considering their diversity and my limitations. Of course, I understood perfectly that this was not in any way a contest between opposing forces; but simply an effort to get the points of view of those who had been differently situated, and whose experiences varied, the hope being that out of this seed might spring a great tree which would be of service to humanity. Everybody to-day listens with the utmost interest to what is said by any of our great professors: partly because they know so little about what the professors are doing, and mystery is always attractive, and partly because they justly have a great respect for anything they say, knowing that they are picked men, not actuated by selfish motives, and who rarely advertise themselves.

When I was a youngster, if you will pardon a personality, those who were interested in my progress concluded, after painful thought, that I was utterly unqualified for any business occupation, and that the only rôle which I held out any promise of being able to fill with credit was that of professor of some sort not specified. This shows that the professor in those days was sometimes looked upon as a kind of a humdrum person whose duties were to explain, more or less lucidly, to budding minds what some other professors had put into books, and, where their own experience justified it, which was seldom the case, delivering lectures of their own. I had a very different view, however, and felt that while I admitted the premise that I was entirely unqualified for business work, I did not see any reason for supposing I was qualified for the alternative; and so, on my own motion, without taking anybody's advice, I proceeded to do the best I could to acquire an education as a technical chemist—a profession which in those days had very few followers.

Immediately on graduation I proceeded, with the assistance of one workman, to enter the field of technical chemistry, and have been more or less employed in that field ever since. One of the very first discoveries I made was that college professors would be apt to know a great many things which I did not, and

I took occasion more than once to accept the kindly invitation of Dr. Chandler to consult him, without charge, on any problems confronting me. I remember, in this connection, another man who was not a university professor, but who was qualified to be one, who also rendered any advisory service which I called upon him to undertake. That gentleman was Dr. Manuel Alsberg, long since passed away. The only thing like a quarrel which I ever had with Dr. Alsberg resulted from his complaint that I did not consult him often enough, as, for some reason or other, he seemed to have taken an interest in my progress. So you see that the subject of the coördination of the universities with industries, as far as I am concerned, began practically with the beginning of my business life, and has been prominent in my thoughts ever since. While this does not qualify me particularly to discuss the question before us, it at least shows that I approach it with friendly feelings, and that it is not a novel proposition with me.

The first address of this series was delivered by President Butler of Columbia, and will well repay preservation. In the first paragraph he makes a statement that has an immense bearing on the whole subject, although I think he put it in as a mere pleasantry. He said that he had an impression that there had been so many changes in chemical knowledge during the thirty-five years which had elapsed since he had listened to Dr. Chandler's lectures, that if he were to attempt to reproduce any of this excellent instruction you might think him a student of archaeology rather than of chemistry. While, without any derogation of Dr. Chandler's lectures of that day, it must be admitted that the period alluded to by President Butler has produced the most astounding changes, it must not be forgotten that thirty-five years hence any speaker being educated in Columbia to-day, and who should not follow up the work, would surely have to make a similar confession, for the science of chemistry has gone forward with such leaps and bounds, and is of such limitless extent, that it has long since been impossible for anyone to fill all of the fields. In fact, many of the fields are, themselves, divided up into several departments, so that the great chemist of to-day is usually a specialist, and sometimes a specialist in quite a narrow area. The importance of this lies in the fact that the nation which is generally credited with having made the greatest advance during the past fifty years, may not be the nation which will make the greatest advance during the next half century. No one can tell who will have the honor then; but it is perfectly safe to state that whichever country stands at the head, it will be only after tremendous efforts made by the others. There is, therefore, no reason, whatever, why the American chemist, with his conceded ingenuity and imagination, may not well look forward to being the chemist in the lead a half century hence, even though he be engaged in fields which do not bring him so prominently before the eye of the public



as if he were making dyes and colors. Thus President Butler's pleasantness is really a word of hope.

I also like the way he described the problem, and I cannot do it better than in using his own language:

"The problem—if I may use a military term—is from one point of view a problem of mobilization of resources, of facilities, of opportunities for a peaceful war in the interest of science and of industry. The problem from another point of view is a problem of conservation—the conservation of our natural, our human and our institutional resources. From still another point of view it is a problem in efficiency engineering, applied on a great national scale through an organized undertaking to care for the thousand points of contact between theoretical knowledge and practical life."

I do not believe that the problem could be better stated, and I shall certainly not attempt the task. A careful consideration of it leads to so many trains of thought, that an address of the length permitted in this cannot possibly touch upon many of them. Fortunately it is so clearly stated that any man, whether a chemist or not, giving it his careful thought, can think out along lines with which he is familiar, and arrive at results.

#### THE INDUSTRIAL VISITING BOARD

President Butler's device to bring about the coöperation through an industrial visiting board, which seems to him to be practical, makes a different impression on my mind, as far as the field of chemistry is concerned. On more than one occasion I have alluded to the fact that the chemical engineer in the making is very much more hampered than the electrical, civil, mechanical, or mining engineer, because the latter have great operations which have been conducted by masters of the work, which they, as well as their teachers, can see and study, which is not often true in the field of chemical engineering. President Butler's suggestion that those who are in the industrial chemical field should form themselves, or be formed, into representative bodies of visitors, advisors, and counsellors, so that the student would have the benefit of contact with those engaged in the industry, and learn the problems with which they are confronted, or which they have solved, I fear would not be practicable, however desirable from the educational standpoint. It would take too long to get results, and depends for its value upon a degree of altruism to which the manufacturers, as I see them, have not yet attained. If such a committee can be formed, however, by all means set about forming it.

#### IMPORTANCE OF THE SMALL UNIVERSITY

President MacLaurin, of the Massachusetts Institute of Technology, in his able address of this series, lays a good deal of emphasis on the fact that his institution, while not called a university, is one, just the same, for reasons given by him, and which are all perfectly sound and conclusive. I allude to this merely to point out that in a full discussion of this matter we must not anywhere let the impression go abroad that only the coöperation of large universities is desirable. Nothing could be further from the truth than this view of the subject. After all is said, it is the individual professor, himself, and not the university with which he happens to be at the moment connected, who will have to solve many of the problems submitted. Of course, it is of untold value to the individual that he have the backing of a great institution, with all of its laboratories and other equipment, to say nothing of the *esprit de corps* inseparable from such an organization. It may well happen, however, that the very best man capable of following out a given line of research, may be found in one of the smaller institutions, and may be, himself, almost unknown. In a discussion of this question we must not lose sight of these men; but, on the contrary, must make it appear to them that they will be cordially welcome, not only in the discussion, but in any subsequent movement that may grow out of it. I am quite sure that President MacLaurin would agree with me in this, and had no idea of stating

the contrary—but I think it wise to mention it, to prevent any possible mistake. After alluding to several matters which the war has brought sharply to our attention, he goes on to say we have the schools of applied science here, to contribute to a solution of the problem, which must be along the line of giving their support to the organization of industry, so as to meet the needs of the nation as a whole, though their main contribution, here as elsewhere, must be in the supplying of men properly trained for the task. He naturally points out that there are great differences in the students themselves, and that the most that can be expected from the school is that it gives them three things—a knowledge of the fundamentals, the method of attack, and the spirit of industry and alertness for improvements. It is quite true, as has been so well stated by him, and others, in this discussion, that the universities have to take such material as comes to them, and make the best they can of it. Some graduates I have seen have plainly shown that they have not been worth the time and expense which they have cost the university, and it has seemed to me that while it is true that an institution of higher education cannot select the students which come to it originally, it ought to be very well able at the end of the first year, or sooner, to decide whether a student should be permitted to cumber the ground any longer in that institution, or whether it would be an act of kindness to all parties, to inform him that he does not hold out sufficient inducements to encourage the institution in proceeding further with his education. In some such way as this, while the original material could not be selected, it could at least be culled more thoroughly than is done at present; and while a smaller number of graduates would result, I think a larger amount of benefit to the world would be forthcoming. This is at least one way in which the university can contribute to the industries. In concluding his address, President MacLaurin says: "The universities are animated by the spirit of service, and anxious to do all they can to help. Let the industries tell us clearly what they want." This is a fair challenge, and deserves a concrete reply.

In Professor Talbot's address, delivered on the same evening, we find much of great value, and worthy of the careful study which it will doubtless receive. The reference to Professor Mann's investigation, resulting in fourteen hundred replies, mainly from members of the engineering societies, to questions designed to bring out the factors which the engineers regard as contributing most certainly to success in personal work, and also to learn the opinions of the same men as to the efficiency of our educational institutions at the present time with respect to those factors, Dr. Talbot finds that in certain very important matters the output of the universities seems to be lacking. Of course we all know that one of the most important kinds of knowledge that it is necessary for a man to acquire, is a knowledge of human nature. This proposition has only to be stated to receive immediate assent. As everyone knows, its possession is essential to great usefulness in many fields, if not in all. I do not see how a university can be expected to teach this important branch, nor why it should be blamed because its students do not enter life fully posted in this regard. It is one of the great elements of education which come to a man after he has left the college walls, and has commenced to associate with the world at large and rub up against those who are not interested in his success, or, for that matter, not interested in him at all, except in so far as he makes himself of value, or a nuisance. Its possession, however, is necessary if a man is to make even a good foreman, and even more necessary if he is to make a good superintendent, or, possibly, later, a manager of a great concern. Let us not hold the universities to blame because they cannot do the impossible. There are so many splendid things they can do, that we should confine our work to these. I can say, for the encouragement of the young graduate, who is full of a knowledge of facts and theories, that this post-graduate study will be found

to be one of the most interesting in which he can possibly engage, and when acquired will be of the utmost value to him in the application of what he has hitherto learned. Though the whole of life should be a school, and no man should graduate from it until his spirit leaves his body, it will be found that the schooling is none too long to acquire a working knowledge of human nature.

#### SUMMER WORK IN FACTORIES

Professor Talbot's suggestion that chemistry students should have the advantage of summer work in factories, while doubtless of great value to the student, has sometimes been found, when tried, to be something of a nuisance in the plant—provided it be a chemical plant. I am sure he will not forget that these are not educational institutions, except in so far as they are providing for a permanent staff. I have little doubt, however, that the chemical student would receive great benefit from spending his vacations in plants of general character, where he could not fail to learn a great deal which would be of subsequent value, and at least gain in the study of human nature.

Professor Talbot thoroughly appreciates the importance of arranging some way by which able men should serve both industries and universities. He alludes to the advantages which the industries have in being able to offer greater emoluments to bright men, and thinks it is possibly too much to ask of the industries to refrain from securing their services; but, he says, "It seems very desirable to make an effort to devise some plan of coöperation which will, in a considerable number of cases, permit able men to serve the industries without severing their connection with the educational institutions." I think that is one of the questions which we are trying to solve in this series of talks, and is a natural sequence to President MacLaurin's challenge.

Professor Walker, in his excellent address, makes some well-deserved criticisms of the industries, hoping that he may elicit corresponding criticism of the universities when the industries have their inning. As I said at the beginning, this is not, as I understand it, a competition between the universities and the industries, but rather a discussion leading to further and better coöperation. Hence I will acknowledge the force of some of Professor Walker's criticisms, and make no effort to excuse the industries. It is true the latter do not disclose all their problems, and it is equally true that they are foolish for not doing this, unless they are satisfied that they have within their own staff men who are capable of satisfactorily solving them. I do not believe that they hide their problems because they lack faith in the universities; but rather on the theory the ostrich is popularly supposed to entertain.

#### PUBLICITY FOR INDUSTRIAL RESEARCHES

I also acknowledge Professor Walker's point that scientific advantage obtained in industrial research should be made public, and heartily agree that no scientific man should be satisfied with a purely monetary return for his labor. Professor Walker points out that this publicity need not result in any way in injury to the particular industry which directed the research, and mentions Professor Gies' admirable example of Pasteur. I also acknowledge the force of the criticism that technical directors are needed in our industries, and it has always been a mystery to me how any concern would expect to succeed without such intelligent direction. I might say, however, that whatever may be their shortcomings, they make safe competitors.

Professor Walker's suggestion that universities must supply intelligent foremen, is worthy of careful consideration, and may have in it a suggestion of considerable value.

Mr. Little has, for a long time, been a real link between the universities and the industries, and has had considerable experience with those residing in outer darkness. His reference to efficiency in government, and certain prevailing notions regarding labor, wealth, and brains, are really refreshing. Re-

garding the subject under discussion, however, I was particularly interested in his remarks about the desirability of students leaving the university with a definite purpose in view. It has always been beyond my comprehension how so many of our young men can prepare for college, and pass through it, and come out with only the vaguest ideas of what they really want to do. To think of spending all of the years necessary to prepare for life, without having some definite line laid out to pursue, would seem impossible if it were not so common. I hope Mr. Little's words, added to those of so many before him, will sink in to enough minds to produce some real specialists of the future.

His remark about the neglect of the English language as a business tool well expresses a thought which has often been in my own mind. It is not only of the greatest value to any kind of an engineer or scientific man to be able to express his thoughts in good English, but sometimes it is absolutely essential. I knew a man who held a high place in the ranks of engineers, who reached that point because of his knowledge of English, and not because of his knowledge of engineering. I do not say this to convey the idea that the former might take the place of the latter; but only to show how it helped at least one inferior engineer to reach distinction.

I have not alluded to Professor Gies' address, as it was extemporaneous, and I, unfortunately, was absent. Professor Lucke's, delivered the same evening, contains much of value to the industries, as does that of Professor Whitaker. Both gentlemen have had much experience in industrial work; they have discovered many weaknesses existing therein, which are generally acknowledged by industrial managers.

#### "PURE" AND APPLIED CHEMISTRY

At this point I would like to inject a few words regarding so-called pure and applied chemistry, as I think their relation has sometimes been misunderstood, and a good deal of harm occasioned thereby. I am a great believer in the enormous importance of work done along lines of pure chemistry, some of which would seem to the casual observer to be of no possible value for the present, or for the future. There is no need of taking a moment of your time to discuss this, as every one of you will readily admit the great importance of work which is done along purely theoretical lines, and without anything in the mind of the worker looking to its application. At the same time I believe it to be impossible to work out any purely scientific theory, or arrive at any scientific fact without either directly, or indirectly, contributing to the good of humanity. I am aware that pure theorists may contradict this view, strange as it may seem to those of us who have been engaged on the practical side. Take the great Dr. Witt, for example. In more than one conversation he expressed to me the contempt he felt for those chemists in his own country who were prostituting chemical science to the making of money; and yet no one would be more ready than Dr. Witt, himself, to admit that the great organic chemical industry of Germany would never have progressed as it has done, without the magnificent work in pure theory done by himself and many others. The right view of the case, in my opinion, is that pure and applied chemistry are simply different phases of the same science, and that one cannot live without the other. Applied chemistry is the bringing out to useful needs of theories evolved by pure chemistry, which, in turn, is pushed forward to further investigation by the results obtained in applying these theories. Some men are better adapted to theoretical work than to practical, and of others the converse is true. Let each man be "fully persuaded in his own mind," and bring forward the results of that which he, himself, can do the best, and the world will be the richer because of the labor of all. If the universities are to assist the industries, therefore, a means must be found whereby not only the ability of the practical minds of the faculty can be utilized,



which is comparatively easy, but the ability of the pure theorist can also be taken advantage of, which is not so easy.

Referring to President Butler's statement of the problem, we find that the whole matter resolves itself into one word—coöperation; and coöperation in its broadest sense, involving government, finance, the industries, and what is pleased to call itself labor. If we are to stand any chance in the peaceful warfare of the future, we must learn how to make all of these forces coöperate better than any other people can do, or at least as well. Our form of government makes it very much more difficult for us than for some others; and yet the result must be reached unless we expect to oppose a rabble to a well-organized army. Germany has given us an instance of government coöperation which has been extremely efficient; but probably goes too far to be followed in this country. I must confess, however, that I was much impressed, not only in Berlin, but in Vienna, when I was travelling in the interest of the Eighth International Congress of Applied Chemistry, by the extremely intelligent and comprehensive knowledge which government officials possessed regarding the chemical industry, and the very great interest which they exhibited in furthering it. I could not help thinking that with that kind of intelligent government coöperation how easy it would be for us to do things in this country, which now seem to be almost impossible. But there are other methods of government coöperation which I believe would be more valuable to us, of which evidences are already appearing, and which I trust we will in time fully enjoy. Efficiency is a great deal; but it is possible to pay too much for one branch of it, at the expense of others.

#### ENGLISH APPRECIATION OF CHEMISTRY

In England, for some reason difficult to understand, the chemist has in the past had very little coöperation from the government, whatever may have been true of other branches of industry. As far as I am advised the government, itself, has never before the war shown any particular interest in, or acquaintance with, our profession, and they are just now realizing their mistake, and taking steps to recover lost time. Dr M. O. Forster, F.R.S., has been working for years in the endeavor to further the English government and people, and is at present presiding over the Technical Committee of British Dyes, Ltd., an institution with which you are doubtless familiar. In a paper read at the Annual Autumn Congress of the Textile Institute, held last October at the Technical College, Huddersfield, he said several things which I will quote, as they will express the attitude I have alluded to, as he has observed it:

"Among the numerous topics which the war, like a huge cauldron of boiling liquid, has brought to the surface of public discussion, is the proper relation between Science and Industry. It is not new, nor is it really more urgent than it has been at any time during the past thirty years, but present circumstances have combined to impress it so deeply upon the public mind that probably for the vast majority of our people its consideration came with an air of novelty. After a year of conflict, even those who never gave much thought to the subject are now agreed that a union, approaching in permanence and intimacy that of matrimony itself, must in future link these two forms of human activity if the commercial prosperity of the British Empire is to be maintained and the social welfare of its citizens augmented. The celebration of this union has been delayed and hampered by some confusion as to which is the bridegroom and which the bride. Another factor which, in my opinion, has operated more strongly, lies in the fact that Industry, bold, assertive and enterprising, has failed to recognize in the modest and retiring virtues of Science any of those qualities which are desirable and helpful in a life-partnership. In some cases Industry has been content to use Science as a handmaiden without admitting her to the privileges of complete union. An exception to this generalization may be claimed for engineering, however, where, in most of its branches, full use has been made of the underlying scientific principles by its practitioners." \* \* \*

"My purpose in thus tracing, as briefly as possible, the manner in which organic chemistry has secured its grip on the textile industry, is to show that each stage has been reached only by

patient research, and that when reached, it has offered a fresh vista of industrial enterprise capable of yielding new sources of profitable development. Among the reasons why this country has fallen so far behind in the application of chemistry to this branch of industry is the fact that it appears to be practically impossible to explain to the busy man of affairs just what chemical research involves, and what it is capable of yielding. The business genius of this country, drugged by the engineering tradition and by fat dividends, has been blinded to the fact that successful chemical enterprise not only yields fat dividends but is completely dependent upon engineering. Hence, even those business men whose horizon is limited by profits and machinery could have wallowed in profits and rioted in machinery during the conduct of a successful courtship of chemistry, either personally or by proxy." \* \* \*

After explaining the subject, he goes on to say:

"This is research, and it is because the few people who, from time to time, have been able to make dyes in this country, have been discouraged from employing chemists in conducting their researches, while such researches have been sedulously prosecuted in Germany, that we and the United States find ourselves where we are, namely, in the cart; happily, the cart has not yet reached the scaffold, although the guillotine is in sight." \* \* \*

"I believe, however, that the color-makers of this country are honestly and industriously attempting this undertaking, and it is of the utmost importance that they should receive the greatest possible encouragement from the consumers, who must rigidly deny themselves the expectation of miracles, for miracles are not on the list of experiments. The neglect of thirty years, with the moral and intellectual damage arising therefrom are not to be repaired by the wave of a magician's wand." \* \* \*

"Reverting, in conclusion, to the textile industry and organic chemistry, it may be worth while to point out that Americans are making a determined effort also to throw off the color-yoke of Germany, and in certain respects they are situated more favorably than ourselves. In the first place, their business elements comprise many alumni of the modern university, and are therefore alive to the importance of employing graduates in their organization. Secondly, they possess a flourishing heavy chemical industry, including the technical skill necessary to the production of oleum, the elixir of chemical life. Thirdly, they have great power of organization, and lastly, when the time comes, they can rely upon whatever type of intelligent Government support may appear at the critical moment most potent in application."

Evidently Dr. Forster has more faith in the ease with which American laws can be made to fit the necessities arising, than many Americans with whom I have conversed, and whose language would not make polite reading here.

#### GOVERNMENT COÖPERATION IN JAPAN

In somewhat sharp contrast with this, let us look for a moment at a law passed in Japan the 19th of June, 1915, called "The Law for the Encouragement of Manufacture of Dyes and Medicines." After defining what is meant by the title, the law proceeds:

"When a joint stock company established in accordance with Imperial Japanese laws and ordinances, more than one-half of whose capital, as well as a controlling number of votes, belongs to Japanese subjects, undertakes the manufacture in Japan of dyes and medicines according to the provisions of ordinance, a subsidy for a period of not more than ten years from the date of enforcement of this law may be granted to such company. The amount of the subsidy shall be such as to make the dividends which the company pays in each business year reach a rate of 8 per cent on the paid up shares."

The law and ordinances connected with it go into particulars as to how profit shall be computed, and how the company shall be made up; but the gist of the matter is, that subject to those rules and regulations the Japanese Government guarantees a return, for a period of ten years, of 8 per cent on the capital. Contrast that action taken promptly when the dye situation began to become acute, with some of the struggling efforts we have seen in our own country, and I think you will agree with me that our Oriental friends have gone much further along the lines of government coöperation than we have in this country, with all of our vaunted superiority.

So much for government coöperation. Without the most

efficient kind, supervised by men who know what they are talking about, and who understand what is said to them, the many problems before us will, in my judgment, never be satisfactorily solved.

So much has been said and written about the importance of coöperation of the other elements alluded to before, namely, finance, the industries, and labor, that it is hardly necessary in an address of this character to dwell particularly upon them. It is, however, absolutely clear to me that some means must be found within a reasonable time, which will bring about such unity of action of all forces, that our country will be working as a unit and not as a disorganized mass. Too much stress cannot be laid upon this matter here, or anywhere, although I am aware that the subject under discussion is far more limited than the great subject of universal coöperation. The point is, that while it is desirable, and necessary, that the universities and industries should coöperate, if they are the only forces that do coöperate, we will not get along very far in the solution of our problems, as a nation. Fortunately, universities teach many things beside chemistry, and it may be that some of them will discover a method for producing intelligent lawmakers, who, on account of their love of truth, will place the old, efficient, almost-forgotten virtue of patriotism above the modern, vicious idea of party.

#### ADVISORY COUNCIL FOR INDUSTRIES

The question we have been discussing is not a new one. It is as old as universities themselves. Much older than industries in their present highly organized state. The universities have always been ready to do their share. The industries have been getting themselves into a condition to reciprocate. Many of them have arrived at a point where the leaders recognize the need of something which they have not got, to help them forward toward the ends which they have in view. Naturally a line of contact which would serve one industry might not serve another. In fact, it is practically certain that different industries would require different methods of contact with the universities. After years of thought I have arrived at a method which, while peculiarly adapted to the needs of the Company over whose Board I have the honor of presiding, has, I think, some points of value for other companies, whether in the same field or an entirely different one. This plan is now in process of evolution, and, to a moderate extent, is an accomplished fact. I trust it will be rounded out completely within a comparatively short time.

Briefly stated, my plan is as follows: We are forming what we call an "Advisory Council," composed of great chemists in their several lines, located in various universities and schools of science. Each member of the Council will receive a modest honorarium, and be expected to attend meetings occasionally, at which specific problems will be discussed, as well as any other subject of interest to any of the members. In order that the touch may be as complete as possible, I hope to attend these meetings myself, and to have the highly valuable assistance of two or three of the best of our staff. Naturally, as the meetings will only be occasional, correspondence between the head office and members of the Council, and between the members themselves, will be frequent. New problems will be referred to the Council, and by it referred to the member best qualified to solve it. The report, if favorable, will, after discussion, be passed along to the Research Department of the Company, which, in time, if thought advisable, will bring it before the engineering staff. Problems originating with the members of the Council, itself, will be treated in the same way, and it is hoped that this will give the members an opportunity of bringing forward the results of their research work, to ascertain if it be practically valuable. Anything of value resulting from this work, whether originating with the Company, or with the members of the Council, will naturally be rewarded with a share of the profits resulting.

Starting with a small number, the Council will elect its own members, subject only to the approval of the highest officials of the Company, thus insuring the most agreeable relationships, without which the best work cannot be accomplished.

You can see at a glance many of the advantages which would accrue to both the Company and members of the Council, from this close touch. The latter will be brought face to face with real problems, will be allowed to work at their share in them in their own way, in their own laboratories, to the great benefit of their own students, and, in doing this, will have the benefit of association, not only with their fellows, but with some of the best minds which have been devoted for years to the more practical side of the question. Thus we will have a completed cycle, and thus the world ought to benefit as a result of the play of all these forces.

There may be many other ways of bringing about the same, or better, results; but after years of thought I have been unable to devise one. I see no reason why this plan should not be just as efficacious in a steel mill, or a silk mill, or any other kind of mill in which the chemist plays a part; but it need not be confined to chemists. Any university man who can contribute something of value would surely find his place in some of the industries.

This is my answer to Dr. MacLaurin's challenge, and to Professor Talbot's suggestion. The problems awaiting solution are many, the difficulties are great, and the call for universal coöperation imperious. I trust that officials of other industries, for whom I have no right to speak, will seriously take up this question, either on the lines we have adopted in our Company, or improve upon them and give us all the benefit of their study. Let coöperation be the watchword of the future.

25 BROAD STREET, NEW YORK CITY

#### DISCUSSION

By MARSTON TAYLOR BOGERT

Professor of Organic Chemistry, Columbia University

To review all that has been said at these meetings and to express any carefully considered opinion upon the many admirable suggestions which have been presented, would require the entire evening, and I am conscious of the fact that there are other speakers upon the program.

Of the many ways in which our chemical industries and our universities can coöperate to mutual advantage, I can discuss but one or two in the few moments available and have, therefore, selected those which appeal to me as deserving of especial emphasis just now, in that they lead directly and speedily to the desired goal, namely, results of immediate practical value to both.

As has often been pointed out, the universities exist for the diffusion and extension of knowledge, and for public service through its application, and it is upon these grounds that they appeal to and receive the support of the community. They are not intended to be money-making enterprises and, in fact, are almost invariably run at a loss, which loss is made good from endowment funds or in other ways, so that the amount of the tuition fees may not exclude capable and deserving students.

Our chemical industries, on the other hand, are organized primarily for the purpose of making money and everything else must be subordinated thereto. The universities are essentially altruistic and philanthropic; the industries, since they must earn dividends for their stockholders, are apt to be egoistic and mercenary, to put the case bluntly.

#### LACK OF COÖPERATION IN THE DIFFUSION OF KNOWLEDGE

In the matter of the dissemination of knowledge, particularly that relating to industrial practice, it must be evident to all that there is but little coöperation between the manufacturers and the universities. It is not strange that the manufacturers



should be averse to the publication of discoveries made in their plants since, in manufacturing as elsewhere, "Knowledge is power," and new knowledge gained in the laboratories of the corporation may often be regarded very properly as among the most valuable assets of the concern.

From the standpoint of the universities, the great disadvantage of the above policy is this locking up of knowledge, for it causes a serious retardation of the general growth and development of the science and renders it much more difficult for the universities to train men properly for such industries, since all textbooks and general information available are far behind actual manufacturing practice. This is a serious handicap to those endeavoring to give up-to-date instruction in industrial chemistry, and one felt keenly by all teachers of the subject. Another immediately harmful effect of the above policy upon the universities is that it not infrequently results in some of their most capable investigators spending many of the best years of their lives and considerable sums of money in attempts to solve problems, the clues or answers to which had been discovered and filed away long before in the laboratory records of the factories.

It is, of course, futile to ask manufacturers to publish to the world their most cherished "trade secrets," or to endeavor to secure from them articles for our chemical journals describing all the manufacturing details of their industries. But in many of the great industries which have been in operation for any length of time, information has been accumulated in the course of the work which could be made known without irreparable injury to the firm concerned and to the considerable advantage of the chemical profession. It may happen, for example, that a corporation decides to abandon a certain line of work, either because conditions have made it no longer profitable or because it wishes to devote itself to other more lucrative ones. In such cases there seems no good reason why the new knowledge gained in the prosecution of the abandoned process or product should not be made public. New analytical methods and new forms of laboratory apparatus are usually published, I believe, without any objection on the part of the corporation.

#### INDUSTRIES AND UNIVERSITIES SHOULD SO COOPERATE THAT THE WORK IN PURE SCIENCE IS NOT SACRIFICED

Any plan of cooperation should be rejected which compels the university chemical department to devote *all* of its energies and resources to the solution of industrial problems, the results of which are never to be divulged except to the manufacturer who has paid for them. The laboratory which follows such a plan has ceased to be a productive unit so far as its university function of disseminating knowledge is concerned, and has become to all intents and purposes a works laboratory run in the interest of the chemical manufacturer who subsidizes it. Research for profit takes the center of the stage, and research for its own sake is driven out. I do not intend to argue here the question of whether research for its own sake and for the discovery of wholly new chemical fields, the so-called "pure" research, is worthy of encouragement or not, as the material progress of that nation where "pure" research is most assiduously cultivated and where it is held in highest honor, namely, Germany, is a sufficient object lesson to any who care to study it, but what I do want to emphasize is that if the universities withdraw from research of this type, there is little likelihood of its being carried on elsewhere. That is a prospect which cannot be regarded with equanimity either by the universities or by the industries themselves, for it means the death of the goose which has already laid many golden eggs.

What the manufacturers should do, then, is not to weaken in any way the work of the universities in pure science by diverting it into other channels, but to *supplement* it by providing additional men and funds for the solution of the industrial problems. This is the ideal combination, pure science and ap-

plied science at work side by side, each reinforcing and adding to the zest and interest of the other, the point of contact being the scientific staff of the university.

#### ADVISORY COMMITTEES OF MANUFACTURERS FOR THE UNIVERSITIES AND OF UNIVERSITY PROFESSORS FOR THE INDUSTRIES

The universities possess staffs of scientific experts, well-equipped laboratories and libraries, all of which they are willing to share with the industries in return for financial and other assistance from the latter, but the proper adjustment of this cooperation calls for some care and thought.

Any method of handling the question, to get the best results, must obviously be based upon close relations of mutual confidence and respect. If the manufacturer is unwilling to take the university officer entirely into his confidence, the cooperation will prove a failure and unsatisfactory to both parties. As Prof. Walker has aptly expressed it, if the university professor cannot be trusted with all of the problem, he is a dangerous man to be trusted with any of it.

The speaker believes that such cooperation should include also, on the part of the universities, the creation of an advisory committee of manufacturers recognized as leaders in those chemical industries most closely related to the work of the particular laboratory concerned; and, on the part of the chemical industries, of a similar advisory committee, composed of those university professors best qualified by inclination and attainments to render service to that particular industry. Whether or not these advisory committees are constituted, the way is open to those manufacturers who wish to establish such cooperative relations with university officers, and the university professor stands willing and eager, in the great majority of cases, to meet the manufacturer half way in all such matters.

#### RESEARCH FELLOWSHIPS AND A RESEARCH INSTITUTE

An excellent method of making cooperation of this kind effective, is for the manufacturer to establish industrial research fellowships at the university for the solution of problems of immediate importance to him, supplying sufficient funds to secure really skillful investigators, and providing raw material and any special equipment needed, the university giving the use of its laboratories and libraries and the services of its scientific staff to supervise and direct the work. The results of these investigations then become the property of the manufacturer who has paid for them, and may or may not be published as the manufacturer and the university agree. As these industrial fellowships multiply in the university, and the special equipment provided therefor increases, they compose a real graduate school of specific industries where advanced students (usually those who have already received their Ph.D. degrees) may receive that special training in the details of manufacturing practice which it is not feasible to include in the regular undergraduate curriculum, and from which the door into the factory stands open for men of demonstrated energy and ability. The university teacher benefits greatly from this contact with the industries by gaining familiarity with manufacturing methods and the industrial point of view, and is enabled to infuse new life and interest into his lectures. As the natural result of his study of many of these industrial problems, he finds important pure science problems cropping up everywhere, and these he refers to his group of pure science investigators, composed mainly of candidates for the Ph.D. degree, a degree which is awarded only on the basis of *published* results. Such a graduate school should be housed preferably in a building of its own, devoted exclusively to chemical research.

It is difficult to conceive of any more beneficent endowment for a great city like New York than the establishment of a properly equipped research institute for pure and applied chemistry, to do for chemistry what the Rockefeller Institute, for example, is now doing for the cause of medicine. Such an institution

could render the community splendid service, not only by the research work which it actually accomplished and by the highly trained men it turned out, but also by acting as a clearing house between the manufacturers on the one hand and the research chemists of the country on the other, to bring together the problems to be solved and the men capable of solving them. Its fine equipment, its distinguished staff, the confidence engendered by its results accomplished, and the prestige it would enjoy among both manufacturers and investigators would make it eminently qualified for such service. In fulfilling this function it would, on the one hand, gather and keep on file, properly classified and indexed, a list of the various industrial problems requiring solution: wastes, by-products, unutilized raw materials, new uses for chemical products, the improvement of wasteful and costly processes, the production of new and useful chemical substances, and the like. On the other hand, it would keep also a full list of the research workers and consulting experts of the country, their special lines of work, equipment, etc. It would then be in position to render the following definite service:

1. TO THE MANUFACTURER—To explain to him in what ways the efficiency of his manufacturing operations seems capable of improvement by the chemist, and to tell him who are the best qualified men in the country to help him with these particular problems.

2. TO THE UNIVERSITY LABORATORIES—To call the attention of the men in charge to those industrially important problems which seem most nearly related to the research work for which the laboratory is noted. There are many laboratories which would attack with eager enthusiasm such problems were they aware of their existence. Most students are particularly keen for problems of just this kind, yet the teacher is often uninformed concerning the character or amount of the by-products going to waste in his immediate neighborhood, a careful study of which might bring the abiding satisfaction of having converted useless substances into something of service to the community, and lead not only to financial reward for the manufacturer as well as for the investigator, but might also save us much of the present pollution of our streams and tidewaters and of the air we breathe.

An institution conducting work of this nature need never fear that it will be giving away all of its research subjects, for there will always be far more than enough to go round and the careful study of any one inevitably leads to the uncovering of a whole new crop of problems. Further than this, the influence of an institution rendering such service can scarcely be overestimated. It would be the handmaid of all, and yet recognized as the leader of all, national in its scope, with a director and advisory council, keeping close watch on the industrial chemical research work of the country, coordinating, assisting, encouraging and stimulating it in every way possible.

The best proof that such work can be done here is that much the same kind of work is now being done with conspicuous success in the applied science field by the Mellon Institute of the University of Pittsburgh, an admirably equipped establishment, founded by the princely generosity of the Mellons of Pittsburgh; and, in the pure science field by the Kaiser Wilhelm Institute, in the Dahlem suburb of Berlin.

The success of the Mellon Institute has been phenomenal, far surpassing the dreams of its most enthusiastic supporters. Although its fine new building was completed but a year ago, it is already filled to overflowing with industrial research fellows, and the Director has announced that they cannot accommodate any more. Nearly forty different fellowships are now in operation there or have been arranged for, occupying the attention of between sixty and seventy graduate workers gathered from all parts of the country, for the support of which the manufacturers will this year contribute over \$130,000, with from \$50,000 to \$60,000 additional offered in bonuses for the successful solution of certain of these problems. The latest addition to this

industrial research institute, and it is a significant one, is a professorship of research in pure chemistry, to which chair Dr. Martin A. Rosanoff has been called.

As to the great Kaiser Wilhelm Institute for research in pure chemistry, I would remind you that it too is supported largely by the chemical manufacturers. In 1913, when I had the pleasure of visiting this establishment, it had two large and imposing stone structures, one for Physical Chemistry, under the direction of Prof. Haber, and one for Organic Chemistry, under the direction of Geheimrat Beckmann and Prof. Willstätter.

There is thus nothing new in the plan of coöperation suggested above, as it is essentially that worked out and first given a practical trial by the late Prof. Duncan, and has culminated in the founding of the Mellon Institute. The reasons why I have picked it out for emphasizing are, as stated, that it appears to me to lead most directly to the goal sought, that it is not an untried experiment but a demonstrated and conspicuous success, and one which has accomplished more in a short time than any other with which I am familiar, and because the chemical manufacturers of this vicinity have not yet availed themselves of it to any great extent.

When it comes to the troublesome question of the publication of the results of industrial investigations and the diffusion of chemical knowledge, the situation must be faced squarely and the fact clearly recognized that manufacturing corporations are not universities, but are organized to turn out a product at a profit. It is unreasonable, therefore, to criticize them as though they had been founded for purely altruistic and philanthropic ends.

President Butler, in his admirable address,<sup>1</sup> points out clearly the distinction between the functions of the college and of the university in the community, and that this problem of coöperation touches both. In this paper the writer has confined his remarks to those features of the problem which concern the universities chiefly.

To sum up, the writer favors closer and more confidential relations between the chemical industries and the university professors, the creation of advisory committees of manufacturers for the university laboratories and of university professors for the industries, the establishment of industrial fellowships by the manufacturers at the universities, to supplement and reinforce the work already being carried on there, or still better, the creation of a great chemical research institute in this world metropolis.

To attain that efficiency which is the only sure path to supremacy in any field of human endeavor, our universities and our industries must work together in entire sympathy and understanding, and it rests now with the manufacturer to decide whether he will seek this closer coöperation or not.

ORGANIC LABORATORY  
COLUMBIA UNIVERSITY, NEW YORK

## DISCUSSION

By ELON HUNTINGTON HOOKER  
President of the Hooker Electrochemical Company

"What can the University do to foster the rapidly expanding chemical industries?"

"What can the Industries do to promote a higher yield of University leaven, to their own uplifting, and to the general good?"

Perhaps no field offers a more promising outlook to the university graduate of to-day than chemical engineering. The demand for him has come with an acceleration which is rendering the supply inadequate. Indeed, a few years since he was hardly to be found.

Of late the universities have tried to produce him "in embryo." The task is a large one and so far as I know has not yet been

<sup>1</sup> THIS JOURNAL, 7 (1915), 1069.



solved. Our own experience to date has been that we must take a chemist and train him by dint of serious moods on the theory to be an engineer or failing this we have been forced to train engineers to be chemists.

I think I speak a thought to which managers of industrial enterprises will respond sympathetically in saying that thus far engineers and chemists show in their work what seems superficially a natural antipathy for one another. Probed under the surface there is disclosed merely a difference in habits of thought, units of measurement, and working materials. It is hard for one to get the viewpoint of the other.

We find a disparity of view in other walks of life. The student trained in the law school to a commendable respect for precedent finds this trend becoming fixed in the early years of his practice. As he ripens to greater usefulness he finds himself fixed as with a gyroscope to certain lines of thought which make precedent and respect for orderly process so nearly an end in themselves that his usefulness as a human factor is impaired. He can only respond with prodigious effort to those rapidly changing conditions which must be wisely met at whatever strain to legal procedure.

It is the human fact, not the orderly process, which is the paramount issue. Along these lines we have suffered much in the field of government these recent years. So it is with chemists and engineers.

Our experience is that chemists are unable to force themselves into forms of procedure which will produce a reasonable estimate of cost; that engineers are unable to work out a problem experimentally on a laboratory scale with glass and rubber but must go to costly steel, concrete, bricks and mortar for trivial experiments and that both fail to carry their experimentation far enough to insure ultimate success, but embark prematurely in operation.

Frank Munsey once explained to me why it was undesirable that young men should go to college. He rounded out his argument by pointing to George W. Perkins' career. One could not help being amused at his deduction. The concentration, continuity of purpose, keenness of mind and prodigious working capacity which Mr. Perkins has always exhibited are qualities which would have brought him to the front with or without college. Mr. Crane of Chicago formerly expressed views similar to Mr. Munsey's, but we may look upon that line of argument as belonging to the past.

The essential thing is that the young graduate should enter practical affairs with humility and with the realization that for business purposes he is at the moment several years behind the man of the same qualities who did not go to college. He will gradually outstrip the other if he concentrates on his work with a willing hand. The first essential in the university man is a trained mind habituated to reach logical and accurate conclusions from the facts at his command. This mental training should be in the main acquired before entering the university.

The chemical industry needs most to-day technical graduates of broader culture. A pithy, succinct, clear and forcible presentation of a mediocre proposal often goes further than an involved presentation of an excellent proposition.

Good general education preceding the technical training has become increasingly important. Emphasis on English and economics has often been laid, but it should be further emphasized and more stress be given to public speaking. To this day the benefit of a course in Roman law at college in teaching habits of analysis is gratefully remembered. The study of sciences can give equal mental training but notwithstanding Dr. Abraham Flexner's new school proposals, there is nothing equal to Greek and Latin for widening the vocabulary.

I have long thought the universities and colleges should teach geography. What elements we received in school made but a passing impression. There is of course a much broader pre-

sentation of this subject to day, but a study in maturer years of physical geography and the resources agricultural, mineral, political and human of the different countries would offer a ready key to stores of information needed by the technical graduate. It could be made a most interesting and inspiring field.

After all what is needed of the student, as in after-life, is single-mindedness and tenacity of purpose. William James has used a term "energizing" to indicate an act of will by which one individual of equal brain capacity with another yet surpasses him by occasionally breaking through, by conscious effort, into a sub-stratum of the brain where activity yields a higher quality of product. The cultivation of this capacity brings results in research as well as in active life.

In urging where possible a liberal foundation before the technical course I have in mind that heretofore most men have secured their university training before they were old enough to appreciate and make the most of it. It has seemed a catastrophe to lose a year during the college period. On the contrary, those men who take a year off to work in some industry have the same advantage in subsequent usefulness which lies with those who are forced to work their way through college. They know what they are after and realize that money is being spent and sacrifices made to acquire a definite asset.

The obvious thing which the university can do for the industries is to send professors on sabbatical years to work in the outside world and draw in increasing measure from men in the industries for lectures to students. Cornell has done this consistently for some time; Columbia and the Massachusetts Institute of Technology have done the same. It should be further emphasized.

Men in after-life remember with an almost personal appreciation or resentment those professors whose lecture field enters into the every-day routine of their particular business or profession. The teacher whose exposition of algebra was dull and depressing to a future engineer, who had enjoyed his preceding mathematics and found keen interest in the ensuing calculus, is remembered through life, rightly or wrongly, as the man who gave him a "game leg."

On the other hand, keen enthusiasm is aroused and lasting benefit secured as at Zürich from the lectures of Conrad Zschokka, who came often to talk on hydraulics, leaving the night train from Marseilles, fairly dripping with experiences of the day before in the construction of the great harbor works there, or the movable dams in the Seine and Rhone.

The obligation of industry to the university is great; the discharge of the responsibility should be a pleasure. Our industries must not only maintain themselves but must forge ahead, particularly in a time of world readjustment and opportunity such as the present. The textbooks of to-day are superseded through the discoveries of to-morrow. Research and scientific scholarship must ever follow the lead of and find their best opportunity through the university organism.

Scientific work is now, of course, appreciated and well remunerated by the more advanced of the industries and it is constantly on its mettle to keep ahead providing new and orderly channels for the investment of capital and of any exuberance of activity. The frequent failure of research to lead to useful ends is offset by that inertia of industry which finds difficulty in keeping pace with the opportunities presented for revision of methods and machinery.

Prizes were once offered to foremen and officials of an industry considered by some of its friends to be in the forefront of technical development. The administration was swamped within two months with enough valuable suggestions for improvements to require five years for installation, and had to withdraw further prizes from pure plethora of invention. It

has not yet caught up with the manifest opportunities disclosed.

Reproach has been made that the industrial managers do not open up problems in their entirety to the universities for fear data may be disclosed to competitors. There is much to be said in reply for certain of the industries.

Every right-thinking man feels the human impulse to offer freely of the result of his labor and brains for the advancement of science and in the interest of education. It is easy to say that by the time your competitor has learned what you are doing and copied it, a wide-awake concern will be several jumps in advance. Most of us, I think, also concede that process and machinery patents are of value in the main only to enable one to bring together capital and afford protection during a formative period. Nevertheless, it is equally true that the details of apparatus operation, the so-called "tricks of the trade," the deductions from accumulated data which serve to guide the driver to keep his engine on the rails—all these are vital and are the inestimable accumulation of the years. In a specialized industry these may represent huge sums of past waste and they are not likely to be disclosed to the advantage of a competitor by an executive who feels his responsibility as a trustee.

There is a very real contribution from the world of industry to the universities which the recently organized Research Corporation aspires to make. I refer to affording a channel through which the output of invention in university faculties and among graduate and research students may be saved to the advancement of industry. Many ideas of undoubted industrial value are thus generated but go no further because opportunity is not at hand for their exploitation.

The Research Corporation, as some of you may be aware, aims to present itself as a nonpartisan element between inventor, licensee, manufacturer, consumer and even the patent office and other government bureaus and departments at home and abroad to aid in working out improvements of advantage to the industrial world and at the same time capable of making money for the further endowment of science.

Here is an opportunity whereby original ideas developed in the universities may become productive, of lasting benefit to science and to industry. The corporation by charter provision devotes all of its earnings and the activities of its notable governing board to the cause of science through gifts to institutions of learning.

40 WALL STREET, NEW YORK CITY

## DISCUSSION

By P. A. LEVENE

Member of the Rockefeller Institute for Medical Research

All through history, from the early to present days, science was, and still is a function of the economic needs of a people.

The science of the early agricultural state was astronomy; mathematics and again astronomy were the sciences of the state economically built on domestic and foreign trade. More advanced agriculture encouraged biology and the present industrial state is founded on the exact sciences. Theodore Richards, as Berlin exchange professor, remarked in his opening address: "If Leonardo da Vinci had lived to-day, he should have chosen engineering for his profession."

All through history science was made to serve society through its two distinct branches: one dealing with the fundamental conceptions of natural (at times supernatural) forces, the other with the problems of practical life. One is science in its larger theoretical aspect; the other science in narrow specialized fields. One led up to reconstruction of social orders, to economic revolutions, to the founding of industries; the other introduced improvements in methods of production of one commodity or another, at times perhaps of a small branch of an industry.

One created the wealth of nations; the other helped in accumulating fortunes which seemed vast only on a scale of personal property.

All through history the two branches of science were housed and nursed by two classes of people distinct in their temperaments, susceptibilities, and reactions. One class was grouped around academies and universities, and the other around the guilds, trades and crafts.

It is important that the leaders of industry of to-day should bear in mind the respective debt for their existence that they owe to every one of these two branches of science. It is still more important for them to realize that in the race for supremacy between nations the victory will belong to the one strongest in scientific attainment.

Up to the present, our own industries, and our chemical industry among them, were built on foreign and on borrowed science. Our contributions were principally in the line of practical improvements in the methods of production. Our schools were professional and technical schools. Conditions are changing rapidly. Our industries are challenging those of the rest of the civilized world. There is a vague awakening of a feeling of the value of science. And judging from the addresses delivered in the meetings of this society there seems to be a tendency to draw the scientific university force into direct service of the industry.

There is grave danger in it for this country where universities are maintained by private endowment. It is important for the industries to realize that discretion is needed also in the employment of our scientific forces. Men of great executive ability are not kept in positions of subordinate clerks. Men endowed with ability for theoretical research should not be made to waste their energies in the improvement of methods of production. This is a matter of ultimate economy. Service on advisory boards of industries necessarily must distract the energies of the university professor. The practice is particularly dangerous for the reason that a president of an industrial corporation may also be a member of the governing board of a university.

Undoubtedly there is need for coöperation between the industries and the university. Industries being the principal beneficiaries of scientific achievement should also be the principal contributors in the maintenance of the theoretical work of the university. Since the teaching duties in our universities are very burdensome, the establishment of research professorships, and research fellowships seems most advisable. The German industries have realized the sagacity of such a plan, for recently there was organized by them a group of institutes for theoretical research under the name "Die Naturwissenschaftlichen Kaiser-Wilhelm-Institute." In order that the institutes may enjoy all the advantages of the university, every institute director is made university professor. The industries provide the endowment. The university does not require teaching duties; the industries do not require service on advisory boards. The gain will be for both university and industry.

NEW YORK CITY

## DISCUSSION

By B. L. MURRAY

Chemist, Merck and Company

In order to bring about the fullest coöperation between our universities and our industries two lines of work seem to be necessary. One is the effort to learn new things, to discover new knowledge: that is, to conduct a campaign of research. The other is to make fuller application of our present knowledge. Neither one of these lines should be minimized, neither belittled nor neglected, for in each lies tremendous possibilities for our national welfare. In the atmosphere and company of scientists one may hear so much about investigation, about origi-



mal work, about research that this line would seem to be the only one of importance. But in the society of the industries is found a constant study of how to increase efficiency—that is, how to apply our present knowledge and appliances to better advantage.

If you inquire which of these two lines is of greater importance and along which our efforts shall be expended it will be necessary to make a guarded answer, for a single successful researcher in a single piece of work may revolutionize a whole industry or do far more. He may discover something as important as the telephone or electric light. He may do this. Of course it is uncertain, but it becomes very important if successful, and so is worth trying. On the other hand, the better application of our present knowledge is *sure* of success. It lacks the element of uncertainty and has in addition a breadth wholly unrealized by most of us. I think it would be safe to say that our most pressing need is for cooperation in the use of the information already at hand. Work of this nature would furnish relief to industries almost from the outset, and it could easily continue for years without wearing itself out. But our country is large enough, and our resources sufficient for us to carry on research at the same time; and that is advisable.

In reviewing the papers of the various educators that we have had the pleasure of hearing on this subject during the past winter it is found that almost every one feels the need of more funds the better to further the ends of teaching. Indeed one educator feels that with money we could so expand our present methods of teaching as to make them all-sufficient. The second note sounded by the speakers is the call for more intimate contact between the universities and the industries. It is evident that both these points are well taken. Funds and still more funds are necessary: Contact, friendly contact, intimate contact is just as necessary; they go together; neither will accomplish much alone. Imagine a condition in which the university, while drawing its funds from industry, makes no adequate return to it. Imagine industry in close contact with and in large measure dependent upon the university, but still refusing to support it. Both conditions are intolerable and fortunately are only imaginary. The question at hand is how to promote both funds and contact to a greater extent than at present. I am satisfied that with contact carried to the proper extent, almost if not quite to intimate contact, funds will become available. This is said because it is felt that with fuller acquaintance leaders of industry will acquire greater confidence in our educators and be ready to exchange their funds for improvements in their industrial operations. Is it not purely an exchange proposition?

There is in fact a great lack of contact, of fellowship, or comradeship, even a great lack of acquaintanceship between the officials and teachers of our schools and the officials and responsible men of our industries. If one stops to consider the subject, the impression grows that to a great extent, perhaps even generally, these two groups are essentially strangers: They are working so independently of each other in what should be a common field. Examples will readily come to mind on reflection. The condition is aggravated by many small things often overlooked. The atmosphere of life in the profession of teaching is so utterly different from that of the business world. Surely no elaboration of this point is needed; nor is there need of an attempt to place the responsibility for the situation on either side. It is simply a question of how to bring the two together in harmony.

What are the means of developing this contact? What suggestions can come from the industries to the universities that will help out in our present time of need? Six ways of developing contact have come to my attention and will be briefly reviewed.

One of the means of producing the desired contact, that has been tried on a more or less extensive scale, is the fellowship

idea. Fellowships and scholarships have been established at universities by numerous industries. At times, perhaps, it has been done merely as an advertisement for the party making the grant of the funds, although in some cases, at least, the fellow is supposed to study problems of interest to, and finally to join the ranks of, the firm involved. The success or failure of this seems to depend in large part on the relations existing between the professor and the members of the firm. Disagreement may arise, since it is necessary for some one to decide what particular work is of interest to the firm and just what the fellow shall do. In some educational institutions this means of contact is discouraged, and it is thought to be of limited value. Yet it is not always so. In some cases the student spends part of his time with the firm and part with the teacher. This means of contact should be continued, but only limited results seem to be promised by it.

This leads naturally to the second means of improvement in contact, which I shall call intermittent training. Prof. Talbot says that teachers often marvel at the more intelligent and receptive attitude noted in students who for one cause or another have been obliged to spend a year, or even a summer, in some industry before or during their student career. It is usually the poor boy's privilege to "stay out a year and earn some money." And in all seriousness it is generally better for him than going to school that particular year. Let the boy go to his classrooms for two or three years and then go into industrial work for a few months. He'll soon find out what he wants to study when he goes back to his classes. He will have a much keener appreciation of what is going to be useful to him.

Why not encourage or require the students to get some practical experience before they graduate? It is well worth trying on an extensive scale. In some lines it has long been the custom. It is in vogue to-day in many schools of pharmacy, in some schools of commerce, in partial effect at least in dentistry and in medicine.

I would not, however, have the movement stop with the students. It would be an excellent idea, as already suggested by others, for teachers to try a few months in industrial life. The universities could well afford to grant the necessary leaves of absence, regularly, if they are necessary. In some cases, no doubt, the teachers would welcome such an opportunity during the vacation months, although it must be confessed that in an experience of many years an application from a teacher for vacation employment cannot be recalled. Still there is undoubtedly in this an opportunity for real improvement in the teaching force of the universities.

We have heard from the speakers at previous meetings that the university cannot select the raw material from which to produce *graduates*. The *teaching force* is drawn from the same raw material. And we are told in addition that the best material for teaching cannot be held in the universities because the industries pay higher. This in effect amounts to saying that the teaching force of our universities is apt to be less efficient than the graduates that enter industrial life. It is thought too that faculties many times are inbred. An inquiry made in one large university chemical laboratory sometime ago discovered only one teacher that had seen service in the industries. How can teachers fit students for industrial life without a knowledge of it themselves? How can they give to students a positive leaning or properly direct them to specific fields without such fields being wholly familiar to the teachers?

Another means of contact that is excellent takes the form of lectures or addresses delivered by capable men selected from the industries. Such speakers can supplement the teacher's lectures in a way that is especially interesting to the students. They can be instructive as well. Organize this movement and it can be made important, and worthy of much more extended

application than it enjoys at present. It can be made something more than a pleasant diversion from the routine of student lectures.

If the industries at times furnish speakers to address the college students, why not reverse the situation and have the teachers address the industries? Nearly all industries are organized, and nearly all have occasional meetings. Such meetings provide appropriate occasions for good rousing addresses by prominent educators. They must, of course, be in sympathy with the audience. Industries should invite such speakers. If this suggestion were followed out hundreds of opportunities for contact of this kind would occur during the course of a year.

The visiting committee mentioned by President Butler would also seem to be an excellent means of contact. The various departments of the university are visited by a body of men, appointed from industrial life, whose duty it is to examine the teaching and offer constructive criticism. It requires broad-minded men for good work on such a committee, and to adopt suggestions from such a committee requires broad-minded teachers. Our country is full of both. May I suggest that the members of such visiting committees be recruited in part at least from the various organizations of the industries.

The extension work of our universities is regarded by me as a most important method of cooperation with our industries. It may be made a *powerful* means of contact between university and industry. Such a form of cooperation will not appear at first sight as very promising, because it is so modest in its nature. It does not seek to furnish information to the captains of industry or to the captains of research; nor does it seek to solve the difficult problems of investigation that are more properly solved by other means. But it does greatly increase efficiency; and at the very point in industry where efficiency needs an increase. That is, it helps the humble worker, the foreman, the boss, or perhaps the superintendent or chemist.

There are in the ranks of industry thousands of men to whom the opportunity of a college or university training never came. But these men are none the less deserving of such a training. They often have a keen desire for learning and self-improvement. They are our sturdiest citizens and will usually be found direct-

ing the work of others. Attendance for a few weeks at extension courses, especially if those courses cover subjects with which the men are daily occupied, will quicken and keen and hearten them to a remarkable degree. Such students will often gather from an extension teacher just the stray bits of information that will help them in their daily tasks. It leads to their advancement in the works. Hope is newly awakened in them, they see some progress, and their futures assume new and brighter aspects. It does not usually take long for such men to command greater respect from their associates, and in addition to encourage the latter to greater efforts on their own part. Increased efficiency results, and it comes to the attention of the employer.

It is impossible to escape the feeling that this matter is not fully understood and not fully appreciated by our educators. It may even be unattractive to some of them. It does not result in a long list of graduates when Commencement Day comes around. It does not increase the number of original papers that may be published in the university press. In fact, it is not showy at all. It is just simply effective. It may well be called the mustard-plaster form of contact between universities and industries. It takes hold. And it is on ideas similar to this that Benjamin Franklin, Peter Cooper and others founded such excellent schools of practical training.

I know men who, after working all day, will snatch a quick supper and travel two hours to attend extension courses; and, after the evening has been spent under the reassuring and encouraging influence of the teacher, bringing with him the atmosphere of a different world, the homeward journey must be made, again at the expense of two precious hours. Students of this kind are always eager to take subjects to the very limit of their physical endurance.

I heartily suggest to our regents, trustees, and other educators to bring their teaching more fully within the reach of these eager students. If the courses offered bear directly on practical work of every-day industrial life one of the most powerful means of contact will be found, and certainly a great step in cooperation will be accomplished.

RAHWAY, N. J.

## ADDRESSES

### A DIAGRAM FOR THE CALIBRATION OF VOLUMETRIC APPARATUS AND THE REDUCTION OF THE VOLUMES OF LIQUIDS TO A STANDARD TEMPERATURE OF 20° C.<sup>1</sup>

By HORACE G. DEMING

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It is surprising how many chemists fail to correct for the variation in the density of standard solutions due to changes in temperature. The fact does not seem to be generally known or remembered that errors of as much as a fifth of a per cent may easily be introduced by such neglect.

It is believed that a part of the nonobservance of this precaution is due to the difficulty that is experienced in making the necessary computations, for it is human nature to seek to avoid that which is found to be difficult. For this reason anything that tends to make easy the introduction of corrections for errors of this kind has a tendency to raise the average standard of analytical work throughout the world. A chart is here presented that serves to reduce the calculation of temperature errors to a simple mechanical operation. It is hoped that its publication will lead to a somewhat more general observance of desirable precautions in routine analytical work.

<sup>1</sup> See also Bureau of Standards, *Circular 19*, for tables from which the corrections in the calibrations can be quickly derived. [EDITOR'S NOTE.]

A recent paper<sup>1</sup> explained the underlying principles of a number of charts or diagrams, among others the so-called alignment chart, of which the chart here presented is an example. The latter has been accurately constructed, and readers who wish to make use of it will be able to employ a tracing. But it is thought worth while to describe the principles of its construction, in order that the same method may be applied to other similar problems, such as the reduction of weights to a vacuum, and the correction of refractometer readings for changes of temperature. The chart about to be described is really a combination of two charts, that will be explained separately.

#### CALIBRATION OF VOLUMETRIC APPARATUS

The chart consists of three parallel scales, *A*, *B*, and *C*, equal distances apart. Along *A* is plotted a logarithmic scale, from 5 to 100, each number representing the apparent weight, in grams, of water weighed in the air with brass weights at any given temperature. The point representing 10 g. is marked *p*. Unit distance on the logarithmic scale, namely, the distance from 10 to 100, was taken as  $33\frac{1}{3}$  cm. in the drawing from which the chart on this page was reduced, the reduction being about one-half.

Along the right side of *C*, toward its upper end, is plotted a logarithmic scale of temperatures, from 10° to 33°, for use

<sup>1</sup> THIS JOURNAL, 8 (1916), 264



on the consideration of volumes in cubic centimeters. Each numbered degree of temperature appears at a point measured off from a reference point,  $r$ , and situated at a distance from the latter that is proportional to the logarithm of the volume

$V$  by which a kilogram of water, weighed in the air at the given temperature, exceeds the capacity of a flask holding exactly 1000 cc. at a standard temperature of 20° C. The quantities that need to be considered are the apparent loss of weight of a kilogram of water, due to the buoyancy of the air (taken as 1.05 g.); the density ( $d$ ) of water at the temperature at which it is weighed; and the cubical coefficient of expansion of glass (taken as 0.00027). The latter is needed because it is desired to know the volume of the flask, not at the temperature at which it is calibrated, but at the standard temperature of 20° C. It is evident that

$$V = \frac{1000 + 1.05}{d} - 1000[1 + 0.00027(t - 20)].$$

If  $V$  is expressed in cubic centimeters, it will be convenient to take the unit logarithmic distance along  $C$  equal to that adopted in laying down the graduations of  $A$ .

The scale  $B$  is placed exactly midway between  $A$  and  $C$ ; and a point,  $q$ , lying in a straight line passing through  $p$  and  $r$ , is taken as the reference point in laying off the graduations of  $B$ . These graduations are carried in both directions from  $q$ , unit distance being half that adopted in laying off the two outer scales. A more convenient way of locating the points on the middle scale is to connect each point on scale  $A$  in turn with the point  $r$ . The intersections of the lines thus drawn with  $B$  give the graduations of the latter.

Now since  $0 = \log 1$ , the point  $r$ , which has been taken as the zero point of scale  $C$ , represents a temperature at which 1000 g. of water exceed 1000 cc. by 1 cc. namely, by 1 part in 1000. Connecting this point with  $p$ , which has been taken as 10 g., we intersect the middle axis at a point  $q$ , which, therefore, corresponds to the product of  $1/1000$  and 10, namely, to 0.01 cc. (See the principle of the alignment chart, as explained in the former paper.)

The point  $r$  is, therefore, labelled with the value 0.01, and the other points of the middle axis are given values proportional to the numbers of scale  $A$  to which they correspond.

The chart is now ready for use in the calibration of volumetric apparatus for a standard temperature of 20° C., by weighing water at any temperature. Let us suppose that a graduated pipette has been found to discharge 49.85 g. of water at 30° C. Connect 50° (approximately 49.85) on scale  $A$ , with 30° on the right side of scale  $C$  by a straight edge. Note that scale  $B$  is intersected at 0.26. The true capacity of the pipette at 20° C. is, therefore,  $49.85 + 0.26 = 50.11$  cc., its capacity at the temperature at which it was calibrated being a trifle more.<sup>1</sup>

By following this method, all the pieces of volumetric apparatus in the laboratory will

have been adjusted to the same temperature. This seems to be preferable to the method described in some textbooks, in which no allowance is made for the change in volume of the apparatus with change of temperature. The result of the latter plan is that each piece of apparatus has its volume determined at the temperature that the water used in calibration happened to have. The error involved is about 0.01 per cent for every difference of 3° between the temperatures at which the vessels are standardized.

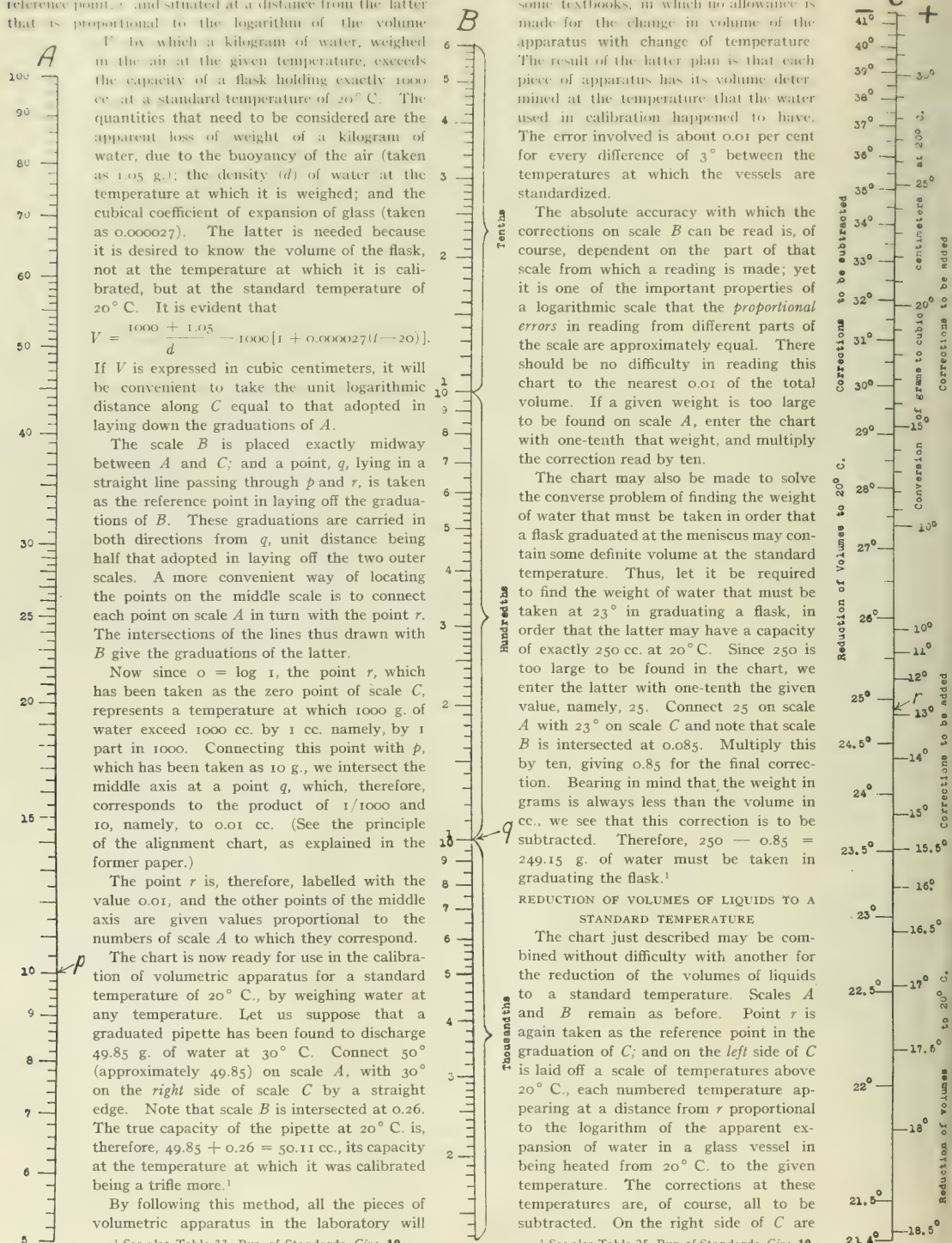
The absolute accuracy with which the corrections on scale  $B$  can be read is, of course, dependent on the part of that scale from which a reading is made; yet it is one of the important properties of a logarithmic scale that the *proportional errors* in reading from different parts of the scale are approximately equal. There should be no difficulty in reading this chart to the nearest 0.01 of the total volume. If a given weight is too large to be found on scale  $A$ , enter the chart with one-tenth that weight, and multiply the correction read by ten.

The chart may also be made to solve the converse problem of finding the weight of water that must be taken in order that a flask graduated at the meniscus may contain some definite volume at the standard temperature. Thus, let it be required to find the weight of water that must be taken at 23° in graduating a flask, in order that the latter may have a capacity of exactly 250 cc. at 20° C. Since 250 is too large to be found in the chart, we enter the latter with one-tenth the given value, namely, 25. Connect 25 on scale  $A$  with 23° on scale  $C$  and note that scale  $B$  is intersected at 0.085. Multiply this by ten, giving 0.85 for the final correction. Bearing in mind that the weight in grams is always less than the volume in cc., we see that this correction is to be subtracted. Therefore,  $250 - 0.85 = 249.15$  g. of water must be taken in graduating the flask.<sup>1</sup>

#### REDUCTION OF VOLUMES OF LIQUIDS TO A STANDARD TEMPERATURE

The chart just described may be combined without difficulty with another for the reduction of the volumes of liquids to a standard temperature. Scales  $A$  and  $B$  remain as before. Point  $r$  is again taken as the reference point in the graduation of  $C$ ; and on the left side of  $C$  is laid off a scale of temperatures above 20° C., each numbered temperature appearing at a distance from  $r$  proportional to the logarithm of the apparent expansion of water in a glass vessel in being heated from 20° C. to the given temperature. The corrections at these temperatures are, of course, all to be subtracted. On the right side of  $C$  are

This seems to



<sup>1</sup> See also Table 33, Bur. of Standards, *Circ.* 19.

<sup>1</sup> See also Table 25, Bur. of Standards, *Circ.* 19.

likewise laid off temperatures below  $20^{\circ}\text{C}$ ., at distances from  $r$  proportional to the logarithms of the apparent contraction of water in glass vessels in being cooled from  $20^{\circ}\text{C}$ . to the given temperature. These corrections are, of course, all additive.

In order to prevent mistakes in the use of the chart, the graduations on scale  $C$  should be marked very plainly in a way that will show whether they correspond to additive or subtractive corrections, and whether they are to be used in the calibration of apparatus by weighing water, or in the reduction of volumes to a standard temperature of  $20^{\circ}\text{C}$ . It is very easy to make an error by reading a temperature from the calibration scale when a correction of volumes is wanted, and *vice versa*. In copying this chart it might be a good plan to construct the calibration scale of temperatures in red ink in order to lessen the danger of an error of this kind.

As an illustration of the use of the chart for the reduction of volumes to a standard temperature, let us suppose that a burette reading of 35.25 cc. has been obtained at  $28^{\circ}$ . Connecting 35 on scale  $A$  with  $28^{\circ}$  on the left side of scale  $C$  we note that scale  $B$  is crossed at 0.06 cc. Because this correction is indicated as being subtractive, it is deducted from the burette reading, giving 35.19 for the volume reduced to  $20^{\circ}\text{C}$ . It will be noticed that 0.06 cc. in a total volume of 35 cc. corresponds to a relative error of about  $1/5$  per cent, and one that is well worth correcting.

Since the rate or expansion of water over small ranges of temperature is approximately constant, it is possible to use the chart just constructed for the reduction of volumes to  $15^{\circ}\text{C}$ . In this case each of the numbers on the left side of scale  $C$  is decreased by 5 units.

An interesting property of the alignment chart is that it permits us to introduce a constant factor without changing anything other than the relative positions of  $p$ ,  $q$  and  $r$ . For example, if it is desired to use the chart just constructed for the reduction to the standard temperature of a liquid having a cubical coefficient somewhat greater than that of water, this may be done by simply moving the scale  $C$  upward a slight distance with respect to the other two scales. For every 10 per cent increase of expansibility over water, scale  $C$  will have to be moved upward a distance of 6 mm. in a chart the size of that here given. For example, if we have to deal with a liquid having a cubical coefficient of expansion about 30 per cent greater than that of water, we may reduce any given volume of it to the standard temperature of  $20^{\circ}$  by means of the chart constructed for water, with the sole difference that each point denoting temperature is to be taken as occurring about 18 mm. above its actual location. As this rule is only an approximate one, true within small ranges, it is sufficient to estimate these distances by eye at the time the chart is read. If more accurate results are wanted, with liquids whose coefficient of expansion is several times that of water, it will be necessary to construct another chart on the principles that have been described.

It is worth noting that the coefficient of expansion of normal sulfuric acid and normal solutions of the alkalis appears to be about 50 per cent greater than that of water, and that of normal hydrochloric acid about 20 per cent greater. For this reason one should be especially careful to make the necessary temperature corrections if solutions of this strength are used in titration. For the ordinary  $N/10$  solutions the coefficient of expansion may be taken as about 10 per cent greater than that of water. Thus with 45 cc. of  $N\text{NaOH}$  at  $28^{\circ}\text{C}$ ., the correction is  $-0.117\text{ cc.}$ , the result being obtained by reading the chart as if the  $28^{\circ}$  mark had been moved upward 30 mm., or else by reading the correction for water and increasing the result by 50 per cent of itself.

Aside from the correct graduation of the scales, the only points that need to be especially observed in the construction of the chart are that the three scales are exactly parallel, that scale  $B$  is exactly midway between the others, and that the points

$p$ ,  $q$  and  $r$  lie in the same straight line. If these conditions are observed, the parallel scales may be any distance apart, and the graduations may begin at any point.

The writer is indebted to Mr. Francisco Quisumbing for the carefully executed drawing that illustrates this article. It is based on the data of Thiesen, Scheel, and Dieselselhorst, as given in Van Nostrand's "Chemical Annual," 2nd Ed., page 459, the corrections for the buoyancy of the air and the expansion of glass between  $20^{\circ}$  and the temperature of calibration being as given above.

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## THE AMERICAN CHEMIST AND THE WAR'S PROBLEMS<sup>1</sup>

By JAMES R. WITHROW

A volume could be written upon this subject if one possessed the power to assemble the material. The new problems which have arisen; the old ones which have become acute because of changed conditions; the splendid way in which the problems have been met where they were a matter of invention or skill; the new methods and processes which have sprung up as though born full-grown; the many old ones which have been improved, altered and utilized in new connections; the way in which the chemists of the country have risen to emergencies which have compelled them to manufacture products in whose manufacture they had had no prior experience—all these would easily fill entire chapters in such a volume. Even so, no earthly progress, achievement or consideration can lift the pall which settles over us when we permit our minds to dwell upon the spectacle of this war. And whose mind can be diverted from it for any length of time? He must indeed exist far below the kindling point who does not resent and despise with all his soul the philosophy and ideals which made it possible. It would be out of place, therefore, to consider our subject from the point of view of achievement, or felicitation, on any alleged good which has come to the science of chemistry because of the war. Surely no one would want progress at such a cost to his fellow man. We approach the subject rather in a spirit of thankfulness that we have been enabled to save something out of the wreck, and that our experience had prepared us in advance so that we have been enabled to prevent the collateral business and economic tragedies of the war from spreading universally. It is not in any spirit of gladness, therefore, at the evil providence which has fallen upon our European neighbors, that we recognize that this war has exalted the importance of chemistry in the minds of those who had not much opportunity hitherto to appreciate its value, nor is it with any jubilation that we take pleasure as chemists in meeting our new problems and emergencies arising from the war.

The satisfaction to many industrial chemists in the last two years of being able to contribute to the solution of these problems and of being conscious of the salvation of many businesses from financial ruin through the exercise of their chemical experience, has seldom been so widely distributed as it now is. What an inspiration it would be to read, spread out upon the pages of such a book as we have mentioned, the chemical successes, big and little, of the past two years. It is not likely that many of them will be known for a while because of the fact that business caution forbids their publicity in many cases, and that the vigorous campaign of destruction of equipment and diversion of supplies in order to hamper export from this country, makes silence a necessity in self-defense.

*The problems of the war are of two kinds, those due to changed conditions, and those arising from supplying munitions at high speed.* Among the former are changes in raw materials made necessary by the failure of imports or by unusual consump-

<sup>1</sup>Address presented before Section C of the American Association for the Advancement of Science, Columbus, Ohio December 30, 1915.



tion of raw material in other channels, such as for products not heretofore manufactured in this country, to the extent made necessary under present war conditions. These changed circumstances were also due in part to new demands for materials and products, which have arisen in the complete rearrangement of things that has come about in many circles since the war began. The other war problems which have arisen, those directly connected with munitions supply, are frequently of a difficult nature. All these various problems, however, have been met in practically every case with a degree of success that has surprised even ourselves.

Naturally one of the first serious effects of the war on American industries was the stagnation produced by the enforced cessation of exports in various lines. Such things as rosin, turpentine, petroleum products, acetate of lime and methyl alcohol were seriously affected for a varying length of time. Then the demand for munitions, for instance, became the wood distillation industry's salvation and with great celerity, acetone plants were attached to many of the works of this industry and the high prices which its products command have brought unprecedented prosperity and have correspondingly hampered progressive improvements. Production, not efficiency, is at present the slogan for this and many other industries. Setbacks of the nature cited usually take time for readjustment and frequently the chemist is a material factor therein. The producer himself is often compelled to add the next manufacturing step to his own operations. Where the new demands were ample, these attempts have succeeded and the war's conclusion will find an increased tendency to manufacture at the source.

The setbacks to industry arising from the disturbance in exports, while they were important financially, were minor matters compared with those arising from such changed conditions as failure of raw materials or their curtailment by absorption in new or abnormally expanded industries. It is here that the chemist is needed most and it is here that he has been of immeasurable service, and has met the problems that have arisen in wonderful style. He was seriously hampered at first by the uncertainty as to the facts. The fundamental thing in every industry is the market. At first much damage was wrought and delay produced by false reports as to stocks on hand and supply, particularly, of imports. Much withholding of goods for higher prices was practiced and even yet the pirates of commerce seek ways and means of evading contracts, even on deliveries of goods which they were receiving without cessation, so as to avail themselves of the inflated market prices. Some clever work by consumers trapped at least some of these unscrupulous brokers and sellers. All manner of fictitious prices were demanded of those unfamiliar with the facts.

As soon as the true status of demand and supply became reasonably certain, many changes were effected which will give gradual and probably ultimate relief. On every hand we see chemical activity without end. Products like synthetic phenol and barium salts, not made in this country before the war, are now made in large amount. Great expansion in production has taken place in the case of such materials as benzol, toluol, aniline products, naphthalene, carbon tetrachloride, acids, alkalis, chlorates, bichromates, and even oxalic acid. With all of these we were largely or in part dependent on imports, but have almost ceased to be so since the war began. Now, fertilizer plants erect their own sulfuric acid works and insecticide makers their own arsenic plants, textile mills make their own bleach. Numbers of manufacturers are replacing potash compounds by sodium compounds and to my own surprise at least, often with great improvement in results. Professor Watts has just told you this afternoon how the ceramist is making this country less and less dependent upon imports in that field by scientific purification and utilization of domestic clays.

Manufacturers of numerous miscellaneous chemicals and pharmaceutical preparations proceed to refine and produce their own crude raw materials and intermediates. The dye famine—for it is real in certain quarters—stirs up corporations with capital of hundreds of millions to enter the field. One of these new companies has installed half a million dollars' worth of machinery in the last few weeks. Indigo and other dyes are being made in nearly half-ton batches which will soon expand to a several-ton size. Where formerly was the most peaceful of occupations, even fertilizer manufacture, every effort now goes to the making of munitions. New plants spring up at the beck and call of new conditions such as the world has never seen. Think of a battery of 100 nitric acid stills each charging 4000 lbs. of sodium nitrate three times a day! Think of the sulfuric acid required and the nitric acid produced! Think of the fact that this one of a number such (the largest nitric acid plant in the world, it is said) is a plant which a year ago did not exist except in the mind and plans of a group of chemical engineers. How little are we able to comprehend the reality of producing 1,000,000 lbs. per day of guncotton where a year ago was merely pine woods. What does it mean with reference to design of plant, erection and operation to anyone who has not managed chemical engineering operations, to recount the engineering operations involved in this enormous production of guncotton in a single plant? Work that is conducted in ten to fifteen parallel procedures or "cotton-lines," which with their accompanying accessories include cleaning and alkali digestion of the cotton; bleaching with chloride of lime; manufacture of sulfuric acid for the production of nitric acid and "mixed acid;" nitration of the cotton in 30-lb. batches; the hazardous wringing and hasty submerging of the cotton in water, to avoid the consequences of heating by too slow dilution of the strong acid held sponge-like by the cotton; the conveying of this material in the "cotton-line" to the washers where the remaining acid in the tube-shaped cotton fibers is removed; and finally the removal from the water as wet or damp guncotton, the commercial product of many plants. This end-product, of course, is but the beginning of raw material for the various nitrocelluloses, smokeless powders and other high explosives. Yet this scale of operations is not going on in just one plant of this kind or even in this one industry. This is a sample of what is happening every day and is the American chemical engineers' answer to the question, "How are you meeting the war's problems?"

At some of these things we are permitted to take at least a peep. No one man can know all of even such gross developments, and practically every chemist we meet has his enthusiastic story of the progress of his own and familiar fields. We all do know, however, that if this is the character of the outward developments, there must be legions of quiet research and other experimental attacks on the new problems, and literally hundreds of solutions being worked out for minor problems in factory and plant, not to speak of the vast amount of work in other departments of chemistry made necessary by all these things. Then, too, there is the ever-verdant crop of interesting suggestions, revolutionary changes and inventions throughout the list of the chemical industries. In fact, they are doubly numerous and aggressive under the stimulation of such a time as this. It is never wise to predict their success or failure in many cases until years even have elapsed. It is true that a large number of these new things *never* make good. It is equally true that some of them *will* make good and that all of them indicate progress, for they are strivings, and progress comes by striving.

It is equally true also that many of the chemical expedients which are in successful use under war conditions will automatically be put aside when normal conditions resume. It is fundamental industrial chemical intelligence that a procedure which is ridiculous under some conditions may be a godsend under

others. We do not expect every change installed to be really normal progress, for it will not be so in the ordinary sense at least. On the other hand, it would be wrong also to say that the mushroom plants producing munitions are not signs of progress. They unquestionably are not such signs in so far as they are temporary. They do not measure true expansion in their respective fields. He would be a novice or singularly blind, however, who did not see that the construction of such plants on the undreamed-of scale I have already mentioned, not to speak of the new materials and procedures which have been incorporated in many of them, makes for greatly enlarged experience in chemical engineering designing, construction and operation. It is easy to see the pressure these things are going to exert upon the future development of American chemical industries. The American chemist's experience is becoming greatly expanded and the significance of this is apparent when we consider that engineering progress is a function of demand and skill or experience in solving problems. The demand increment is ever expanding with the development of the country. In addition, the skill acquired in the production of munitions is a valuable potential asset for defense should such a necessity ever arise. Such preparedness is highly to be desired. Then, too, at the close of the war when the output of these plants is no longer needed for that purpose, their equipment and intelligence will be directed into whatever field promises most. Already some of these concerns are assured that some of their products will find a continuous demand after the manufacturing of munitions ceases, which will be some little time after actual hostilities are at an end. The field of dye production is already attracting some of them. Without doubt the industrial rearrangements to follow the war will leave us much better situated in our ability to cope with the problems of chemical production. At any rate, powerful financial interests will attack these problems as they never have been attacked before. These interests will constitute another great force, which will be particularly effective after the war. When they seek new outlets for materials such as alcohol, benzol and acids, whose production they are greatly accelerating at the present, the gasoline and other problems will be greatly affected. These interests will be found after the war lined up behind the industrial chemists who have been struggling for years against all kinds of unfair competition and disreputable depreciation. Then again, any change in process, be it ever so timeworn or transient in its chemical nature, if it actually is put into successful operation under the then existing conditions, must of necessity push out the boundaries of experience to greater and greater distances and make us better able to meet the problems of the future. Chemical engineering is like any other division of engineering, it grows by what it accomplishes. In this proof of ability to meet a transient emergency the American chemist is certainly reaping a hundredfold as a result of his unadvertised care in the meeting of his industrial problems of the years gone by. Individual cases of progress and development which I have mentioned, it is easily seen, are rarely of great importance in themselves. We have not been revolutionizing on a great scale nor have we been jumping at once into great, new, national industries, but we are rather directing the normal steady gait of our progressive industrial development, with a keener perception toward more complete self-containedness, and thorough industrial preparedness. Some of the industries mentioned which receive much public attention are of relatively little importance compared with many other items affected. The dyestuff shortage appears to annoy many, but the complaint is out of all proportion to the facts and the damage done, compared with that of other commodities. We import normally, for instance, \$9,000,000 in coal-tar dyes per annum, and if we should make them all ourselves—which we will only gradually approximate—we would increase our chemical manu-

factures only 2 per cent and our total manufactures 0.05 per cent.

Though we have made reasonable headway on our problems we are keenly aware that much remains to be done. We do not expect to set the market right in the dye or other matters, in a year or two. These developments take time and have always taken time. Neither should we deceive ourselves or the public with thinking because of what we are doing that we could turn out, without the most careful and detailed previous planning, adequate munitions for our own defense "in sixty days" to supply the "two million men who would spring to arms," as we so often hear would happen in that undesired emergency.

It would be interesting to discuss in detail some of the transient, as well as probably permanent advances, where they happen to be a matter of personal knowledge, if it were wise to hand information to the assassins who lie in wait to hamper some of them, for military reasons. It might be well, therefore, to spend just a little time in emphasizing some general considerations which are connected with this subject.

There is little use in attempting to disguise the fact that the present war is a struggle between the chemical engineering genius of the Central Powers and that of the rest of the world. Quite irrespective of the war's origin, aims, ideals or political circumstances, these are the cohorts from which each side derives its power.

When we consider the strategic position of the Central Powers themselves, their capable education and training, their system of government, which, no matter what we may think of its selfish effect on the world as a whole, we must admit makes for more effective concentration upon its own governmental objectives—when we take into account all these things it must often appear to us that the greatest outstanding feature of the past two years is the miracle of the Entente Powers' resistance to the terribly efficiently prepared onslaught of the Central Powers. This resistance is due, to an extremely large extent, to the efficiency of the chemists of the neutral and Entente nations. The chemists of the Entente Powers and of America have arisen to the emergency as no chemists have ever done before in the history of the world. Confronted at the beginning of the war by antagonists whose munitions industry for years had been developed for just such a contingency, these chemists have in less than two years built up a rival industry at least as strong. Plant after plant has sprung up of such perfection of design and operation that one wonders how the mind of man was capable of such engineering. Though the speed with which these new and unexpected problems have been solved may appear surprising, no one who is informed as to the progress and development of industrial chemistry in this country could have reason to doubt that American chemical engineers and industrial chemists would rise to any emergency which it was within human power to meet. They have already and will continue to live up to what we have a right to expect of them, in view of their past successes. We would be surprised if a similar degree of success did not crown the efforts of the chemists of the other countries, France, Britain, Italy, Germany, Austria and Russia; for it has never been the habit of American chemists to boastingly claim superiority because of any advantage, real or imaginary, with which they, like any group, are apt to be blessed for a greater or less period of time. We have always appreciated chemical contributions to progress from whatever source they have come and praised unstintingly the individual, wherever he may be, who has taken a distinct step forward, for we firmly believe this is an important help in advancing the progress of the science.

These general developments are naturally not a matter of public information, except when attention is called to them. The chemist works almost entirely beneath the surface of things, and only in a few spectacular cases is public attention drawn to



his work. It is quite natural, therefore, that appreciation and praise of foreign chemical achievement and particularly our consistent praise of German achievement to our students by our university teachers of chemistry have been misunderstood, and have prepared a fertile field for foreign propagandas to establish a false impression of the superiority of certain groups of foreign chemists. We would scarcely object to a good natured adulation of anyone's fatherland and its achievements. Such things always contain good and are stimulating to every one, and it is a pleasure to hear them when free from arrogance, even when the adulation contains little that is new or even strictly true. When, however, this privilege is abused so that the point of superiority must be made by depreciating American efforts it has a vicious, positive result upon the minds of the uninformed, and at times causes great financial loss to them.

If the shortcomings of American chemistry were frankly discussed and compared with foreign successes in a chemical publication, some help might be given to those who could derive benefit from it. When this is *not* frankly done, but simply issued as an incidental *depreciation* of American chemistry, particularly when discussing foreign chemical achievement, and still worse when in a non-chemical publication, the object can scarcely be rated as creditable.<sup>1</sup>

If the myth of the overwhelming industrial chemical superiority of German chemists ever was really believed in that country, the military forces of the Central Powers at least must marvel at the way the supposedly inferior foreign industrial chemists have displayed such astounding ability and speed in meeting the problems of munitions production, particularly, too, in countries where governmental mobilization of industries was unknown before the war and, in America at least, still is unknown. At any rate it has become evident that lack of self-advertisement is no sign of lack of ability or activity, and that ability to handle science skillfully and powerfully is not confined to any one race or nation. We do not feel that there is much to be gained by confuting claims of the chemical superiority of foreign countries in this and other similar articles, for it is curious how this war has developed farsightedness to the extent that some *Americans* can see only the chemical developments abroad.

I hope I have made it clear that it is the abuse of a privilege against which I speak, and not against individuals, for we do not let narrow-minded attacks affect our regard for individual Germans any more than we allow our opinions on the history of the past two years to affect this regard for such individuals. Everyone of us know Germans who are the most whole-souled and kindly men—who we are grateful to know and who scorn to be guilty of, or take advantage of, chauvinism. Depreciations of American efforts will bury themselves, without any assistance from us, and I emphasize them here only to call the attention of teachers of chemistry to the fact that we

owe protection to the business community and the public against such misrepresentation. We should never cease our appreciation of foreign chemists of whatever nation, but in addition it is our duty first to inform *ourselves* and then our students as to what our own chemists have done to solve our problems in this country. We have been able to blame our shirking this duty in the past upon the fact that it was easy to get information about foreign chemical achievement and no one seemed anxious to give publicity to American development. We, as teachers, have certainly done little to remedy this condition. The *American Chemical Society*, however, has spread the results of American efforts before us and made them accessible in its *JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY* for the last two years, in the shape of a series of addresses on the chemist's contributions to American industries. There are other addresses in these same volumes profoundly informing along these lines and this is particularly true of the Perkin Medal addresses each year in the same Journal. In addition, Professor S. P. Sadtler, in the *American Journal of Pharmacy*, for October, 1915 (an address before the National Exposition of Chemical Industries), in giving popular information along this line limits himself entirely to chemical industries *originated* as well as developed by the American chemist, and Edgar F. Smith's "History of Chemistry in America," but recently issued, should be read by every student of chemistry.

None of this work is in any sense a vain, glorious adulation of the chemist as some superbeing, nor is it an attempt to compete in the questionable game of lauding one nationality above another. It is merely a matter of a belated form of education which our universities and chemists hitherto have largely denied to the American business man, and which he has a right to expect of them. The record is one for which we have good reason to be thankful and, as we teachers no longer have the excuse of ignorance about American progress, we are at fault, if the rising generation has not an appreciation of the progress of chemistry in America, commensurate with the high level of its development.

In conclusion then, let us take courage from the fact that though much damage has been done to us and our industries by the war, our efforts at salvage benefit us as experience, power and preparedness. We have seen that the chemists of America have met the war situation well and do not require defense at the hands of anyone. It becomes increasingly evident that business has been awakened to the value of chemistry as a source of power and wealth as business has never had occasion or opportunity to be hitherto. Let us hope also that not only the spectators but also all the combatants may learn, even if impelled by bitter war's experience, to appreciate the worth, each of the other, and that all nations are "made of one blood to dwell on the face of the earth."

THE OHIO STATE UNIVERSITY, COLUMBUS

## CURRENT INDUSTRIAL NEWS

### A YEAR'S WORK IN FOREST SERVICE INDUSTRIAL INVESTIGATIONS

The annual report of the Office of Industrial Investigations of the Forest Service shows developments in its work of direct interest to the wood-using industries and consumers of forest products generally.

One new phase of this work is the formation of a wood waste exchange and the collection of detailed information regarding the supply of wood wastes and the demand for it. This information is made available in the form of specific quotations from *bona fide* buyers and sellers of waste who cooperate by supplying complete information regarding the exact form,

<sup>1</sup> Specific reference omitted by editor with consent of author.

species, sizes, and amounts of waste available or desired. Schedules requesting this information were sent to a number of wood-using establishments and a list was gradually built up. It now contains the names of several hundred manufacturers. Lists of opportunities to buy or sell waste are published every three months and sent to the various coöperators. Manufacturers have coöperated heartily and reports of sales are being received regularly.

A large amount of specific information has been made available to the public regarding the location of manufacturers, buyers, sellers, importers, and exporters of forest products. Detailed information has also been collected regarding the forms of raw material needed or available at various establishments

and the value of various products f. o. b. mill and at the principal markets. Records of lumber prices secured in cooperation with various lumber associations from mills throughout the United States were issued quarterly. Besides the records that have been issued in former years for the important woods in the principal producing regions, quarterly records were added for spruce and hemlock in West Virginia, New York, and New England, and for cedar poles in Minnesota and chestnut poles in the East. Information as to the conditions involved were obtained whenever possible. A directory of American sawmills was compiled in cooperation with the Department of Commerce, showing the kind of lumber cut by each mill, the forms and dimensions of its products, and the railroads over which the material is shipped.

In cooperation with the Bureau of Crop Estimates, statistics on the lumber production of the United States were collected and a report published covering the year 1913, which showed the production of nearly as much lumber in that year as in 1912. Steps were taken, in cooperation with the American Wood Preservers' Association, to secure for the coming year statistics on the number of poles and ties and the amount of various other kinds of forest products purchased by the principal railroad, telephone, and telegraph companies; and a report on the amount of wood preservatives used and the amount of timber treated in the United States in 1914 was published. Approximately 100 plants cooperated in supplying information regarding the amount of wood preservatives used, including practically all of the establishments of importance engaged in the industry.

Data were also compiled on the veneer, box, and cooperage industries. A preliminary report on the box industry was published in cooperation with the National Association of Box Manufacturers. This report furnished information of use to the industry, and to the Interstate Commerce Commission in their investigations of shipping containers. It was also made use of by the American Society for Testing Materials in working out standards for shipping containers.

The Office has also enlarged its activities in cooperation with various other branches of the Federal Government. The work has been chiefly the inspection of lumber, the revision of specifications, the furnishing of information regarding prices and the suitability of various woods for particular uses, the suggestion of better methods of handling and storing lumber, and the preparation of lists of bidders on various products. At the request of the Navy Department, a study was made of the methods of handling and piling lumber at various navy yards, and a report was prepared in which recommendations were made regarding the best means of preventing deterioration. A large amount of lumber was inspected for the Navy Department at various points east of the Mississippi. Generally the object of the inspection was to determine whether the shipment was up to the grade called for in the specification; but occasionally the Forest Service was called upon for the identification of species. Specifications for grading hickory handles were prepared and were adopted by the Navy Department, the War Department, and the Panama Canal. The Panama Canal used these specifications in the purchase of a large number of handles during the year. The specifications are coming more and more into commercial use, and eleven large railway systems have adopted them in one or more of their divisions.

A field study of southern pines in the Carolinas, Georgia, Florida, Alabama, Mississippi, Louisiana, Arkansas, and Missouri was conducted to determine the quality of wood grown in the various parts of the Southeast and the quality of lumber in the typical markets in the East and Middle West. The work resulted in the collection of data of immediate practical use in connection with the preparation of more satisfactory rules for grading structural timbers.

The reports on the wood-using industries of the various States were continued, and three new reports were published—Pennsylvania, New Jersey and Georgia. This makes a total of 33 State wood-using industry reports issued so far. Reports for Indiana and West Virginia were completed and placed in the hands of the publishers. Data on the wood-using industries of the remaining States have been collected. A final report on the wood-using industries of the United States is in preparation, in which combined data collected in the various studies will appear by species and by industries.

Many requests were received from the public for information regarding the most profitable uses of certain woods, the markets for them, the most satisfactory woods for certain uses, where they may be obtained, etc. Inquiries come from small sawmill owners, timber owners, and manufacturers of finished and semi-finished forest products. Through the wood-using industry studies the Office is well equipped to give such information. A large amount of utilization data is compiled monthly, including lists of wood-using establishments and specifications for raw material, and will be used for the benefit of lumbermen, woodlot owners, and the Forest Service cooperators throughout the United States.

In connection with the general lumber industry study now being carried on by the Forest Service, the Office of Industrial Investigations has studied the adaptation of grading and manufacturing to consumers' needs, particular attention being given to yellow pine and oak. Data were compiled also on the relative values of oak logs in lumber, veneer, cooperage, and ties.

#### NEW COAL FIELD

According to the *London Evening Post*, a Stavanger morning paper states that a Norwegian Company has been formed for the purpose of exploiting the extensive coal fields of Beeren Island, near Spitzbergen. Geologists and engineers, who have investigated the deposits, report that the quantity of coal obtainable is practically inexhaustible, while it seems to be of very good quality, its heating power being greater than that of ordinary British coal. Beeren Island is always accessible, so that export trade can be carried on during the whole year. It is expected that no difficulty will be experienced in finding good harbors.—McMILLAN.

#### TREATMENT FOR DISCOLORED CHINA CLAY

According to the *Dyer and Calico Printer*, the yellow discoloration of clay is due to presence of iron and, to remedy it, a blue coloring agent such as a soluble aniline dye is added. This neutralizes the yellow and makes the clay appear whiter. It has also been proposed to remove the iron altogether by chemical treatment. An entirely new method has been patented by Messrs. Feldheimer and Gee, London [B. P. 894 (1915)]. To nullify the discoloration, some of the clay is first washed to free it from impurities and to this is added a very dilute solution of ferrocyanide (less than 1 per cent) to produce sufficient prussian blue to neutralize the discoloration of the remainder of the clay.—M.

#### MINERAL RESOURCES OF CHINA

Iron ore can be found, according to an article in *Engineer* (121, No. 3142), in almost every province in China, but the working of the ore on an extensive scale has been carried out in only a few. The annual production of pig iron in Hupeh in the last two years was almost 160,000 tons, while the total amount produced in all the other provinces together was also about 160,000 tons. If up-to-date, thoroughly modern, methods of smelting were employed, the production of pig iron would be sufficient to supply the needs of the country and also to permit of large shipments being sent to foreign countries, especially Japan and the United States. Tin ore is found to some ex-



cent in China, the most important deposits being those of Yunnan, Kiangsi, Honan, Kweichow and Szechwan. The output of pure tin is about 1,000 tons without taking into account the considerable quantity of tin ore mined in other provinces.

Copper comes from the districts of Yunnan, Szechwan, Kium, Anhui, and Kansu, the annual production of pure copper being about 5,000 tons. China is the largest producer of antimony in the world, no less than 20,000 tons crude antimony, 1,000 tons refined antimony, and 15,000 tons of the ore being produced annually. The chief centers of the antimony industry are Hunan, Yunnan, and Kwantung.

Lead deposits are found in Hunan, Yunnan, Kwangsi, Szechwan and Kweichow, the annual production of ore being about 10,000 tons.—M.

### BRITISH ALCOHOL TRADE

According to the *Engineer*, it is authoritatively stated that the British Government has decided to take over all the patent-still distilleries. The requirements of strong spirits in connection with the manufacture of munitions are still under 15,000,000 gallons per annum, whereas the total output of patent-still distilleries is over 40,000,000 gallons. This output will, however, be substantially reduced by the curtailment of the imports of raw materials. The Government scheme was discussed at a meeting of the distillers of the United Kingdom in London recently, but the proceedings were not divulged. It is understood that nearly all the great distilleries have hitherto been making for the Government spirit at 60 per cent overproof for the manufacture of high explosives. The time has now been reached when it is felt that a larger supply and more expeditious production are urgently needed with the result that it is proposed to commandeer all the grain distilleries.—M.

### MINERAL RESOURCES OF GREAT BRITAIN

The British Board of Agriculture and Fisheries gives notice of the publication of three volumes containing special reports on the mineral resources of Great Britain. These reports have been specially prepared by the Director of the Geological Survey in response to numerous inquiries that have arisen through the conditions brought about by the war. In Vol. I, the uses, distribution, treatment and output of tungsten and manganese ores are dealt with and particulars of mines, active and inactive, are given. Vol. II deals with the sources, uses, and treatment of barytes and witherite, the sulfate and carbonate of barium. The mines, from which the minerals are raised, are described in full. Vol. III gives a description of the properties, uses, treatment and modes of occurrence of gypsum, anhydrite, celestine and strontianite. Details of the workings in all parts of Great Britain are given with statistics as to output. The price of Vols. I and III is 24 cents, and Vol. II, 36 cents.—M.

### LATEST COKE RECOVERY PLANT INSTALLATIONS

A very complete and modern plant, says *Chemical News* (113, No. 2939), has been installed at Normanby Park Steelworks, Yorkshire, England, for the making of coke, tar, ammonia and benzol. The buildings are of ferro-concrete on the Monchel-Hennebique system and, in addition to an immense washing apparatus, two batteries of 48 generative coke ovens of the Semet-Solvay type, capable of dealing with 3,000 tons of coal per week have been installed. The power for the working of the plant is supplied by gas engines which use up the blast furnace gases. The main washery building is 65 ft. long by 40 ft. wide, two-thirds of it being 77 ft. high, while the remainder rises in the form of a tower 94 ft. high and is surmounted by a huge ferro-concrete tank capable of holding 62,000 gallons. The coking ovens are supplied with washed coal at any required rate up to 100 tons per hour by means of conveyor bands

connected by a runway under which charging machines receive and stamp the slack into compression boxes. Each of the 96 ovens carbonizes 50 tons washed coal per week. The coke is pushed out through the quenchers to an inclined hearth over which it passes to 36 in. tray conveyors which deliver the product to the central screening machine and thence to the blast furnaces. The gases from the ovens are collected into a large main and exhausted through air and water condensers, thence passing through the extractors and scrubbing washers for the absorption of benzol and remaining ammonia. After this treatment the gases are utilized, one-half for heating the flues in the coke ovens, the other half in the steelworks. The tar-ammonia liquor and benzol extracted from the gases are treated in buildings situated between the coal washery and the batteries of coke ovens.—M.

### MALAY STATE WOLFRAM

Reports show that the output last year was 3,940 pikuls (1 pikul = 142.7 lbs.), compared with 3,898 pikuls for the previous year. The chief producer was the Titi Mines Company, which had a yield of 1,199 pikuls. The market price in London was 55/- per unit, but to producers abroad the price was lower, thus, in Melbourne and Sydney, it was 48/1 per unit. A company recently was formed in Melbourne with a capital of £50,000, called the King Island Scheelite Company, for the purpose of treating deposits there. The assay value of the ore is equal to 2.34 tungstic acid.—M.

### RUSSIAN TRADE

The British Vice-Consul at Ekaterinburg reports that, in Ural mining works, a great dearth of machinery is beginning to be felt, and fears are being expressed whether the allied powers will be able to supply the enormous quantity formerly supplied by the Germans. Not to mention new enterprises, machinery at present in use, owing to the difficulty of repairing parts, will likely be run out so that all current business will in all probability require new machinery after the war. The demand for catalogues and specifications in the Russian language has never been so great as at present. Russian buyers are eager to find where reliable information can be had as to where their requirements can be obtained. Great preparations should be made by firms anxious to get a share of the Russian trade after the war. Travellers with a knowledge of the Russian language and technical knowledge of machinery should be sent to the Ural mining district, where the Russians will be glad to give them every assistance.—M.

### THE USE OF POLARIZED LIGHT IN ENGINEERING TESTS

Some interesting and highly important revelations were made by Prof. E. C. Coker in a lecture given before the Royal Institute, London. Recent researches show that polarized light can be made use of in such practical matters as bridge building and aeroplane construction. The stresses and strains in a great bridge and in the different parts of air craft are very hard to work out. The calculations can, however, be simplified if a model be made of transparent material and the strains watched by polarized light. The lecturer showed how a bridge intended to be thrown over a gorge, was first made of glass. Polarized light was passed through every part and in analysis each stress was shown by the colors which different parts assumed. Full brown color indicated 1,000 lbs. per sq. in., while a brilliant red showed enormous pressure. It was found that glass and glass-working were too costly for making models, and xylonite, which could be moulded into any shape, was afterwards selected. Polarized light, if sent through under normal conditions, gives no colors but, if the slightest bend or strain is applied, color effects are produced. Prof. Coker

showed on the screen series of the links of aeroplanes made from xylonite models; the change of color could be watched to indicate how strains affected them. This new method of testing the designs of structures would seem to have a great future.—M.

# POTASH FROM OLIVE OIL RESIDUES

From analytical results published in *L'Italia Agricola* by A. Aita, olive oil residues (the blackish turbid liquid deposited at bottom of sink under oil presses) contained the following:

	Per cent
Soluble in water.....	13.57
Alkaline chlorides.....	1.57
Iron oxide (FeO).....	1.34
Carbon dioxide (CO <sub>2</sub> ).....	1.87
Insoluble in water.....	1.05

The amount of potash in the liquid is given as about 1.5 per cent or slightly more. By the evaporation and combustion of 100 gals. of this residue from 30 to 35 lbs. of ash were recovered. The volume of the liquid is double that of the olive oil produced. If the average yearly production of olive oil in Italy is estimated at 44,000,000 gals., it is calculated that 15,000 tons ash can be recovered from the liquid residuum and the value of this exceeds \$400,000. A Commission has been formed to consider the possibility of utilizing this residuum for the manufacture of potash salts. The Commission informed the *Associazione chimica industriali* of Turin that the process was simple and the expenses of concentrating in ordinary triple action apparatus were not greater than 10 cents per 100 gals., reckoning fuel at about \$6 per ton. The nitrogen content in olive oil residuum is equal to about one-third the potash content and, therefore, of great value. It would be, perhaps, advisable to secure both the nitrogen and the potash by adopting a method other than the incineration one.—M.

# MINING IN MADAGASCAR

According to the *Mining World*, Madagascar seems to be rich in mineral deposits. In addition to gold, which is found in alluvial deposits widely spread over the island, ores of antimony, copper, iron and tin are stated to be in abundance, to say nothing of asphalt, coal, graphite, mica, platinum, precious stones and petroleum. No coal developments have taken place of late in the coal-bearing area discovered in the southern province of Betroka, but a concession for working copper near Ambositra has been granted and also one for working nickel. Alluvial gold deposits have been found in the valley of the Ampasary, a tributary of the Mananjary River about 40 miles east of the town of Ambositra and in the district of Maevatanana. About 5,000 natives are employed in washing auriferous gravel in pans. The production of fine gold for 1912 amounted to only 2,120 kilograms, which showed a decrease of 730 kilograms on the previous year, the decrease being mainly due to the difficulty of obtaining labor in the principal mining districts. Graphite is worked chiefly in the neighborhood of Tananarive and is found disseminated in the form of spangles interstratified in the gneiss and appears to occupy the place of mica. It is easily separated from the gneiss by hand washing. Prospecting for graphite is engaging the attention of many prospectors in Madagascar at the present time. Galena is found at Ankitokazo in the northern province of Diego-Suarez. No work is at present being done in petroleum claims. Small quantities of platinum are being obtained in the province of Vatomandry. The principal workings for precious stones are those of Mount Ibity and of the river Manandona, near Antsirabé.—M.

# EFFECT OF SULFATES ON CROPS

Certain plants, says the *Pharmaceutical Journal*, seem to be benefited by treatment with sulfates, but others show less response to sulfates than to phosphates. Plants belonging to

*Cruciferae* and *Leguminosae* are most favorably affected by treatment with calcium sulfate although the latter appears to stimulate seed production in cereals such as barley and oats, but to have little or no effect on the straw. In the case of clover, the increase of air-dry content due to calcium sulfate was 23 per cent, while with rape, calcium sulfate mixed with complete fertilizer, gave a crop of 17 per cent heavier than with complete fertilizer alone; with radishes, the increase in crop under the same conditions was 9 per cent. The root development of red clover and rape showed a marked increase under the influence of calcium sulfate dressing. Free sulfur is harmful, even in large supplies of calcium carbonate.—M.

# UNITED KINGDOM IMPORT DUTIES

The following list gives the import duties on items of interest to the chemical trade, in accordance with a general order of the Board of Customs and Excise. The tariff quoted in the "Return" is that in operation on January 1, 1916:

ARTICLES	IMPORT DUTIES		Rates of duty	
	£	s d		
Chloral hydrate, per lb.....	1	9		\$0.42
Chloroform, per lb.....	4	4		1.04
Collodion, per gal.....	1 14	11		8.38
Ether, acetic, per lb.....	2	7		0.62
Ether, butyric, per gal.....	1	10		5.04
Ether, sulfuric, per gal.....	1 16	6		8.76
Ethyl bromide, per lb.....	1	5		0.34
Ethyl chloride, per gal.....	1 1	10		5.04
Ethyl iodide, per gal.....	19	0		4.56
Glucose, solid, per cwt.....	5	11		1.42
Glucose, liquid, per cwt.....	4	3		1.02
Motor spirit (a), per gal.....		6		0.12
Saccharin (b) and mixtures containing saccharin or other substances of like action—per oz.....	3			0.72
Soap, transparent, in manufacture of which spirit has been used—per lb.....		3		0.06

(a) In cases where Commissioners of Customs and Excise may approve, motor spirit may be delivered without payment of duty or in payment of half duty.

(b) This substance not to be imported in packages containing less than 11 lbs, must not be packed with goods of any other description and must be specially reported and imported and entered for warehousing at following ports only: Dover, Folkstone, Goole, Grangemouth, Grimsby, Harwich, Hull, Leith, London, Newhaven, Southampton, West Hartlepool.

—M.

# BRITISH BOARD OF TRADE

During the month of March, the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles. Firms which may be able to supply information regarding these things are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall Street, London, E. C.:

Aeroplane fittings	Machinery for shaping vulcanite and galalith rods in cigarette holders
Alloy, ignition for pocket lighters	Machinery for automatically filling sacks and tin boxes
Bottles, gum	Mining plant for output of 300 tons per day of 15 per cent pure NaNO <sub>3</sub> including complete railway equipment, stationary engines, etc
Cane, wanganhee	Masks, dolls, papier maché, faced with silk
Charcoal, stick and lump	Nails, wire, for butter boxes
CHEMICALS:	Neuberg chalk, substitute for metal polish
Acid phosphate of sodium and ammonium	Needles, pearl, machine
Acetic acid, 60 per cent	Paste, soldering, noncorrosive
Bleaching powder	Pith, finely ground
Lactic acid, 50 per cent	Precious stones, agate, onyx, lapis, jade
Potassium permanganate	Rollers, hard tungsten steel
Sulfuric acid	Rollers, for rolling mills, tempered steel
Phosphate for self-raising flour	Straps, chin, rubber
Potassium nitrate	Studs, collar, metal
Sodium bromide	Screws, iron
Catches, silver and nickel-silver for purses	Silk, artificial, 1,000 lbs. required
Celluloid beads	Slide rules
Celluloid caps for pomade pots	Teats, rubber, on cards
Celluloid watch covers	Trunks, metal, for export
Cylinders, mining, rustless	Tortoise shell, real and imitation
Cutlery, rustless, stainless	Vacuum flasks, cheap
Engines, detachable for rowboats	
Hoop-iron, 1/2 in. by 30 gauge	
Hoop-iron, 3/4 in. by 26 gauge	
Hydrogen gas plant, "Linde" system	
Iron clamps, small, cheap	
Jet, raw, for making cigarette holders	
Lifting jacks, screw	

A firm in Brazil is making inquiries regarding sources of supply of the following chemicals, formerly imported from Germany:



Chloride of lime; acetic acid; alum; sodium sulfide; Glauber salt (acidulated); also crystal, Epsom salts; sodium nitrate, aluminum sulfate; dextrin and potato starch. Firms supplying these may apply to Board of Trade, London, reference number [85] should be quoted.—M.

#### UTILIZATION OF PEAT

The economical utilization of peat in the generation of gaseous fuel even with the recovery of the by-products is said to be to-day, an accomplished fact. The tar, on distillation, according to work described in the *Journal of Society of Chemical Industry* [35 (1916), 247], gives neutral oils differing from those obtained from coal tar and from the paraffins by being highly unsaturated. This is shown by the rapidity with which they absorb atmospheric oxygen. When extracted with alkaline solutions, substances with high boiling points and powerful germicidal activity are removed. These oils are sparingly soluble in water but may be used in suspension or emulsified by soap solutions or, as solid disinfectants, when mixed with hard soap, dextrin or similar substances. Small quantities of pyridine bases occur in the crude peat tar oil. The higher fractions of the neutral oils are waxes and resemble montan wax lignite. The residue from distillation of peat tar is a typical soft pitch, suitable for use as asphalt, caulking or electrical insulation.—M.

#### SELENIUM

In a series of articles published in the February numbers of the *Electrician*, W. K. Cooper has given an account of the properties of selenium which will prove of value to any who may be interested in the technical applications of the sensitiveness to light which the substance exhibits. Such information had, previous to the appearance of the above papers, to be sought for in the scientific journals published in all parts of the world, a task sometimes by no means easy. This is now available in a compact and readable form. An account is first given of the various forms of selenium with the modes of preparation. Their sensitiveness to light in general and to the variations of the wave length of the light is then discussed and, although no general theory has been deduced from the experimental facts at hand, sufficient information is available to indicate that, before long, it will be more intensively used than at present, when its use is mainly restricted to the automatic lighting of isolated buoys at sea.—M.

#### NICKEL

From official papers given to the Canadian Parliament, says the *Mining Journal*, it appears that the International Nickel Corporation has agreed to a request from the government and will erect in the Dominion at such point as seems in their judgment most economical for operation, a plant for refining nickel of such initial capacity as will secure to Great Britain and Canada within themselves, a supply sufficient for their requirements. The company is reported to have just concluded a contract with Great Britain for a large tonnage of nickel equal to 20 per cent of the production to be delivered in monthly instalments over one year.—M.

#### MINING DEVICE

A device has recently been patented intended to indicate the slightest movement of ground, when adjusted in stope or tunnel, and thus to give warning of impending falls of roofs. Instant intimation is given to a watchman or to the mine manager's office by completion of a circuit through the instrument. The ringing of a bell and the showing of a red light in the device itself may serve where it is near the miners. The Mining

Commissioners in the South African gold mines and also in Australia state that there is need for such an instrument and, in the latter country, legislation for its use in dangerous mines is about to be made.—M.

#### OIL PROPERTIES IN GUATEMALA

The government of Guatemala is said to have taken measures to retain exclusive right of the oil deposits of the Republic. A recent presidential decree specifies that oil and hydrocarbons may be acquired or worked in no other way than by lease from the government for terms of not more than 10 years and such leases can be made only by native or naturalized residents of Guatemala. Special regulations give terms in which oil fields may be purchased.—M.

#### PHOSPHATES FROM PACIFIC ISLANDS

In a bulletin from the Imperial Institute, London, it would appear that phosphate is the chief mineral product of the German Pacific Colonies. Nauru and Ocean Island of the Marshall group are estimated to contain not less than 50,000,000 tons phosphate rock, while Angaur Island, in the Pelew group, is supposed to contain 2,500,000 tons phosphatic deposit. The total exports of phosphate from Nauru and Angaur in 1912, which went principally to Australia, New Zealand and Japan, were valued at a quarter of a million sterling.—M.

#### NEW PROJECTS IN SPAIN

It is rumored that there will shortly be formed a subsidiary company of the *Compañía Minera de Sierra Menera* with a capital of 20 million pesetas for the establishment of blast furnaces in Sagunto, also, that the *Real Compañía Asturiana* is to lay down at Arnao another large zinc plant but fitted for treating blende.—M.

#### TEMPERING OF STEEL

According to the *Gas World*, gas has come into use in France as a means of heating-up tools of "rapid steel" (chrome-tungsten steel) for the purpose of tempering them. The temperature required is 1000° C. (1,832° F.) and the tool is plunged in a bath of fused caustic soda. The material being rather fragile, any defects in tempering shorten the life of the tool but it is found that with gas tempering the life of the tool is fully twice as long as that of a similar tool tempered with a coke or oil fire.—M.

#### SCIENTIFIC RESEARCH IN AUSTRALIA

Mr. Hughes, the Prime Minister of Australia, who is at present on a visit to England, outlined a scheme for the establishment of an organization for scientific research in Australia, in a recent speech delivered in London. He mentioned the following, especially, as questions for immediate study: The recovery of lanoline and potash salts in the "dross" thrown away after wool-scouring; the cultivation of beet for sugar; the development of fisheries; the improvement of gold recovery and other metallurgical problems; the extraction of valuable oils and resins from negative plants; afforestation and the systematic investigation of diseases affecting stock.—M.

#### SALT MINES IN VENEZUELA

The lease of the Venezuelan salt mines by the River and Coast Navigation Company having expired on December 31, 1915, and no application for another lease having been received in response to a call in November last, the government of Venezuela took over the direct administration of the salt mines on January 1, 1916, in accordance with a presidential decree.—M.

## SCIENTIFIC SOCIETIES

### LAYING OF THE CORNER STONE OF THE CHEMISTRY BUILDING OF THE BUREAU OF STANDARDS, WASHINGTON

On March 23, 1916, the corner stone of the new chemistry building of the Bureau of Standards, at Washington, D. C., was laid by the Hon. William C. Redfield, Secretary of Commerce. The building is about 60 X 200 ft., constructed of brick and stone, and is to be four stories in height, in addition to attic and basement. It will provide adequate laboratory space for about 120 chemists, besides rooms for offices, supplies, etc. It will probably be ready for occupancy early in the spring of 1917.

In his opening remarks, Dr. S. W. Stratton, director of the Bureau of Standards, sketched the early history of the Bureau and the circumstances leading to the selection of the present site, and to the erection of the various buildings, of which the new chemistry building is the seventh. In discussing the work of the chemistry division, he said:

"It can safely be stated that the Bureau of Standards has led all other institutions of its kind in the association of chemis-

render her secrets. They are extracted from her by toil, and of the toilers who draw them forth it may be said with truth, 'to him that hath shall be given and he shall have abundance.' Such work is the triumph of the spirit of man and of the mind of man over material things. The progress that has been made seems slow when measured in its daily march, yet if we look back far enough to get a due perspective we can see that the road that has been traveled is long. It has not been an easy road. It has been conquered step by step. We have had to build the ladders by which we climbed and to mount to our present knowledge round by round. There has gone much of human patience, much of struggle, much of unselfishness, much of enthusiasm for truth for its own sake, into the winning of the way that has thus far been won. A great thinker has said, 'The Universe is plastic in the hands of man in proportion as he brings the power of the Creator to bear upon it.' The work which wins has always a spiritual value. Moral impotence does not achieve permanent successes. The seeker after truth must, in the main, himself be true, else are his conquests limited. \* \* \* \* \*

"So the best of mind and heart and spirit are united here both as we look toward the past and forward into the future. Who knows what shall be when this building shall have wrought its perfect and finished work and made way in its turn to its successor? Thus much we can say of that time, that the things



LAYING THE CORNER STONE OF THE NEW CHEMISTRY BUILDING OF THE BUREAU OF STANDARDS, WASHINGTON

try with physics and engineering in the solution of problems arising in connection with standards and standardization. By this gathering together the chemical work of the Bureau in a single building equipped with apparatus and utilities peculiar to chemical work, the work of the chemical division will be greatly facilitated. It is hoped that this concentration of the chemical work will not prevent the segregation of its application to the various fields of the Bureau's activities—for the Bureau's success in all lines will ever depend upon the close coordination of chemistry, physics, and engineering."

In his address, the Secretary of Commerce, in speaking of the work of the Bureau of Standards, said:

"I have often thought of this service as one which pushes back more and more each day the shades of darkness which limit our present knowledge. Nature does not readily sur-

that then shall be will be based upon the work that is here to be wrought out. The foundations of our present knowledge were laid by the great investigators of the past. On them you are here to build that which in its turn shall sustain the structure of the future. Let us hope that the chemists of a future day shall find their work for mankind more effective and their efforts in that work more inspired by what is here to be done."

After the corner stone was laid by the Secretary of Commerce, Dr. W. F. Hillebrand, chief chemist of the Bureau, first referred to his early associations with government chemical work, in the Denver laboratory of the Geological Survey, and then said:

"What the dim future may have in store in the way of successors or additions to the structure we are now dedicating,



each one may try to picture for himself, but there is no doubt in my own mind that this future foreshadows credit for the Bureau and the chemical profession if we and our successors hold fast to the guiding principles that have been established already—seriousness of purpose, never-ending study, open-mindedness, largest willingness and intention to cooperate, accuracy in work, and entire honesty and fairness in presenting the results of that work."

He then read a list of the articles enclosed in the copper box, which had been hermetically sealed and deposited in the corner stone. This list included photographs of the personnel, with autographic signatures, various reports and publications showing the Bureau activities, especially of the chemistry division, a few standard analyzed samples, specimens of paper, written upon in ink (included to test their lasting qualities), and also a bottle of lime to absorb moisture.

In conclusion, Dr. Hillebrand paid tribute to the interest and cooperation of the Secretary of Commerce, the director of the Bureau, the building committee, the engineer of the Bureau, and the architects who designed the building.

## ORGANIZATION FOR INDUSTRIAL PREPAREDNESS

To the Members of the American Chemical Society:

Complying with President Wilson's request of January 13, 1916, published in the February number of THIS JOURNAL, the following members of our Society have been appointed representatives on the State boards of the Organization for Industrial Preparedness:

B. B. ROSS	Alabama	W. L. HOWELL	Louisiana
	Auburn, Ala.	Room 315, Custom House	New Orleans, La.
W. P. LASS	Alaska	R. H. MCKEE	Maine
	c/o Speer River Project		Orono, Me.
F. N. GUILD	Arizona	W. B. D. PENNIMAN	Maryland
	Tucson, Arizona	6 E. Franklin Street	Baltimore, Md.
J. B. RATHER	Arkansas	A. D. LITTLE	Massachusetts
	Agric. Expt. Station	93 Broad Street	Boston, Mass.
EDMUND O'NEILL	California	H. T. GRABER	Michigan
	Univ. of California	697 Trumbull Avenue	Detroit, Mich.
R. B. MOORE	Colorado	G. B. FRANKFORTH	Minnesota
	502 Foster Building	Univ. of Minnesota	Minneapolis, Minn.
E. W. MORLEY	Connecticut	W. F. HAND	Mississippi
	West Hartford, Conn.		Agricultural College, Miss.
CHARLES L. REESE	Delaware	L. F. NICKELL	Missouri
	Box 424, Chester, Pa.		Washington University
CHARLES L. PARSONS	District of Columbia		St. Louis, Mo.
	Box 505, Washington, D. C.	E. P. MATHEWSON	Montana
			Anaconda, Mon.
E. R. FLINT	Florida	C. F. CROWLEY	Nebraska
	Gainesville, Fla.	3315 Burt Street	Omaha, Neb.
F. N. SMALLEY	Georgia	MAXWELL ADAMS	Nevada
	R. F. D. 2, Box 20		University of Nevada
	Savannah, Ga.		Reno, Nev.
J. S. JONES	Idaho		New Hampshire
	Agric. Expt. Station	H. K. MOORE	New Jersey
	Moscow, Idaho		Box 165, Berlin, N. H.
WILLIAM HOSKINS	Illinois	H. S. MINER	New Mexico
	2009 W. Monroe Street		Wellsbach Light Company
	Chicago, Ill.		Gloucester City, N. J.
H. E. BARNARD	Indiana	J. D. CLARK	New Mexico
	State Laboratory of Hygiene		Univ. of New Mexico
	Indianapolis, Ind.		Albuquerque, N. M.
W. F. COOVER	Iowa	T. B. WAGNER	New York
	Iowa State College		17 Battery Place
	Ames, Iowa		New York, N. Y.
W. A. WHITAKER	Kansas	F. P. VENABLE	North Carolina
	University of Kansas		Chapel Hill, N. C.
	Lawrence, Kan.		North Dakota
A. M. BRECKLER	Kentucky	E. F. LADD	North Dakota
	1801 First Street		Agricultural College
	Louisville, Ky.		Fargo, N. D.

I. R. WITHEROW	Ohio	G. W. GRAY	Utah
	Ohio State University		The Texas Company
	Columbus, Ohio		Houston, Tex.
EDWIN DEBEVER	Oklahoma	W. C. BRADSHAW	Utah
	Norman, Okla.		908 Douglas Street
O. F. STAFFORD	Oregon	G. W. BURROWS	Vermont
	Eugene, Ore.		299 S. Union Street
R. F. BACON	Pennsylvania	F. B. CARPENTER	Virginia
	Univ. of Pittsburgh		Virginia Carolina Chem. Co.
	Pittsburgh, Pa.		Richmond, Va.
J. B. BECHER	Rhode Island	H. K. BRESSON	Washington
	Brown University		Univ. of Washington
	Providence, R. I.		Seattle, Wash.
R. N. BRACKETT	South Carolina	A. R. WHITEHILL	West Virginia
	Clemson College, S. C.		Box 394, Morgantown, W. Va.
W. J. SHAWWOOD	South Dakota	C. F. BURGESS	Wisconsin
	Lead, S. D.		625 Williamson Street
J. F. NORRIS	Tennessee		Madison, Wis.
	Vanderbilt University	R. B. MOODY	Wyoming
	Nashville, Tenn.		Laramie, Wyoming

The work of this organization is about to begin. The details have been thoroughly prepared. It is extremely desirable that the work should be promptly completed. To accomplish this the earnest cooperation of each member of the Society with his state representative is absolutely necessary. With the work distributed among our nearly 8,000 members the burden should not prove unduly onerous upon any individual member.

I feel it is unnecessary to make any special plea for loyal effort in this patriotic service.

CHARLES H. HERTY

President American Chemical Society

CHAPEL HILL, N. C.  
March 25, 1916

## FIFTY-SECOND MEETING AMERICAN CHEMICAL SOCIETY, URBANA-CHAMPAIGN, ILLINOIS APRIL 18 TO 21, 1916

### PROGRAM OF PAPERS

#### GENERAL PROGRAM

Address of Welcome. EDMUND J. JAMES, President of University of Illinois.

Response. CHARLES HOLMES HERTY, President of American Chemical Society.

General Addresses: The Composition of Corn as Affected by Nineteen Generations of Seed Selection. L. H. SMITH

The Manufacture of Chemical Apparatus in the United States. ARTHUR H. THOMAS. (See THIS JOURNAL, 8 (1916), 437.)

The War and the American Chemical Industry. RAYMOND F. BACON.

On the Influence Exerted by Electrolytes on the Equilibrium of Emulsions, Jellies, and Living Cells. G. H. A. CLOWES  
Some Effects of High Pressures. JOHN JOHNSTON.

University Convocation and Dedication Exercises. HON. EDWARD F. DUNNE, Governor of Illinois, presiding. Addresses: PRES. EDMUND J. JAMES, University of Illinois; PROF. ALEXANDER SMITH, Columbia University; DR. W. R. WHITNEY, General Electric Company, and member of the United States Naval Board.

Public Lectures: Production of Radium. CHARLES L. PARSONS  
Use of Radium in Treatment of Cancer. CURTIS F. BURNAM

#### AGRICULTURAL AND FOOD CHEMISTRY DIVISION

L. M. TOLMAN, Chairman GLEN F. MASON, Secretary

#### Chemist in Food Control

##### A. Manufacturing Standpoint:

1. Cattle Foods. CARL S. MINER.
2. Starch and Glucose. A. P. BRYANT.
3. Canning. W. D. BIGELOW.
4. Gelatine. J. R. POWELL.
5. Flour. HARRY SNYDER.
6. Salt Purification. W. W. SKINNER.
7. Flavoring Extracts. GEORGE LLOYD.
8. General. W. M. HOSKINS.

##### B. Distributing Standpoint:

9. General Foods. A. V. H. MORY.

##### C. Law Enforcement Standpoint:

10. City. LUCIUS P. BROWN.
11. State. DAVID KLEIN.
12. National. L. M. TOLMAN.

## Food Investigations

13. Preventing the Staling of Bread by Cooling in a Predetermined Atmosphere. ARNOLD WAHL
14. The Use of Picric Acid in Meat Sugar Solutions. W. B. SMITH
15. Analysis of Maple Products. VIII. J. F. SNELL.
16. Chinese Preserved Eggs. PIDAN. CHI CHE WONG AND KATHERINE BLUNT.
17. A Study of American Beers to Show the Effects on Their Composition of Various Raw Materials Used in Their Production. L. M. TOLMAN AND J. G. RILEY.

## Agricultural Chemistry

18. The Effects of Plant Foods upon the Amount and Quality of Substances Used for Foods, Particularly Fruit and Vegetables. H. A. HUSTON.
19. Does the Oxidation of Tetrathionate to Sulfate Affect the Accuracy of the Estimation of Thiosulfate by Means of Iodine? P. L. BLUMENTHAL AND S. D. AVERITT.
20. Separation and Estimation of Polysulfides and Thiosulfate in Lime-Sulfur Solutions. S. D. AVERITT.
21. Some Studies on Liquid Fertilizer. G. D. BEAL AND D. T. ENGLIS.
22. The Detection of Lime Used as a Neutralizer in Dairy Products. H. J. WICHMAN.

## BIOLOGICAL CHEMISTRY DIVISION

C. L. ALSBERG, *Chairman* I. K. PHELPS, *Secretary*

1. On the Formation of Soap Jellies and the Process of Blood Coagulation. C. H. A. CLOWES.
2. The So-Called Caseinates. W. D. BANCROFT.
3. Action of Rennin on Casein. W. D. BANCROFT.
4. On Electrolyte Antagonisms in Physical and Biological Systems. C. H. A. CLOWES.
5. On Anesthesia. G. H. A. CLOWES.
6. Further Observations on the Surface Tension of Saponin Solutions. C. L. ALSBERG AND H. E. WOODWARD.
7. Relative Sensitivity of Some Commercial Litmus Papers. A. VIEHOEVER AND C. O. EWING.
8. The Aeration Method for Total Nitrogen Determinations. R. S. POTTER AND R. S. SNYDER.
9. Titrimetric Determination of Nitrite N. B. S. DAVISSON.
10. Determination of Ammonia by Aeration. B. S. DAVISSON.
11. Investigation of the Kjeldahl Method for Determining Nitrogen. A New Aeration Apparatus. I. K. PHELPS AND H. W. DAUDT.
12. Remarks on the Physical and Biological Chemistry of Fat. MARTIN H. FISCHER.
13. Mutarotation of Gelatine and Its Significance in Gelation. C. R. SMITH.
14. Studies upon the Effects of Acids on the Swelling of Certain Colloids. A. D. HIRSCHFELDER.
15. Brain Lipids as a Haemostatic. A. D. HIRSCHFELDER.
16. The Pharmacological Action of Citrates. R. A. HALL AND R. E. MORRIS.
17. The Fate of Methylene Disalicylic Acid and Derivatives in the Body. R. A. HALL AND E. D. BROWN.
18. The Role of Cystine in the Maintenance of Nitrogenous Equilibrium in Dogs on a Low Protein Diet. H. B. LEWIS.
19. The Excretion of Uric Acid after Ingestion of Sodium Benzoate in Man. H. B. LEWIS AND W. G. KARR.
20. A Comparative Study of the Urea Content of the Blood and Tissues of Some Vertebrates. W. G. KARR AND H. B. LEWIS.
21. On the Esterification of Amino Acids. H. A. SHONLE AND H. H. MITCHELL.
22. Feeding Experiments on the Nutritive Value of Casein. E. M. K. GEILING AND H. H. MITCHELL.
23. On the Determination of the Digestibility of the Constituents of a Mixed Diet. H. H. MITCHELL AND H. S. GRINDLEY.
24. The Hydrogen Electropotentials of Phthalate, Phosphate, and Borate Buffer Mixtures. W. M. CLARK AND H. A. LUBS.
25. Chemical Studies on the Decomposition of Red Oak by *Fomes applanatus* and of Red Spruce by *Trametes pini* var. *abietis*. E. J. PIPER, C. J. HUMPHREY AND S. F. ACREE.
26. Some Observations on the Bacterial Metabolism of Sulfur Compounds. F. W. TANNER.
27. A Colorimetric Method of Estimating Amylolytic Activity. V. C. MYERS.
28. The Colorimetric Determination of Glucose, Sucrose, Dextrin, and Starch in Food Stuffs. V. C. MYERS AND A. R. ROSE.
29. On the Citric Acid Production of *Aspergillus niger*. J. N. CURRIE.
30. The Equation of Fermentation of Glucose by *Bacillus coli communis*. O. KAMM.
31. The Liberation of Ammonia from Ammonium Salts by *B. coli communis*. R. BENGIS AND A. R. ROSE.
32. The Change in Urinary Constituents Following the Feeding of *B. coli communis*. A. KNUDSON AND A. R. ROSE.
33. A Study of the Etheral Sulfates of the Urine in Certain Chronic Diseases. J. ROSENBLUM.

34. The Ammonia Content of Human Gastric Juice. J. ROSENBLUM AND JENA MILTAN.
35. Some Autoamylases. E. W. ROCKWOOD.
36. A Chemical and Bacteriological Study of Some Non-Pathological Gastric Residuums. C. C. FOWLER, M. LEVINE AND S. B. MORE.
37. A Study of Eighty Samples of Gastric Residuums Obtained from Apparently Normal Women. C. C. FOWLER AND Z. ZENTMIRE.
38. The Preparation of a Synthetic Milk for Use in Infant Metabolism Studies. A. W. BOSWORTH.
39. Concerning the Utilization of Inositol in the Animal Organism. The Effect of Inositol upon the Metabolism of Man. R. J. ANDERSON AND A. W. BOSWORTH.
40. Concerning the Utilization of Inositol in the Animal Organism. In the Dog. R. J. ANDERSON.
41. The Analysis of Urine as a Part of the Physical Examination of the College Man. G. O. HIGLEY.
42. The Non-Protein Constituents of Foods and Feeding Stuffs. H. S. GRINDLEY AND H. C. ECKSTEIN.
43. Swine Feeding Experiments to Determine the Nutritive Value of the Amino Acids. J. C. ROSS.
44. Chemical Methods in Diagnosis. I. Renal Function. L. J. DESHA.
45. Contributions of the Chemist to the Science and Art of Medicine. L. J. DESHA.
46. The Reaction of the Pancreas and Other Organs. J. H. LONG AND F. FENGER.
47. The Chemical Aspect of Photosynthesis in Plants. H. A. SPOERH.
48. The Growth of Isolated Plant Embryos. G. D. BUCKNER AND J. H. KASTLE.
49. Plant Immuno-Chemistry. R. W. THATCHER.
50. The Presence and Origin of Volatile Fatty Acids in Soils. E. H. WALTERS.
51. The Organic Phosphorus of Soil. R. S. POTTER AND T. H. BENTON.
52. The Changes in the Amino Acid Nitrogen and "Soluble Non-Protein Nitrogen" in Heated Soils. R. S. POTTER AND R. S. SNYDER.
53. Studies on the Distribution of Nitrogen in Egg Lecithin. M. L. FOSTER.
54. The Nitrogen Distribution in Certain Seeds. C. L. ALSBERG AND F. BREWSTER.
55. Oxalic Acid and Its Salts in Foods and Spices. A. VIEHOEVER AND J. P. CLEVERING.
56. On Some Proteins from the Jack Bean, *Canavalia ensiformis*. C. O. JOHNS AND D. B. JONES.
57. On an Alcohol-Soluble Protein from Kafir Corn, *Andropogon sorghum*. C. O. JOHNS AND D. B. JONES.
58. A Synthesis of Tetracarbinimid. D. E. WORRALL AND M. K. McNAMARA.

## Special Program for Home Economics

59. Diet in Its Relation to the Treatment of Diabetes. E. E. BUTTERFIELD.
60. A Study of Carbohydrates as Milk Modifiers. RUTH WHEELER.
61. The Occurrence of Creatin in the Urine of Children. LOUISE STANLEY.
62. The Relation of a Diet High in Calcium to the Calcium Content of the Tissues. AMY L. DANIELS.
63. Phospholipins, Lecithin, Cephalin, and Similar Substances. M. LOUISE FOSTER.
64. Digest of Data on Mineral Substances in the Diet. GRACE MACLEOD.
65. Title announced at the meeting. F. W. HOWE.
66. Title announced at the meeting. ALICE F. BLOOD.
67. Report of a Survey of the Food Conditions at Sing Sing Prison. EMILY B. SEAMAN.
68. The Relation of Biological Chemistry to Problems of the Community. EMILY B. SEAMAN.
69. A Bacteriological Study of Hamburger Steak. EDWIN LEFEBVRE.
70. The Temperature of Potatoes while Cooking and a Method of Measuring Temperature during Cooking and Canning. R. D. MILNER.
71. Washing and Cleaning. W. D. BANCROFT.
72. Whipped Cream, Etc. W. D. BANCROFT.
73. Mayonnaise. W. D. BANCROFT.
74. Cleaning Silver by Contact with Aluminum in Alkaline Solution. H. L. LANG AND C. F. WALTON, JR.
75. Iron Rust and Its Removal—New Methods. H. L. LANG AND ANNA H. WHITTLESBY.
76. Solution of Antimony from Some Enamelled Cooking Utensils. ELIZABETH W. MILLER.

## FERTILIZER CHEMISTRY DIVISION

- J. E. BRECKENRIDGE, *Chairman* F. B. CARPENTER, *Secretary*
- Plant Food Deficiencies of Coastal Plain and Piedmont Soils. C. B. WILLIAMS.
- Reports of Committees.



## INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS DIVISION

H. F. HOWA, *Chairman*S. H. SALESBURY, JR., *Secretary*

1. The Determination of Ash in Coals with a High Percentage of Calcium Carbonate. S. W. PARR.
2. The Mechanical Sampling of Illinois Coal. S. W. PARR.
3. A New Form of Adiabatic Calorimeter. S. W. PARR.
1. Report on Last Year's Progress of the Industrial Fellowship System of the Mellon Institute. R. F. BACON.
5. An Investigation of Composition Flooring. R. F. BACON AND R. R. SHIPLEY.
6. A Contribution to the Chemistry of Laundering. H. G. ELLEDGE.
7. On the Use of Certain Yeast Nutrients in Bread Making. H. A. KOHMAN.
8. On Hydrated Lime. J. F. MACKAY.
9. On the Prevention of Glass Pot Corrosion. S. R. SCHOLES.
10. On the Behavior of Manganese in Glass. S. R. SCHOLES AND H. W. TILLOTSON.
11. Further Experiments on the Volatilization of Platinum. G. K. BURGESS AND R. G. WALTENBERG.
12. History and Present Methods of Fluorspar Production in Illinois. CARL C. LUEDERKING.
13. Chemistry and Technology of Glass. ALEXANDER SILVERMAN.
14. New Volumetric Determination of Nickel and Cobalt. W. D. ENGLE AND R. G. GUSTAVSON.
15. Copper Deposition in Electrotyping Baths. (Preliminary Report.) W. BLUM, H. D. HOLLER, H. RAWDON AND E. L. LASIER.
16. Our Unnecessary Waste of Potash Compounds. JAMES R. WITHROW.
17. Experiments on the Corrosion of Iron and Steel. W. D. RICHARDSON.
18. Ethyl Alcohol from Wood Waste. IV. Yields from Various Species of Wood. F. W. KRESSMANN.
19. Notes on Tar from Some Mid-Western Cannel Coals. J. C. INGRAM.
20. Comments on the Krebitz Process of Soap Manufacture and Glycerol Recovery. G. S. WRISLEY.
21. An Unusual Explosion in Connection with Potassium Chlorate. F. E. ROWLAND.
22. Laboratory Control in the Manufacture of Corn Syrup. A. P. BRYANT.
23. Effect of Aging upon the Constants of Chinese Wood Oil. D. F. McFARLAND AND H. R. LEE.
24. Effect of Fillers in Synthetic Molding Compounds. L. V. REDMAN, A. J. WEITH AND F. P. BROCK.
25. Printing Plates from Phenol Resins. L. V. REDMAN, A. J. WEITH AND F. P. BROCK.
26. The Effects of Moisture Introduced into the Digestor in the Cooking of Soda Pulp. SIDNEY D. WELLS.

## ORGANIC CHEMISTRY DIVISION

C. G. DERICK, *Chairman*H. L. FISHER, *Secretary*

1. The Synthesis of *p*-Cymene Monocarboxylic Acids and of Certain of Their Derivatives. M. T. BOGERT AND J. R. TUTTLE.
2. Benzoylene Urea and Some of Its Nitro Derivatives. M. T. BOGERT AND G. SCATCHARD.
3. A New Group of Azo Dyestuffs. M. T. BOGERT.
4. Methylene Disalicylic Acid and Derivatives. ROBERT A. HALL.
5. The Addition Compounds of Phenols with Organic Acids. JAMES KENDALL.
6. Derivatives of Isomaphoric Acid—An Unusual Formation of a Methyl Ether of a Hydroxy Acid. G. S. SKINNER AND W. A. NOYES.
7. Researches on Pyrimidine-Nucleotides. New Developments. TREAT B. JOHNSON.
8. The Action of Ferric Chloride and Other Ferric Compounds upon Cellulose. LOUIS KAHLENBERG.
9. The Isomeric Lactones, Caryophyllin and Urson. FRANCIS D. DODGE.
10. Tautomeric Equilibrium Constants and Chemical Structure. A Measure of Valence in Terms of Energy. C. G. DERICK.
11. Preparation and Characterization of Trimethylene Oxide. D. W. BISSELL AND C. G. DERICK.
12. The Action of Metallic Oxides on Trimethylene Halides and of Heat upon  $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{O-Mg-I}$ . E. H. VOLLWEILER AND C. G. DERICK.
13. The Preparation and the Characterization of  $\epsilon$ -Acetylcaproic Acid. ST. ELMO BRADY AND C. G. DERICK.
14. The Behavior of  $\beta$ -Phenoxy Ethyl Bromide in the Wurtz Synthesis. ST. ELMO BRADY.
15. The Preparation and Characterization of  $\delta$ -Acetylvalerianic Acid. R. W. HESS AND C. G. DERICK.
16. A Study of the Isomeric Aminoethylbenzenes and Certain of Their Derivatives. O. S. KEENER, O. KAMM AND C. G. DERICK.

17. Syntheses in the Naphthalene Series. OLIVER KAMM AND H. B. MULLIGAGE.

18. A Study of the Equilibrium in the Friedel and Crafts Reaction. OLIVER KAMM AND S. D. KIRKPATRICK.

19. On the Reactions of the Formamidines. V. On Some Pyrazolone Derivatives. F. B. DAINS, H. R. O'BRIEN AND C. L. JOHNSON.

20. Contribution to our Knowledge of Dichlorether. Part II. G. B. FRANKFORTER AND S. J. REICHERT.

21. The Action of Aluminum Chloride on the Alcohols and Carbohydrates Alone and in the Presence of Other Organic Compounds. G. B. FRANKFORTER AND V. KOKATNUR.

22. A Catalytic Decomposition of Some Phenol Salts. W. H. HUNTER.

23. Some Work on the Reimer-Tiemann Reaction. W. H. HUNTER.

24. Notes on the Use of the Multiple Unit Electric Furnace and of a Modified Carbon Dioxide Generator in the Dumas Method for the Determination of Nitrogen. HARRY I. FISHER.

25. The Relations in Composition of Petroleum, Coal, and Natural Asphalts. C. F. MABERY.

26. The Occurrence of Esdragol in Rosin. CHARLES H. HERTY AND V. A. COULTER.

27. On the Phenolsulfonphthalene Dyes and the Quinonephenolate Theory of Indicators. E. C. WHITE, H. A. LUBS AND S. F. ACREE.

28. On the Use of Viscose as a Dialysis Membrane. H. A. LEWIS AND S. F. ACREE.

29. On the Tautomeric Reactions of the Silver and Mercury Salts of 1-Phenyl-4,5-dihydro-5-oxo-3-triazolyl Methyl Sulfone with Alkyl Halides. E. H. WIGHT AND S. F. ACREE.

30. On the Reactions of Both the Ions and Molecules of Acids, Bases, and Salts: The Inversion of Menthone by Sodium, Potassium and Lithium Ethylates. W. A. GRUSE AND S. F. ACREE.

31. The Galactan of *Larix occidentalis*. R. W. SCHORGER AND D. F. SMITH.

32. Further Evidence for the Electronic Formula of Benzene and the Substitution Rule. H. S. FRY.

33. Reactions in Non-Aqueous Solvents: Chromyl Chloride and Phosphorus Halides. H. S. FRY AND J. L. DONNELLY.

34. Electronic Tautomerism: The Existence of Electromers in Dynamic Equilibrium. H. S. FRY.

35. Partial Hydrogenation of Cottonseed Oil. BEN H. NICOLET.

36. The Reaction between Alcohols and Hydrochloric and Hydrobromic Acids. JAMES F. NORRIS.

37. The Nitro Phenyl Esters. H. I. JONES.

38. Esterification of Acids by Isomeric Mercaptans. J. W. KIMBALL AND E. EMMET REID.

39. Esterification of Isomeric Acids by Mercaptan. J. H. SACHS AND E. EMMET REID.

40. Catalytic Preparation of Nitriles. G. D. VAN EPPS AND E. EMMET REID.

41. The Preparation of Nitriles. G. D. VAN EPPS AND E. EMMET REID.

42. The Identification of Acids. E. EMMET REID.

43. Some Anomalies in the Solidification Points of Fats. B. H. NICOLET AND L. M. LIDDLE.

44. On the Nitration of Toluene. I. W. HUMPHREY.

45. The Hydrolysis of Chloropentanes as Affected by High Pressures: Synthetic Fusel Oil. H. ESSEX AND B. T. BROOKS.

46. The Effect of Sulfur on the Auto-Oxidation of Organic Compounds. B. T. BROOKS, I. W. HUMPHREY AND B. Y. LONG.

47. Two New Methods of Determining Acetylene in Gaseous Mixtures. G. O. CURME, JR.

48. Note on Lead Propionates. S. FRANK COX.

49. Crystalline  $\beta$ -Methyl Fructoside and Its Tetracetates. C. S. HUDSON AND D. H. BRAUNS.

50. A Fourth Crystalline Pentacetate of Galactose and Some Related Compounds. C. S. HUDSON AND J. M. JOHNSON.

51. The Isomeric Pentacetates of Glucosamine and of Chondrosamine. C. S. HUDSON AND J. K. DALE.

52. Indirect Measurements of the Rotatory Powers of Some of the Alpha and Beta Forms of the Sugars by Means of Solubility Measurements. C. S. HUDSON AND E. YANOVSKY.

53. Some Numerical Relations among the Rotatory Powers of the Compound Sugars. C. S. HUDSON.

## PHARMACEUTICAL CHEMISTRY DIVISION

JOHN H. LONG, *Chairman*GEO. D. BEAL, *Secretary*

1. The New Features of the U. S. P. IX. JOSEPH P. REMINGTON.
2. The Toxicity of the Volatile Principles of Coffee, with Comments on Coffee Substitutes. L. E. SAYRE.
3. The Pancreatin Tests of the Pharmacopoeia. J. H. LONG.
4. Rennett: A Note and a Correction. HOWARD T. GRABER.
5. Pepsin: A Résumé of Tests. HOWARD T. GRABER.
6. Relative Toxicity of Different Species of Digitalis. ROBERT A. HALL, E. L. NEWCOMB AND R. E. MORRIS.

13. Activated Sludge Experiments at the Baltimore Sewage Disposal Plant. CALVIN W. HENDRICK.
7. On the Apparent and Real Ash Content of Digitalis. NORBERT MUELLER and EDWARD KREMERS.
8. Alkaloidal Assay by Immiscible Solvents. H. F. LEWIS and G. D. BEAL.
9. The Preparation and Characteristics of Emetine. FRANK O. TAYLOR.
10. Some Unexpected Reactions in Pharmaceutical Mixtures. FRANK O. TAYLOR.
11. The Strength of Fluid Extracts. H. A. LANGENHAN and EDWARD KREMERS.
12. On Tincture of Peppermint for Coloring Purposes. NORBERT MUELLER and EDWARD KREMERS.
13. Further Notes on the Identification of the Emodin-Containing Drugs. RUTH E. OKEY and G. D. BEAL.
14. Determination of Small Amounts of Water and Alcohol in Ether for Anaesthesia. E. MALLINCKRODT, JR.
15. The Detection of Minute Quantities of Unsaturated Hydrocarbons in Liquid Petrolatum. C. H. BRIGGS and W. L. IRWIN.

#### PHYSICAL AND INORGANIC CHEMISTRY DIVISION

IRVING LANGMUIR, *Chairman*

JAMES KENDALL, *Secretary*

1. The Chromic-Chromous Potential at Mercury Electrodes. GEORGE SHANNON FORBES and H. N. RICHTER.
2. Heterogeneous Equilibria between Aqueous and Metallic Solutions: A Study of Mixed Sodium and Potassium Salt Solutions at Total Concentrations Varying from 0.2 N to 4.0 N. G. McPHAIL SMITH and T. R. BALL.
3. The Contamination of Precipitates in Gravimetric Analysis: Solid Solution and Adsorption vs. Higher-Order Compounds. G. McPHAIL SMITH.
4. An Electrically Controlled Calorimeter for Measuring Heats of Dilution. D. A. MACINNES and J. M. BRAHAM.
5. On the Evolution of the Elements According to the Hydrogen-Helium System. W. D. HARKINS.
6. Theoretical Relations of the Atomic Weights. W. D. HARKINS.
7. A New Gravimetric Method for the Separation of Aluminum from Zinc, Manganese, Nickel, Cobalt, Iron, and Chromium. LOUIS KARLENBERG and K. P. YOUNG.
8. The Electromotive Forces of Concentration Cells and Their Relation to the Transference Number. D. A. MACINNES.
9. The Complete Solubility Curve of Calcium Carbonate. JOHN JOHNSTON.
10. The Specific Conductivity of Pure Water in Equilibrium with Atmospheric Carbon Dioxide. JAMES KENDALL.
11. An Apparatus for Determining Freezing Point Lowering. R. G. VAN NAME and W. G. BROWN.
12. The Colloidal Phosphates and Arsenates of Iron. HARRY N. HOLMES.
13. The Formation of Crystals in Gels. HARRY N. HOLMES.
14. The Potential of Iodine Concentration Cells. GRINNELL JONES.
15. A Supposed Effect of the Form of Container upon the Density of a Gas. WILLIAM A. NOYES and LAURENCE C. JOHNSON.
16. A Demonstration of the Selective "Action" of Clay on Soluble Sulfides. JOHN C. INGRAM.
17. The Theory and Mechanism of Adsorption. IRVING LANGMUIR.
18. The Oxides of Iron. II. Magnetic Properties of the System  $\text{Fe}_2\text{O}_3\text{-Fe}_3\text{O}_4$ . R. B. SOSMAN and J. C. HOSTETTER.
19. The Dissociation of Ferric Oxide in Air. J. C. HOSTETTER and R. B. SOSMAN.
20. On the Measurement of the True and Apparent Electrical Conductivities of Solutions: Inductance, Capacity, Frequency, and Resistance Relations. H. P. HASTINGS, W. A. TAYLOR and S. F. ACREE.
21. Separation of the Elements of the Tin Group. J. M. WELCH and H. C. P. WEBER.
22. Differential Iodimetry. III. Determination of Vanadium in the Presence of Iron and Uranium. O. L. BARNEBEY.
23. Differential Iodimetry. II. Determination of Chromium in the Presence of Iron. O. L. BARNEBEY.
24. Precipitation of Magnesium Ammonium Orthophosphate. EDWARD G. MAHIN.
25. Some Laboratory Experiments on the Extraction of Radium from Carnotite Ores. A. G. LOOMIS and HERMAN SCHLUNDT.
26. A System for Reports on Quantitative Analysis to be Used in Teaching. E. GILL.
27. The Action of Anhydrous Aluminum Chloride upon Unsaturated Hydrocarbons. W. E. HENDERSON and W. C. GANGLOFF.
28. The Determination of Solubility Curves by the Method of Flotation. W. E. HENDERSON and GEBHART STEGMAN.
29. Determination of Transition Points by the Measurement of Electromotive Force. W. E. HENDERSON and I. W. CRIGER.
30. A Systematic Procedure for the Separation of the Anions. First Group. H. A. WINCKELMANN and H. C. P. WEBER.
31. On Some Molecular Compounds in Glass. E. W. TILLOTSON.

32. On the Variable Rotatory Power of Dissolved Organic Substances. M. A. ROSANOFF and H. A. MORTON.
33. On the Constant  $\alpha$  of Van der Waals' Equation. M. A. ROSANOFF and H. C. CORLISS.
34. On the Change of Transition Points with Pressure. M. A. ROSANOFF.
35. A Rational Process of Fractional Distillation. M. A. ROSANOFF.
36. A Study of Some of the Physical Properties of Mixtures of Dielectric Oils and Water. (Preliminary Report.) L. I. SHAW and L. A. PAPPENHAGEN.
37. Change of Conductivity with Time in the System  $\text{MeOH} + \text{I}_2$ . (Preliminary Report.) L. I. SHAW and J. P. TRICKY.
38. Atomic Weight of Yttrium. C. W. BALKE and B. S. HOPKINS.
39. The Potassium Iodide Reaction for Platinum. W. J. PRINCE and H. C. P. WEBER.
40. The Viscosity of Alcoholic Solutions. O. F. TOWER.
41. The Relation between Molecular Cohesion and Surface Tension. EÖTVÖS LAW. ALBERT P. MATHEWS.
42. Determination of Aluminum as Oxide. WILLIAM BLUM.
43. A Study of Tantalum Pentachloride for Atomic Weight Purposes. G. W. SEARS and C. W. BALKE.
44. A Study of the Dialysis of a Colloidal Solution of Hydrous Chromic Oxide in Chromium Chloride. MARKS NEIDLE and J. BARAB.
45. The Temperature Effect in Dialysis, and a Simple Rapid Dialyser. MARKS NEIDLE.
46. Production of Triatomic Hydrogen by Radium Rays. G. L. WENDT.
47. The Effect of Dissolved Substances on the Velocity of Crystallization of Water. J. H. WALTON and A. BRAUN.
48. The Atomic Weight of Dysprosium. EDGAR W. ENGLE and C. W. BALKE.
49. Potassium Lead Tartrate. R. S. DEAN.
50. Density of Aqueous Copper Sulfate-Sulfuric Acid Solutions. H. D. HOLLER and E. L. PEPPER.
51. An Electrical Insulating Material for Use in Moist Atmospheres. EDWARD W. WASHBURN.
52. Types of Wheatstone Bridges for Alternating Current Work. EDWARD W. WASHBURN.
53. Induced Reactions in the Analytical Chemistry of Lead. V. H. GOTTSCHALK.
54. An Attempt to Combine Nitrogen and Chlorine Directly. B. R. HONOVSKI, L. C. JOHNSON, F. O. ANDEREGG and W. A. NOYES.
55. The Nernst Luteration Constant in Gaseous Systems. N. HOWELL FURMAN.
56. The Reactivity of Acids. HUGH S. TAYLOR.
57. The Specific Heat and the Specific Molecular Energy of Chemical Elements and Compounds. FRED P. SIEBEL.
58. Vapor Pressures of Ethyl Alcohol and Alcohol Water Mixtures at 25° and Composition of Vapors in Equilibrium with the Mixtures. I. H. DERBY and F. DANIELS.
59. Complete Dissociation in Concentrated Solutions of Sodium Chloride and Potassium Chloride. I. H. DERBY, D. MAYARD and E. T. FERGON.
60. The Dissociation Pressures of Various Salt Hydrates and the Vapor Pressures of Their Saturated Solutions. I. H. DERBY and V. YNGVE.
61. The Swelling of Rubber in Various Liquids and the Nature of the Process. I. H. DERBY, P. D. SCHULTZ and O. D. CUNNINGHAM.
62. A Study of 0.1 Normal HCl Calomel Electrodes. N. E. LOOMIS.

#### WATER, SEWAGE AND SANITATION DIVISION

EDWARD BARTOW, *Chairman*

H. P. CORSON, *Secretary*

1. Sanitary Surveys as a Feature of Public Health Work. H. E. BARNARD.
2. Sanitary Survey Methods. J. C. DIGGS.
3. A Sanitary Survey of Logansport, Ind. J. C. DIGGS.
4. Swimming Pool Sanitation. W. LEE LEWIS.
5. The Rate of Ammonia Distillation in Water. F. W. BRUCKMILLER.
6. A Modification of the Whipple Method for Direct Nesslerization. F. W. BRUCKMILLER.
7. The Determination of Carbonic Acid, Combined and Free, in Water. JOHN JOHNSTON.
8. The Numerical Treatment of *B. coli* Values in Water Analysis. EARLE B. PHELPS and WILLIAM F. WELLS.

#### Symposium on the Activated Sludge Method of Sewage Purification:

9. The Development at Lawrence, Mass., of the Method of Sewage Purification by Aëration and Growths—Activated Sludge. H. W. CLARK.
10. Composition of the Effluent Air from an Activated Sludge Tank. F. N. CRAWFORD and EDWARD BARTOW.
11. Experiments with Activated Sludge at Milwaukee, Wis. W. D. COPELAND.
12. The Aëration of Sewage in the Presence of Activated Sludge from the Standpoint of an Engineer. E. J. FORT.



14. Chemical Observations of the Activated Sludge Process as Applied to Stock Yards Sewage. ARTHUR LEDERER.
15. The Activated Sludge Process. W. D. RICHARDSON.
16. The Sewage Experiment Station of the Illinois State Water Survey. J. F. SCHEIDT and EDWARD BARTOW.
17. The Experiments with Activated Sludge at Brockton, Mass. ROBERT SPIER WESTON.
18. Some Results on the Treatment of Packing House Sewage by the Aeration Process in the Presence of Activated Sludge. PAUL RUDNICK and G. L. NOBLE.
19. The Saving Effected by Using a Softened Water in Boilers. G. S. COOPER.
20. The Treatment of Industrial Wastes. HARRISON P. EDDY.
21. Some Studies on Chemical Self-Purification in the Ohio River. EARLE B. PHELPS and HAROLD W. STREETER.
22. Oxygen Demand Determination in the Field. F. W. BRUCK-MILLER.
23. The Determination of Nitrates in Sewages by the Ortho-Toluidine Reagent. EARLE B. PHELPS and H. L. SHOUB.
24. Studies on the Removal of Manganese from Water Supplies. H. P. CORSON and EDWARD BARTOW.
25. The Value of Softened Water to a Railroad. R. C. BARDWELL.
26. Softened Water and Its Benefits in Laundry Work. JOHN H. RYAN.
27. Some Features of Swimming Tank Control. W. LEE LEWIS.
28. Final Report of the Committee on Standard Methods of Analysis

### AMERICAN ELECTROCHEMICAL SOCIETY, TWENTY-NINTH GENERAL MEETING, WASHINGTON APRIL 27 TO 29, 1916

The Twenty-Ninth General Meeting of the American Electrochemical Society was held at Washington, D. C., April 27 to 29, 1916, with headquarters at the New Willard Hotel. All of the sessions were held at the New Willard Hotel except the Saturday (29th) morning session, at the Bureau of Standards, Assembly Hall of the Electrical Building. The annual business meeting of the Society was held at the Thursday (27th) morning session.

#### PROGRAM OF PAPERS

- Presidential Address. LAWRENCE ADDICKS.  
Symposium on Coöperation in Industrial Research: The Professional Society. LAWRENCE ADDICKS, F. A. LIBBURY.  
The University. W. D. BANCROFT, W. H. WALKER.  
The Government. D. A. LYON.  
The Corporation. L. H. BAEKELAND, W. R. WHITNEY.  
The Detectors in Wireless Telegraphy. W. D. BANCROFT.  
Hydrogen for Military Purposes. E. D. ARDERY.  
Liquid Chlorine. G. ORNSTEIN.  
Magnesium. W. M. GROSVENOR.  
Symposium on Niagara Falls Power and the American Industries:  
The Power Development. I. R. EDMANES.  
Electric Furnace Products. F. J. TONE.  
The Chemical Industries. A. H. HOOKER.  
The Nitrogen Question. W. S. LANDIS.  
Reclamation Service Water Power. A. P. DAVIS.  
The Brittleness of Annealed Copper. W. E. RUDER.  
Cobalt as an Element for Thermocouples. O. L. KOWALKE.  
Electrical Resistance of Copper-Nickel Alloys. F. M. SEBAST and G. L. GRAY.  
Faults in the Small Electric Arc Furnace. W. M. MCKNIGHT.  
The Rennerfelt Electric Arc Furnace. C. H. VOM BAUR.  
Water Power Development for Electrochemical Purposes. J. H. PIERCE.  
The Passive State of Metals. C. W. BENNETT and W. S. BURNHAM.  
Overvoltage. C. W. BENNETT.  
Overvoltage and Monatomic Hydrogen. W. D. BANCROFT.  
Depolarization by Electrical Waves. W. D. BANCROFT.  
Electrode Surface Phenomena. W. C. ARSEM.  
Contact Resistance of Metal Electrodes. N. K. CHANEY.  
Contact Potentials and Electrochemical Potentials. I. LANGMUIR.  
Polarization in LeClanché Cells. D. A. MACINNES.  
Electrolytic Formation of Perchlorate. C. W. BENNETT and E. L. MACK.  
Unstable States in Arc and Glow. W. G. CADY.  
Electric Arcs in Vapors and Gases at Low Pressures. W. A. DARRAH.  
The Moore Tube for Color Matching. W. M. F. MOORE.  
Corrosion and the Engineer. W. H. WALKER.  
Effect of Rust upon the Progress of Rust. J. ASTON.  
Influence of Frequency of Current on Electrolytic Corrosion. B. MCCOLLUM and G. H. AHLBORN.  
Some Unsolved Problems of the Electroplater. G. B. HOGABOOM.

- Nickel Plating. F. C. MATHERS, E. H. STUART and E. C. STURGE.  
VAN T.  
Rapid Nickel Plating. O. P. WALES.  
Tests of Tin Plating Baths. F. C. MATHERS and B. W. COCKERAM.  
Peptone as an Addition Agent in Stannous Ammonium Oxalate Baths. F. C. MATHERS and B. W. COCKERAM.  
Addition Agents in Electrodepositing Silver from Silver Nitrate Solutions. F. C. MATHERS and J. R. KNEIBLER.  
Electrolytic Zinc. W. R. INGALLS.  
Recent Progress in Electrolytic Iron. O. W. STOREY.

The American Institute of Electrical Engineers held a meeting on Wednesday, April 26th, at the New Willard Hotel, to which the members of the American Electrochemical Society were invited. The program was as follows:

- Address. PRESIDENT JOHN J. CARTY.  
Electrochemical Industries and Their Interest in the Development of Water Power. LAWRENCE ADDICKS.  
Water Power Development and the Food Problem. H. S. CUSHMAN.  
Relation of Water Power to Increased Transportation. L. B. STILLWELL.  
The Relation of Water Power to the National Defense. W. R. WHITNEY.  
The Water Power Situation, Including Its Financial Aspect. GANO DUNN.

Reciprocally, the members of the American Institute of Electrical Engineers were invited to the sessions of the American Electrochemical Society, those on Thursday having been arranged to be of particular interest to electrical engineers.

### STANDARD METHODS OF SAMPLING AND ANALYSIS AND STANDARD SAMPLES

By W. F. HILLEBRAND

Received April 13, 1916

The writer presented to the Second Pan-American Scientific Congress a paper bearing the above title, the ultimate publication of which is uncertain. The greater part of the paper discussed the subject in its relations to the countries participating in the Congress, in the light of certain resolutions which the Congress had received as a legacy from its immediate predecessor. Certain portions of this might be of somewhat general interest, but cannot well be divorced from their context. The latter part of the paper, however, may have sufficient interest to chemists of the United States to warrant immediate and separate publication, and is herewith presented in its original form, except as to a few minor changes necessitated by the present form of publication.

#### PRINCIPLES ON WHICH STANDARD METHODS AND SAMPLES SHOULD BE BASED

The fundamental principles that should guide in establishing standard methods and standard samples, principles that have been oftentimes in the past too little considered in spite of the warnings of various writers, may be stated as follows:

#### CRITERIA FOR STANDARD METHODS

What are the criteria by which a standard method for commercial use should be judged? The chief of these appear to be:

- 1.—That its limits of accuracy and applicability are clearly defined and understood.
- 2.—That it should yield sufficiently accurate and concordant results in the hands of different analysts.
- 3.—That it should not demand such close adherence to detail or such manipulative skill and judgment, or such time consumption as to affect seriously its usefulness.
- 4.—That it should have been tested upon material of high purity or upon material carefully analyzed by independent and reliable methods.
- 5.—That the results obtainable upon a given class of materials should not be too dependent upon the composition (steel, iron).

Based upon these and perhaps other criteria it is probable that

many methods used as standard fail to measure up to our ideal requirement.

#### CRITERIA FOR STANDARD SAMPLES

In fixing the criteria by which to judge the fitness of standard samples we have to distinguish between those (A) which serve merely as a check upon analytical procedure and those (B) which find use as primary standards in volumetric and polarimetric analysis or in calorimetry. Samples of the first class are usually more or less complex mixtures of chemical (mineral) individuals, while those of the second are single chemical individuals of the highest attainable purity.

CLASS A: 1—The material must be similar in all essential characteristics (physical and chemical) to the commercial materials that are to be tested in comparison with it.

2—The sample should be so homogeneous in all its parts that the variations are negligible for the purposes in view.

3—Its composition should have been determined by independent and reliable methods affording agreeing results.

4—It must be so stable under all ordinary conditions that no detectable change of composition will occur during the anticipated life of the sample.

This last proviso excludes at once substances that are prone to oxidation (most, if not all, sulfide ores and all coals) and those whose moisture content varies with that of the atmosphere (coals and many ores, etc.).

CLASS B:<sup>1</sup> 1—There must be reasonable ease of preparation and accurate reproducibility.

2—The purity must be determinable with sufficient accuracy and the purified material must be stable indefinitely under ordinary conditions of the laboratory.

3—The use of the material in regular work must demand neither complex apparatus nor difficult manipulation.

4—Such precision must be attainable when it is used with ordinary care, that one or at the most few determinations suffice for the fixing of the value of a standard solution or to calibrate an instrument.

5—The accuracy obtained under ordinary conditions of its use in standardization must be at least as great as that required in the use of the solution or instrument to be standardized.

Going still further back we must presuppose for the attainment of results of high accuracy, both in the study of primary methods and in the application of these to standard samples, that the ultimate standards upon which they are based are of an accuracy commensurate with the needs of the case. Thus, there should be used only reagents of the highest quality, instruments of accuracy calibrated on the same basis, the same units of measurement, and, last but not least, the question of atomic weights should not have been overlooked.

In explanation of the expression "the same units of measurement" only one example need be mentioned. We have the Mohr liter and the true liter. Manifestly these cannot be used interchangeably. Then the temperatures of standard solutions must be approximately alike if comparable results are to be expected. With this last condition is closely connected the temperature at which the measuring vessels have been calibrated. Wide difference may result from the use of some with reference mark 15° and others with 25°; hence the need for uniform calibration.

The question of atomic weights is of peculiar interest and has been urged by others in times past. It is also perhaps the one most often overlooked. For some gravimetric work it is of no significance whether or not the atomic weights are accurately known or the latest accepted ones are used, as for instance, when the amount of aluminum oxide in a material is sought and it is eventually to be weighed as such. The case is differ-

ent when an elementary substance sought is weighed as part of a complex molecule or when the determination of an element or compound is based on volumetric analysis, the primary standard for which is not the same element. Neglect to take this consideration into account may make a large difference in the valuation of cargo lots of materials based on volumetric analysis, as when different atomic weights are used by cooperating analysts.

Fortunately we have as to atomic weights a body of recognized authority in the International Committee on Atomic Weights, whose annual revisions are known to all chemists.<sup>1</sup>

Finally, it should be borne in mind that to some of the atomic weights uncertainties attach which are larger than the differences or errors of some methods of analysis. It is, therefore, a waste of effort to try to refine a commercial method so far that its probable error falls below that of the atomic weights that are involved.

#### MATERIALS COVERED BY METHODS OF LEGAL OR OTHER AUTHORITY STANDING IN THE UNITED STATES

The use of methods that have been proposed as standard is very seldom binding upon anyone, not even upon members of societies which may have adopted them formally. To certain of them, however, there has been given legal standing, recognized in courts of law, either through act of some federal, state, or municipal body, or of departmental officers whose action may be regarded as having the force of law. It is proper, therefore, in a list of so-called standard methods, to discriminate between those which have been legalized in the above sense and are mandatory under certain circumstances and those which have no mandatory or legalized character, although they may have been recommended formally by some competent body. There may be considered, further, a class of methods whose use is compulsory in the laboratories of certain large industrial concerns or which are put forth by others as the methods by which the composition or quality of goods contracted for shall be determined. In cases like the last, the method of test may form part of the specification for the article or material in question. It has been difficult to decide for some methods in which of the above categories they should be placed, or even if they should find place at all. The list which follows includes no methods that were published merely as reports of progress. It is, however, probably not exhaustive and may not be free from error in some of its details, but it is believed that it embodies no flagrant omissions or imperfections. The author will esteem it a favor if those who may be aware of omissions or other imperfections will bring them to his attention.

A word of warning may not be amiss as to the real standing that should be accorded a given method in this or any other list that may yet be prepared. Some organizations put forth no method that has not been either critically studied experimentally or else formulated by experts on the basis of special knowledge and information. Others throw no such safeguard about the method they recommend, but copy from other bodies or adopt methods that may be in more or less common use but have never been critically tested. Methods of the last type are necessarily less to be trusted than the others. Again, unfortunately, instances are not lacking where methods have been formulated by committees not well qualified for the task. Against such as these the average user is without protection.

#### 1—METHODS RECOGNIZED BY COURTS OF LAW IN THE UNITED STATES

1—METHODS OF THE UNITED STATES PHARMACOPOEIA COVERING THE TESTING OF DRUGS AND MEDICINES, as given in the Eighth Decennial Revision. The Ninth Revision is in press

<sup>1</sup> It will perhaps be known to most readers that the 8th International Congress of Applied Chemistry recommended that for commercial transactions the atomic weights put forth by the above committee should remain in force from one Congress to the next and should not change from year to year.

<sup>1</sup> S. McBride, *J. Am. Chem. Soc.*, **34** (1912), 394; Bureau of Standards, *Circ.* **40** (1912), 4.



and should appear within the next few months. The specifications and methods of the Pharmacopoeia are compulsory in the enforcement of the Federal Food and Drugs Act of 1906, in so far as they are applicable, and of laws of many states regulating drugs and medicines.

2—METHODS OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS, as published in *Bull.* 107 (revised), 1908, of the Bureau of Chemistry, Department of Agriculture, and about to appear freshly revised in the February, 1916, and subsequent numbers of the *Quarterly Journal of Official Agricultural Chemists*, Carl L. Alsberg, *Secretary*, Washington, D. C.

The use of these methods, in so far as they apply, is compulsory in the enforcement of the Federal Food and Drugs Act of 1906, and of the Insecticide Act of 1910. Some of the methods are provisional only, not having been subjected as yet to sufficient trial to justify final adoption, but they are none the less recognized by the Federal Courts. They are also recognized by the legislatures of some states and by some public organizations, and are followed rather generally wherever applicable. The materials for which methods are provided in the forthcoming publication are:

Baking Powder	Organic and Inorganic Phosphorus in Foods, Feeding Stuffs, and Drugs
Beer	Phosphoric Acid
Cereal Products	Potash
Cocoa and Cocoa Products	Saccharine Products
Coffee	Soils
Coloring Matter	Spices
Condiments other than Spices	Sugars (see also I-4-a, below)
Dairy Products (Adulteration)	Tanning Materials
Dairy Products (General)	Tea
Fats and Oils (Edible)	Testing Chemical Reagents
Feed Adulteration	Vegetables (Canned)
Flavoring Extracts	Vinegars
Foods, Feeding Stuffs, and Drugs	Water in Foods and Feeding Stuffs
Foods (General)	Water (Potable, mineral, industrial, irrigation from the chemical point of view. See also II-4, p. 469)
Fruits and Fruit Products	Wine
Heavy Metals in Foods	
Inorganic Plant Constituents	
Insecticides	
Liquors (Distilled)	
Meat and Fish	
Medicinal Plants and Drugs	
Nitrogen: Separation of Nitrogenous Substances: Milk and Cheese, Meat Proteins	

3—UNITED STATES GOVERNMENT SPECIFICATIONS FOR PORTLAND CEMENT—Established by order of the President of the United States, April 30, 1912, and published in *Circ.* 33 of the Bureau of Standards. The specifications and methods of testing are obligatory upon all branches of the Federal Government in testing Portland cement intended for government use, and they are subject to modification from time to time as necessity arises.

#### 4—METHODS OF THE UNITED STATES TREASURY DEPARTMENT

(a)—*Sugar and Molasses*: Treasury Department Document No. 2470 (1907), Division of Customs. Regulations governing weighing, taring, sampling, classification, and polarization of imported sugars and molasses.

There is an International Commission for Uniform Methods of Sugar Analysis whose methods are followed by the European countries represented on the commission. In the United States their use is wholly optional, notwithstanding that this country has representatives upon the commission from governmental as well as industrial ranks. A summary of the methods of the International Commission is given in Wiechmann's "Sugar Analysis," J. Wiley & Sons, New York, 1914.

(b)—*Denatured Alcohol*: Regulation No. 30—Revised (Appendix), Bureau of Internal Revenue.

(c)—*Alcohol*: In Revised Statutes 3249 the legal specific gravity of proof spirits is defined as 0.7939 at 60° F. This statute practically compels the chemists of the Bureau of Internal Revenue to use this specific gravity in all their work on alcohol. In Treasury Document No. 34543, the use is authorized of the alcoholometric table No. 7, as given in the Gaugers' Manual of 1913. There are slight variations from earlier editions of the table.

(d)—*Sampling of Ores and Crude Metals*: Treasury Depart-

ment Document No. 35216 prescribes regulations under Sub-section 1 of Paragraph N of Section 4, Tariff Act of October 3, 1913. As to assay of the materials covered by the regulations, it is directed merely that this shall be by "the wet assay, with out deduction." The procedure for determining moisture in imported ores is briefly outlined. Treasury Document No. 35219 extends the use of the "wet assay" to lead-bearing ores.

(e)—*Tea*: Treasury Documents Nos. 34256 and 34411 give the latest directions for the testing of tea by the Read method.

(f)—*Number of Yarn in Cotton Cloth*: Treasury Document No. 34255. An addition of 8.5 per cent is to be made to the bone-dry weight in ascertaining the number of yarn in cotton cloth, instead of 7 per cent as formerly.

#### II METHODS NOT HAVING LEGAL RECOGNITION BUT APPROVED BY SCIENTIFIC OR TECHNICAL ORGANIZATIONS

1—METHODS RECOMMENDED BY THE AMERICAN CHEMICAL SOCIETY, Charles L. Parsons, *Secretary*, P. O. Box 505, Washington, D. C.

(a)—*Glycerine*: THIS JOURNAL, 3 (1911), 679. Methods for glycerine were formulated by a committee of the American Chemical Society acting in cooperation with British, German, and French committees or representatives. In the United States the methods are not generally employed, there being no organization of soap manufacturers or glycerine distillers, but in England, where there is a powerful organization, the acetin method recommended by the committee is followed in all commercial transactions. The writer is unable to say what is the practice in Germany and France.

(b)—*Resin in Shellac*: *J. Am. Chem. Soc.*, 29 (1907), 1221.

(c)—*Copper (Battery Assay)*: THIS JOURNAL, 7 (1915), 546.

(d)—*Spelter (Zinc)*: *Ibid.*, 7 (1915), 547.

2—METHODS RECOMMENDED BY THE AMERICAN SOCIETY FOR TESTING MATERIALS, Edgar Marburg, *Secretary*, University of Pennsylvania, Philadelphia, Pa. Year Book, 1915.

(a)—*Methods Adopted as Standard*: Plain Carbon Steel (p. 201); Alloy Steels (p. 225); Spelter (p. 345); Cement (p. 375) (previously approved by the American Society of Civil Engineers and the American Railway Engineering Association); Raw Linseed Oil from North American Seed (p. 417); Boiled Linseed Oil from North American Seed (p. 420); Raw Chinese Wood Oil (p. 423); Turpentine (p. 428); Soluble Bitumen (p. 444); Penetration of Bitumen (p. 446); Oil and Asphaltic Compounds (Loss on Heating) (p. 447); Cotton Rubber-Lined Hose (Analysis of Rubber Lining) (p. 449).

(b)—*Methods Adopted as Tentative*: Pig and Cast Iron (p. 519); Paint Thinners other than Turpentine (p. 567); Bleached Shellac (Moisture) (p. 571); White Pigments (p. 579); Coal (p. 591)—Large Scale Sampling (p. 596)—Laboratory Sampling and Analysis; Creosote Oil (p. 625).

The method for laboratory sampling and analysis of coal was formulated jointly by committees of the American Society for Testing Materials and the American Chemical Society, revising the methods originally put forth by the latter.

The tentative methods for Pig and Cast Iron are intended to replace the methods heretofore in common use by foundrymen<sup>1</sup> and were in fact originally intended to serve as basis for discussion of methods for international use, representatives of Great Britain, Germany, and the United States participating under the auspices of the International Association for Testing Materials.

The method for cement is essentially that proposed originally by a committee (on Uniformity in the Analysis of Methods for the Portland Cement Industry) established by the New York Section of the Society of Chemical Industry, the procedure having been first published in the *Journal of the Society of Chemical Industry*, 21 (1902), 12, and a year later in the *Engineering News and Engineering Record*.

<sup>1</sup> *Trans. Am. Foundrymen's Association*, 16 (1907), 44

The method for cement under I-3 (p. 468) is also based upon the same original procedure, but has undergone more modification than that approved by the American Society for Testing Materials.

3—METHODS RECOMMENDED BY THE AMERICAN FOUNDRY-MEN'S ASSOCIATION, Richard Moldenke, *Secretary*, Watchung, N. J.

*Coke*: *Trans. Am. Foundrymen's Association*, 20 (1911), 559. These methods are under revision by the above Association, cooperating with the American Society for Testing Materials.

4—METHODS RECOMMENDED BY THE AMERICAN PUBLIC HEALTH ASSOCIATION. Office 289 Fourth Avenue, New York City.

*Water* (from the sanitary point of view): "Standard Methods for the Examination of Water and Sewage," 1912, 2nd Edition. To appear in revised form in 1916. The methods cover physical, chemical, microscopical, and bacteriological examination. The methods for the third edition have been compiled and revised in cooperation with a committee of the American Chemical Society and representatives of the Association of Official Agricultural Chemists (see I-2, *ante*, for the reference to the publication by the latter organization). It is expected that they will also be approved by the American Chemical Society.

5—METHODS RECOMMENDED BY THE AMERICAN LEATHER CHEMISTS' ASSOCIATION, H. C. Reed, *Secretary-Treasurer*, 227 Fulton St., New York City.

*Journal American Leather Chemists' Association*, 10 (1915), 110: Methods official in the Association for 1915 cover analysis of vegetable matters containing tannin, sampling of tanning materials, and analysis of leather. There is also a provisional method for sulfonated oils.

6—METHODS RECOMMENDED BY SOCIETIES INTERESTED IN COTTON PRODUCTS.

*Methods of Analysis of Cotton Seed Products*, printed in the following pamphlets:

(a)—Report of the Proceedings of the Sixth Annual Meeting of the Society of Cotton Products Analysis, G. C. Hulbert, *Secretary*, Augusta, Ga.

(b)—Minutes of the meeting of the Chemists' Committee of the Interstate Cotton Seed Crushers Association at Asheville, N. C., August 10, 1914, F. N. Smalley, *Secretary*, Savannah, Ga.

(c)—Proceedings of the Twenty-first Annual Session of the Texas Cotton Seed Crushers Association, Robert Gibson, *Secretary*, Dallas, Texas.

(d)—Methods of Analysis of the New York Produce Exchange, W. A. Storts, *Chairman*, Cotton Seed Products Committee of the New York Produce Exchange, New York City.

The first (a) of the above is the latest publication that contains the Interstate Cotton Seed Crushers Association's official methods, including minor changes and additions adopted by the Association in September, 1915.

7—METHODS RECOMMENDED BY THE AMERICAN RAILWAY ENGINEERING ASSOCIATION. Office, 900 South Michigan Avenue, Chicago, Ill.

(a)—*Cresote Oil*: Manual American Railway Engineering Association, 1911, p. 441.

(b)—*Zinc in Treated Timbers*: *Ibid.*, p. 451.

(c)—*Cement*: *Ibid.*, p. 478. The method is that recommended by the Committee on Uniformity in Technical Analysis of the New York Section of the Society of Chemical Industry. See also I-3 (p. 468) and II-2 (p. 468).

### III—METHODS IN USE IN LABORATORIES OF CERTAIN INDUSTRIAL ESTABLISHMENTS

The number of industrial organizations that have standardized methods of analysis for use in their business is unknown, but is probably not at all large. A few of the more notable instances are here given.

1—METHODS OF THE UNITED STATES STEEL CORPORATION FOR THE SAMPLING AND ANALYSIS OF:

(a)—*Gases*: Pamphlet. Also *Metallurgical and Chemical Engineering*, 9 (1911), 302, 356.

(b)—*Iron Ores*: Pamphlet, 1914, superseding that of 1909 and the reprints of that year in the technical press.

(c)—*Pig Iron*: Pamphlet, 1912. Also *Eighth International Congress of Applied Chemistry*, 1 (1912), 91, and *THIS JOURNAL*, 4 (1912), 801.

(d)—*Plain Carbon Steels*: Pamphlet, 1915.

(e)—*Alloy Steels*, Pamphlet, 1915.

(f)—*Coal and Coke*, including the by-products. In preparation.

(g)—*Ferro-Alloys and Bearing Metals*. In preparation.

(h)—*Slags, Fluxes, and Miscellaneous Materials*. In preparation.

The pamphlets are to be had at the price of one dollar (\$1.00) each from Mr. Camp, *Chairman*, Chemists' Committee, Carnegie Steel Company, Pittsburgh, Pa.

2—METHODS OF THE UNDERWRITERS' LABORATORIES, under the direction of the National Board of Fire Underwriters. Principal office, 207 East Ohio St., Chicago, Ill.

(a)—*Rubber Compounds Used for Electrical Insulation*. Pamphlet, 1915.

(b)—*Rubber Compounds Used for Rubber-Lined Fire Hose*. Pamphlet, 1914.

(c)—*Rigid Conduit*. In press. Contains chemical methods of determining the quantity of zinc per square foot and the copper sulfate test method.

3—RAILROADS.—The Pennsylvania Railroad was probably the first railroad to include in its specifications methods by which purchases should be tested and it has a very complete list of such methods.

### ACKNOWLEDGMENTS

To the many gentlemen who have been of help to me in the preparation of this paper, colleagues in the Bureau of Standards, fellow workers in the Agricultural and other Federal Departments, and others in university and industrial life, my cordial thanks are tendered.

BUREAU OF STANDARDS, WASHINGTON

## NOTES AND CORRESPONDENCE

### ON THE EXTRACTION OF RADIUM, ETC., BY THE U. S. BUREAU OF MINES

*Editor of the Journal of Industrial and Engineering Chemistry:*

I have read with interest the letter of February 16th, by Dr. Charles H. Viol, of the Standard Chemical Company, page 284 of the March issue of your Journal. I am especially interested to know that Dr. Viol concedes that some of the statements issued by the Bureau may have been altered or abbreviated in the public press, but I regret that I feel it necessary

to add that no one has so fostered misstatement as Dr. Viol himself and other employees of the company which he represents. To attempt to show up all the errors and misstatements they have issued is quite unnecessary and beyond the limit of space which you can allow me. I shall accordingly confine myself to two instances only—the article referred to above and one other which appeared in "*Radium*," the proprietary publication of the Standard Chemical Company, of which Dr. Viol is editor.



In this publication (page 54, November, 1915, issue) the following appeared, only such portion being reprinted as is pertinent to the point at issue:

#### "THE COST OF RADIUM"

"Below we quote in full a letter from L. O. Howard, of Salt Lake City, to the editor of *Mining and Scientific Press*, which was published in that journal September 25, 1915:

"*Editor*—Sir: On page 406 of your issue of September 11, it was stated that the fact the Bureau of Mines has reduced the cost of producing radium to \$36,050 per grain of bromide will perhaps make a visit to the radium booths interesting."

"Assuming this statement to be correct, except for the supposedly typographical error which substitutes *grain* for *gram*, we are again subject to the skillful exaggeration which the Bureau used so successfully in its campaign against the radium producers last year. This statement was connected with the fact that radium was selling at \$120,000 per gram. \* \* \* \* The price at which radium is sold is given in terms of radium element whereas the cost that you report is given in terms of the salt, radium bromide. \* \* \*

In the latter part of July Dr. Viol had been sent the original statement by Secretary Lane to which Mr. Howard refers and which read as follows:

"The cost of one gram of radium metal produced in the form of bromide during March, April, and May of the present year was \$36,050."

Dr. Viol acknowledged the receipt of this statement and expressed his interest in it. On reading the statement in "*Radium*," I wrote Dr. Viol and called his attention to what I supposed to be an unintentional error, to the original statement sent him, and to his acknowledgment thereof—only to receive his reply, that the letter of Mr. Howard was published in his periodical with his knowledge and approval. When Mr. Howard's attention was brought to the misstatement he very courteously acknowledged his error and offered to publicly correct it. Up to the present time, however, Dr. Viol has made no correction in "*Radium*" of this gross misrepresentation nor has he ever published any original statement whatsoever issued by the Bureau of Mines regarding the mining or plant operations of the Bureau or referred thereto without falsification. I must accordingly assume that he intentionally publishes what he knows to be untrue.

Dr. Viol in an article on "The Radium Situation in America" *Radium*, page 106, March, 1915, says:

"By taking the cost of production on the basis of a mg. of hydrous bromide (for which the present selling price is \$64.32 per mg.) and comparing their figures on this basis with the present market price of radium element (\$120 per mg.), the Bureau of Mines officials are able to secure very startling comparisons."

The Bureau of Mines has invariably used the terms "radium element" or "radium metal," and the "comparisons" of bromide to element have originated in the imagination of Dr. Viol or in the misstatements of reporters for newspapers who have been unfamiliar with scientific terms.

On page 108 of the same issue Dr. Viol says:

"Repeated requests by members of the Congressional Committee for the written agreement between the Bureau of Mines and the National Radium Institute brought forth the promises that the agreement would be made a matter of record. So far, however, it has not been made public."

The full agreement was printed on page 195 of the very document from which Dr. Viol was quoting and had been in print for over a year.

The rest of the article makes interesting reading to those familiar with the situation. His extended quotations are quite characteristic of his journal.

It has not been the policy of the Bureau of Mines to authorize replies to any attacks in the public press or in periodical literature, although many have been made by employees of the company which Dr. Viol represents. In the present instance, however, the article appears in a journal which reaches all

parts of the world and is a public and permanent record in all the large libraries. To the many chemists in this country interested in the radium industry and to whom the *raison d'être* of Dr. Viol's letter is well known, no reply is even now necessary. The *JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY*, however, will be consulted in the future for references to radium, and many unfamiliar with conditions may accept Dr. Viol's statements as facts. Therefore, for the sake of the history of the industry these statements should be corrected. It is not, however, my intention to enter into any argument of a controversial nature. Fortunately, Dr. Viol himself and others of his company are on record, especially in testimony given before the Senate and House Committees on Mines and Mining, although those hearings are not readily available to any one searching the literature.

#### THE COST OF MINING

At the hearings before the Committee on Mines and Mining, House of Representatives, January 19 to 28, 1914, practically all of the chief producers of uranium ore and chief brokers were present and gave testimony. The following testimony was given regarding the cost of mining:

Pages 62 and 65, *Hearings before H. R. Committee*, Mr. J. M. Flannery, President of the Standard Chemical Company, testified:

"The average cost of mining carnotite ore would be \$15 or \$20 a ton; sacking and hauling, \$22.50; freight to Pittsburgh, \$12 per ton."

Page 166, *same Hearings*, Thos. F. V. Curran testified that the mining costs averaged \$42 per ton and transportation costs to Placerville \$20 per ton, giving a total ore cost laid down in Placerville of \$62 per ton.

Page 267, *same Hearings*, a signed statement from K. D. Hequemour gives the following figures:

	Per ton average
Development work.....	\$ 6.00
Ore mined, sorted, sacked, etc.....	20.00
Packing to wagon road.....	5.00
Wagon haul to railway.....	20.00
Loading and unloading.....	1.50
Assaying.....	3.00
Total average per ton.....	\$55.50

"Costs depend largely on size, continuity and grade of ore body and the experience of the men sorting the ore to the grade for shipping. Above prices are based on sorting to a grade of 2 per cent or less of  $U_3O_8$  contained. If a higher grade is wanted, the cost per ton would be materially higher for the items of 'mining' and 'development.'"

I believe these costs of mining were underestimated, but they are the best we have. In view of this testimony, the cost of the ore from the mines operated by the National Radium Institute appears high rather than low as claimed by Dr. Viol. The Maggie C claim, operated by the National Radium Institute, was one of the four or five most extensive pockets found in the Paradox region. It was, however, no more extensive than claims such as the Last Chance, Copper Prince, etc., owned and mined by others. Mining on the Maggie C claim has been more costly than on some of the smaller pockets worked by the National Radium Institute, where much less barren rock had to be moved.

#### PRICE OF ORE

At both the Senate and House Hearings referred to, extended testimony was given regarding the market price of ore:

Page 50, *H. R. Hearings*, Mr. Thos. R. Henahan testified that the round figures for the present price (January, 1914) of 2 per cent ore, Placerville, were about \$80 per ton.

Page 150, Mr. O. B. Willmarth testified that \$50 a ton at the mine was a fair average price for 2 per cent uranium ore.

Page 105, Mr. Thos. F. V. Curran testified, referring to ore shipments, "We get for it (delivered in France) at the present time about \$3.30 a pound of  $U_3O_8$ ."

Page 267, Mr. K. D. Hequemour in a signed statement gave the prices received by miners at railway as follows:

## PRICES BASED ON PER CENT URANIUM OXIDE

Per cent $U_3O_8$ . . .	11.2	14.4	2	21.1	21.2	24.4
Price per ton, net.	\$45	\$60	\$80	\$90	\$105	\$120

"The grade most frequently shipped is about 2 per cent. Very few shipments have been found in the  $2\frac{1}{4}$  per cent grade. The miner had great difficulty in getting a tonnage of the 2 per cent grade."

The Report of the Mines and Mining Committee, February 3, 1914, on these hearings, found as follows:

"Many foreign agents have been in this country seeking supplies for shipment abroad and a much stronger demand for ores has caused prices to advance so that ore containing 2 per cent uranium oxide readily brings \$80 per ton at the railroad at Placerville, Colo."

Mr. A. M. Wilson, of Nucla, one of the largest individual producers, wrote Secretary Lane, February 2, 1914, page 59, *Senate Hearings*, that the prices offered him at that time f. o. b. Placerville, Colo., were as follows:

Per cent Uranium oxide	Price offered by Standard Chemical Co.	Price offered by German broker
2 . . . . .	\$ 64.00	\$ 80.00
$2\frac{1}{2}$ . . . . .	82.50	110.00
3 . . . . .	110.00*	138.00
4 . . . . .	148.00	200.00

No offer by the Standard Chemical Co. on any ore under 2 per cent  $U_3O_8$ ."

Page 109, *Senate Hearings*, W. L. Cummings, another producer of carnotite, testified that February 17, 1914, the price of ore had been advancing and that he was then paid \$2 per pound  $U_3O_8$  f. o. b. Placerville, Colo. (\$80 per ton of 2 per cent ore.)

Page 128, *Senate Hearings*, written statement, February 17, 1914, from David Taylor, a large ore broker: "For a standard ore 2 per cent uranium oxide the market price is about \$125 per ton delivered in Europe on a basis of complete payment on a valuation usually less than the American valuation at probably 6 months from the date of shipment."

The price of ore advanced slightly between February and August when the European war began. The price quoted by the Standard Chemical Company to producers as late as July 10, 1911, for ore delivered at the railroad station Dolores, Colorado, was \$98 per ton for 2 to 2.24 per cent, incl., and \$114 per ton for 2.25 to 2.49 per cent, incl. These prices average approximately \$2.35 per pound  $U_3O_8$ . The contract which they offered contained the following clause:

"The buyer shall be under no obligation to take or pay for any ore running less than 1.75 per cent uranium oxide."

It further contained the clause:

"The 'seller' has sold to the Standard Chemical Company, hereinafter called the 'buyer,' all carnotite ores on the dumps, or hereafter mined or produced, on the following described mining claims."

If the contract was legal this practically tied the seller up to furnish all of the ore he might in future produce, at the prices named, to this company.

Dr. Viol, with his usual desire for accuracy, quotes on page 284 of THIS JOURNAL, March, 1916:

"Before the war carnotite containing 2 per cent  $U_3O_8$  was sold to French buyers at \$3.30 per lb.  $U_3O_8$ , and offers went as high as \$4.00 for this ore."

As his company was actively purchasing ore, Dr. Viol must have known that the statement of Mr. Curran (half again as high as any other) which he selected for quotation was exaggerated. The magnitude of the exaggeration should, however, not trouble Dr. Viol, who testified before the House Committee on Mines and Mining (page 116) that in his opinion radium could be extracted from ordinary soils commercially.

It will probably interest Dr. Viol still further to learn that there was a misunderstanding between Mr. Curran and the purchaser of the ore, who bought on the basis of the radium content "One hundred francs per mg. of hydrous radium bromide delivered in France for all ore running over 6-10 mgs. (*Senate Hearings*, p. 73)." Mr. Curran supposed that he was selling on the basis of radium actually present in the ore, while the purchaser was buying on the basis of the radium he was able to extract. As the extraction was later found to be less than 70 per cent, the net price received for the ore, deducting

freight to France, insurance, dust losses in transportation, etc., was essentially in accord with the testimony of the other ore dealers.

It was distinctly pointed out in *Bull.* 104 of the Bureau of Mines just what effect an increase in the market price of ore would have on the cost of radium produced by the Bureau of Mines process. This again Dr. Viol conveniently forgets in his article in THIS JOURNAL. There has been no market price for ore since the war in Europe began, as there have been no purchases until the National Radium Institute recently bought some lots that had been held in storage for many months. The Institute then became, until quite recently, the only corporation making offers for ore.

## EFFICIENCY OF EXTRACTION

In view of Dr. Viol's statements that nothing has been gained by the Bureau of Mines process, although that process has succeeded in producing at a plant in Colorado several grams of radium at a cost of approximately \$37,000 per gram, with an efficiency averaging above 85 per cent, and indeed over 90 per cent, on many carload lots, the following predictions and statements taken from the *Hearings* referred to above may prove enlightening:

Page 54, *House Hearings*, Mr. J. M. Flannery, President Standard Chemical Company, testified:

"We worked on it 3 years and endeavored to develop a process for the extraction of radium from these ores, and found it a very difficult and costly proposition. We have spent to-day, including our property and all, up to the first of January, \$650,000, divided about as follows:

\$100,000 for properties; \$225,000 or \$230,000 for labor and materials used in the process; and for plants, machinery, equipping the mill, etc.

We have, up to the first of January, 1914, produced 2 g. of radium, the market price of which is \$120,000 a gram, or a total of \$240,000. We figure this radium has cost us about \$480,000 and we received for it about \$240,000; not any more."

Page 65, Mr. Flannery further states: "It would be practically an utter impossibility to produce in the State of Colorado radium at anywhere near the price we can produce and sell it. I think it would cost more than \$100,000 a gram for anybody to-day to go into Colorado and undertake it."

Page 93, Mr. Flannery: "I want to say from my knowledge of the extraction of radium as it goes to-day, that if they have not a process as good as one I know of, those claims (claims leased by the National Radium Institute) they have will never produce 7 grams of radium."

Page 19, *Senate Hearings*, Mr. Flannery stated: "I said that with the knowledge they have now I don't think they could go out and build a plant and equip it, and with that \$450,000 produce a gram of radium."

Page 22, *Senate Hearings*, Mr. Flannery stated: "This work has cost the Standard Chemical Company thus far \$700,000 without as yet yielding any profit."

Page 23, *Senate Hearings*, Mr. Flannery: "It took the Standard Chemical Company two and three-quarter years to work out such a process at an expenditure of approximately \$400,000 for this alone."

Page 29, Mr. Flannery: "We spent approximately \$700,000 up to Jan. 1, 1914, and we have realized out of that expenditure only \$300,000 for our total production of radium."

On page 118, of *Radium*, for March, 1915, Dr. Viol, referring to the work of the Bureau of Mines, states:

"One thousand tons of picked ore would probably average not much better than 2 per cent  $U_3O_8$  and would contain *en toto* about 9,500 mgs. radium bromide. On this basis it would require about 74 per cent efficiency in extraction if even 7 g. of bromide are to be obtained. This is an efficiency that will be difficult to obtain, and it is very doubtful whether the government will ever receive any radium from the 1,000 tons of ore."

Page 119, *Radium*—"Certainly those results hardly justify the belief in the statement that 7 g. of radium (bromide) will be produced by the Bureau of Mines by the end of 1915 at a cost of \$40,000 per gram of radium element, as the statement would lead one to expect. It is a trite saying that the government production of anything is notoriously inefficient, slow and expensive."



The efficiency of extraction secured by the Standard Chemical Company has never been definitely stated, but can be calculated from the following testimony: "It varies from 1,000 tons of 1 per cent  $U_3O_8$  ore to 400 tons of 1 1/2 per cent ore, required to produce 1 g. of radium, being an efficiency varying from 26 to 65 per cent. Most of the statements show an efficiency of extraction by this company approximating 55 to 60 per cent. The extraction figures of a number of foreign plants have been reported to the Bureau of Mines, and no one of them has obtained an efficiency of more than 70 per cent."

Page 66, *House Hearings*, Mr. Flannery testified: "If you purchase a mine of 1 per cent ore it would take you somewhere between 1,000 and 1,600 tons. If you purchase a mine of 2 per cent it would probably take 400 to 500 tons (to produce 1 gram of radium). That has been found out by actual spending of money so far as we are concerned." This would indicate a radium extraction of less than 50 per cent.

Page 105, *House Hearings*, Dr. Viol stated: "To produce that quantity of radium chloride, containing a gram of radium element, would require from 350 to 400 tons, or even more—it depends, of course, on the quality of your ore, but as a minimum it would require from 350 to 400 tons of carnotite ore."

Page 107, Dr. Viol stated, referring back to his previous statement that the quality of the ore would have to be "somewhere around 1.5 or 2 per cent—that is, taking the ore as we get it."

On 1 1/2 per cent ore, 400 tons would be an efficiency of 65 per cent; 2 per cent ore, 350 tons would show an efficiency of 55.7 per cent.

As before stated, the radium extraction efficiency of the Bureau of Mines process has averaged above 85 and, indeed, above 90 per cent on many carload lots.

Dr. Viol's statement regarding the Bureau of Mines extraction of vanadium on page 284 of *THIS JOURNAL* is incorrect, although he quotes correctly on page 285. The facts are that between 29 and 30 per cent of the vanadium has been recovered in merchantable form as iron vanadate and that 85 per cent of the uranium has been recovered, not as crude sodium uranate, but as high-grade black oxide of uranium.<sup>1</sup> While it is true that the Bureau's process in its regular course does not obtain as large a proportion of the vanadium as might be wished, *Bull. 104* carefully points out that vanadium was sacrificed at this point in order to increase the radium extraction. Nothing was said about the further treatment of the residues to obtain the vanadium they contained, for at that time the work had not been done. Dr. Viol will, however, be relieved to know that the vanadium can be easily and profitably extracted from the residues. The method will be described in a later bulletin.

In regard to the operations of the company with which he is connected, Dr. Viol testified before the House Committee (page 106), regarding the value of the by-products from the uranium ore, as follows: "We have not gotten a cent from that. Our ore is a rather low-grade uranium and vanadium ore. It is an expensive proposition to recover vanadium from low-grade ore."

On page 284 of *THIS JOURNAL*, Dr. Viol states:

"When it was evident that the National Radium Institute was in the field to buy ore, the State Commissioner of Mines in Colorado made public announcement advising the miners to hold their ore for at least \$2.50 per lb.  $U_3O_8$ ."

In this statement Dr. Viol refers to a telegram printed in the *Norwood Post* which was sent under date of December 3, 1915, and signed "CARROLL." Mr. Fred Carroll is the mining commissioner of Colorado, but he did not send the telegram. This he has definitely stated to the Bureau and afterwards in

<sup>1</sup> An error which inadvertently crept into *Bull. 104* may be corrected here. In describing the electric furnace used in experiments on uranium oxide it was stated, page 66, that "the iron pot, cooled with water externally, was used as one electrode and container, the other electrode being made of Acheson graphite." The facts are that the iron pot was simply a container and two Acheson graphite electrodes were used in the form of a double arc therein. The voltage on each arc would therefore be approximately one-half that to be expected from the data on page 67 of the bulletin.

the *Norwood Post*. Mr. Carroll's public denial Dr. Viol conveniently overlooked. The author of the telegram is unknown.

Dr. Viol is quite correct in his statement that it is highly desirable that low-grade ores obtained in connection with the mining of the higher grade ores should be directly and profitably treated. This was one of the chief reasons why the Bureau of Mines undertook its radium investigations. He was present at my lecture at the Chemists' Club in New York on December 17, 1915, and, as usual, correctly quotes me in part only. The Bureau of Mines is using a slightly modified Raymond mill for the concentration of the low-grade ore obtained in connection with regular mining operations. At the Chemists' Club, Dr. Viol stated that ore which he had treated averaged 1.7 per cent (not 1.6 per cent as he now states) uranium oxide and that his company had up to that time extracted 14 grams of radium element. In reply to his question, I answered in the presence of 100 or more of my colleagues that the concentration experiments on low-grade ore were successful, that we were able to treat ore containing 0.8 of 1 per cent uranium oxide, concentrating 6 tons to 1 and obtaining a concentrate of approximately 3 per cent  $U_3O_8$  and that the concentrate so obtained would cost us less per pound of uranium oxide laid down in Denver than the regular ore we had been operating upon. I further stated that methods had been developed for treating this concentrate direct and although it was harder to filter, the difficulty had been overcome by special pressure filters. I further publicly stated that so far as his contention was concerned the Bureau of Mines method could not treat 1.7 per cent ore successfully. I was prepared to say that there was no question if he would furnish the same amount of 1.7 per cent ore, which they had used in producing 14 grams of radium element, at the highest price per ton at which they had purchased a single car-load of this grade of ore, it would be a simple matter to treat the ore for a cost not exceeding \$35,000 per gram of radium element extracted and in my opinion some 16 to 18 grams of radium element could be recovered therefrom instead of the 14 actually produced.

I am rather surprised to note that Dr. Viol acknowledges that the mill for low-grade ore his company built on the San Miguel River in the Paradox, which uses air separation and which cost, according to the statements of the president of his company, approximately \$100,000, has not been a success—especially as the successful concentration mill built by the National Radium Institute has cost less than \$9,500 including repairs. So far as I am able to determine, there are three reasons for this difference in cost and in results. One is the technical control of the mill of the National Radium Institute; another, certain auxiliary arrangements preventing losses of carnotite dust; and the third is that this mill is small and is planned to be moved from one center of low-grade ore to another so that hauling charges to the mill will be minimized.

If statements made to me by persons familiar with conditions in the Paradox are correct, the transportation charges to the large mill built by Dr. Viol's company must be a large item of the cost of treating the 6 tons of ore necessary to yield 1 ton of concentrates. If the details reported to me are correct, the cost of haulage is itself nearly as much as the total cost of concentration at the mill of the National Radium Institute. In my opinion the failure, if such, to obtain commercial results has been due to business reasons of this kind and not to any essential fault in the method of air separation involved which, as Dr. Viol states, was much the same in both instances.

I wish to assure Dr. Viol and any others interested in the production of radium that the treatment of the concentrate from low-grade ores obtained incidental to mining higher grade ores and heretofore wasted, presents no real difficulties. It can be treated successfully by itself. However, the radium

producer who wishes to obtain the greatest profit from a carnotite deposit will continue to separate as much high-grade ore as possible from the low-grade in order to save radium values, for there is a considerable loss of carnotite in any process of mechanical concentration. The most efficient method of operating by the Bureau of Mines process will be to directly treat without concentration all ore rich enough to stand transportation costs to some plant near to the source of the necessary chemicals. There should be mixed with this 20-mesh ore, when treated, the carnotite dust obtained by concentrating at the mine the low-grade ore obtained.

BUREAU OF MINES, WASHINGTON  
March 22, 1916

CHARLES L. PARSONS

### ON SYNTHETIC PHENOL RESINS

*Editor of the Journal of Industrial and Engineering Chemistry:*

The account of the presentation of the Perkin Medal by the New York Section of the Society of Chemical Industry at the Chemists' Club to Dr. Leo Hendrik Baekeland January 21, 1916, as described in *THIS JOURNAL* for February, 1916, from pp. 177 to 190, contains some inaccuracies which have crept into the presentation address and should be corrected, if we are to preserve an accurate record of the scientific and industrial development of synthetic phenol resins. These inaccuracies refer particularly to the discoveries in the art of phenol condensation products.

One method of producing these resins was developed by Dr. Baekeland and the resulting resin he named "Bakelite." This improvement consisted in adding to equal volumes of phenol and commercial formaldehyde (40 per cent) a basic condensing agent in the proportions of less than one-fifth of a mol. of the basic condensing agent per mol. of phenol used. The basic condensing agent was added at the beginning of the reaction. As difficulty was experienced in preventing the escape of formaldehyde at times, counter-pressure was used at the same time that heat was applied to prevent the escape of the formaldehyde gas and to prevent bubbling.

The two steps which resulted in the production of bakelite consisted in adding the basic condensing agent in certain proportions at the beginning of the reaction, in place of adding the basic condensing agent after the reaction had proceeded for a short time in an acid solution as Luft had done, and in the use of increased heat and counter-pressure where it was necessary to prevent the escape of formaldehyde and in this way also preventing porousness or bubbling in the mass due to formaldehyde and water escaping. Luft used an acid condensing agent at the beginning of his reaction, he washed out the acid completely and added a basic condensing agent to finally transform the resin. Dr. Baekeland deviates from Luft's process in one step only. Luft added an acid at the beginning of the reaction and later washed out the acid and added a basic condensing agent, while Dr. Baekeland adds the basic condensing agent at the beginning of the reaction; Luft's process is more rapid and gives the same type of insoluble resins.

With regard to the amount and kind of basic condensing agent which could be used, it will be interesting in this connection to quote Dr. Baekeland's patent No. 942,809, applied for October 15, 1907, renewed application September 17, 1908, and patent granted December 7, 1909. On p. 2, col. 1: "It is therefore essential that the proportion of base should not exceed certain definite limits, and the maximum permissible proportion has been found to be less than one-fifth of the equimolecular proportion of phenolic body present. If larger proportions of base be used there are formed in the mass such amounts of disturbing bodies as serve to render the product technically inferior or worthless for the purposes of this invention."

In view of this point it seems rather remarkable that Dr.

C. F. Chandler in his presentation address should have made the statement found on p. 179, col. 2, line 26: "Instead of formaldehyde, other substances which have the same functions may be utilized, as, for instance, methylal "paraform and HEXAMETHYLENETETRAMINE."

Dr. Baekeland's scientific and patent publications do not show that he was aware that hexamethylenetetramine could be combined directly with phenol until long after we had performed such reaction and the fact was quite generally known. Dr. Baekeland's main process explicitly states that less than one-fifth mol. of the condensing agent must be used per mol. of phenol, and if the nitrogen in the hexamethylenetetramine be calculated and regarded (for argument's sake) as a condensing agent, then hexamethylenetetramine contains 300 per cent more than the maximum permissible proportion for the purpose of his invention. If the nitrogen is not regarded as a condensing agent, then no condensing agent is added. In either case, the use of hexamethylenetetramine clearly does not fall within the Doctor's specific improvement on the well-known wet formaldehyde process. The use of hexamethylenetetramine in the presence of water was mentioned in Wetter's British patent No. 28009 applied for December 19, 1907, and granted July 20, 1908, in which he states: "the 40 per cent formalin may be replaced by the polymerization products as well as by substances which yield formaldehyde, such for example as hexamethylenetetramine;" and, the U. S. Patent Office has ruled against the patentability of claims which would cover such use in wet solution.

The case was argued exhaustively by the contestants in person before the Patent Examiners and the patent office has taken the position and ruled that Dr. Baekeland was not entitled to make claims in which hexamethylenetetramine and phenol are used in the anhydrous condition giving as the *only* by-product ammonia and presenting such a reaction as is completely anhydrous. We may mention here that there is not even a trace of water formed when phenol crystals are used, and *no trace of formaldehyde is formed at any time during the anhydrous process.*<sup>1</sup>

The decision of the U. S. Patent Office was rendered November 11, 1914, on the subject of synthetic resins, interference No. 34995, quoting from the last paragraph: "The claims submitted above cannot be made by Baekeland. . . . because they have elected to claim a process involving the presence of water and because their specifications afford no indication of a distinction between a process in which water is present and one from which water is excluded."

In fact it appears the Doctor was not only not aware of the use of hexamethylenetetramine but even warns against the excess use of ammonia lest hexamethylenetetramine be formed which he mentioned as a detrimental substance. To quote from his patent No. 942,809 granted December 7, 1909, col. 2, line 95: "The proportion of bases used as condensing agents has a preponderant influence on the nature of the ultimate products. For instance, if a large amount of ammonia be used, hexamethylenetetramine is formed, which is a crystalline body of definite chemical properties. Likewise, if large amounts of caustic soda be used there are obtained alkaline derivatives of phenol-alcohol. It is therefore essential that the proportion of base should not exceed certain definite limits, and the maximum permissible proportion has been found to be less than one-fifth of the equimolecular proportion of phenolic body present. If larger proportions of base be used there are formed in the mass such amounts of disturbing bodies as serve to render the product technically inferior or worthless for the purposes of this invention."

To quote Dr. Chandler further on p. 181, col. 1, line 6: "the action of ammonia in presence of formaldehyde in this process is entirely similar to that of the use of hexamethylenetetramine." This cannot possibly be true, as the formaldehyde and ammonia

<sup>1</sup> *THIS JOURNAL*, 6 (1914), 3.



would leave 60 per cent of water present in the reaction which is troublesome at any time. Further it would be impossible to use formaldehyde and a small amount of ammonia in the same way in the reaction where phenol resins are hardened by the action of hexamethylenetetramine. The use of free formaldehyde and a small amount of ammonia makes a resin with a blinding, stifling odor of formaldehyde which can not possibly be used commercially, while the use of hexamethylenetetramine gives an odorless, molding compound which can be used anywhere with the greatest ease. Indeed, it is significant that the phenol condensation products, used for molding, to-day, show the presence of more than two and one-half per cent of ammonia, which indicates that if the ammonia be reckoned as a supposed condensing agent it is used in at least double a fifth of a mol. of the condensing agent to one mol. of phenol.

In Dr. Baekeland's patent No. 1,038,175 on a divisional application filed July 6, 1911, and granted September 12, 1912, lines 78 to 90, Dr. Baekeland adds: "If this base be ammonia, it will immediately react with formaldehyde to form hexamethylenetetramine, as pointed out in my prior U. S. Patent No. 942,809 issued December 7, 1909. So that the technical effect is the same whether hexamethylenetetramine be introduced as such or as a mixture of ammonia and formaldehyde." But this second date of application is subsequent to the work which the writer did in the University of Kansas on hexamethylenetetramine and the patent itself is granted subsequent to many of the patents issued to Aylesworth on the hardening of phenol resins with hexamethylenetetramine, and further in view of the decision of the patent office rendered Nov. 11, 1914, which stated that there was no indication in any of Dr. Baekeland's application that water had been excluded, it becomes impossible to contend further that the Doctor was aware of such a reaction as the use of phenol and hexamethylenetetramine in the anhydrous condition previous to our discoveries.

L. V. REDMAN, A. J. WEITH AND F. P. BROCK

LABORATORIES, REMANOL CHEMICAL PRODUCTS COMPANY  
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## ON THE PRODUCTION OF ALUMINUM

*Editor of the Journal of Industrial and Engineering Chemistry:*

I have noticed in the technical press, references to an address made by Dr. C. F. Chandler and printed in your Journal. The address contains the following:

"Chas. M. Hall, a Perkin medalist, had brought out his beautiful and simple process for extracting aluminum from alumina in 1886, and had given a practically new metal to the world to replace copper, tin, and zinc in many arts."

To the best of my knowledge the above is entirely incorrect. I left the employ of the Cowles Electric Smelting Company January 1, 1887. Hall had at that time not yet come with this Company. I believe he started to work in July, 1887. Romaine Cole was then, and had been for some time, with the company.

When Hall and Cole broke away from the company they attempted to use external heat only and did not produce any aluminum until (1889) they appropriated Cowles' ideas which Heroult and Minet had already appropriated and produced aluminum. Now, as I remember it, using external heating, neither Hall nor Heroult in Europe ever evolved a process that gave an ounce of pure aluminum or that was in any wise different from what Gratzel had been doing three or four years previous at Bremen, where he was employing externally heated crucibles with cryolite and alumina.

In the *Journal of Franklin Institute*, Feb., 1886, pages 118 and 119, there occurs the following:

"The future of the process is one of great promise, and will undoubtedly lead to the production of cheap and pure aluminum itself within a very brief period. Indeed, 'The Cowles Electric Smelting Company' asserts, on the back page of its pamphlet, that it expects to put the pure metal on the market within a year. When you are informed that we can charge iron, man-

ganese, tin, copper, nickel, etc., with a very high percentage of metallic aluminum in this furnace, and that, also, without any base metal in the furnace, we can saturate the charcoal contained therein with metallic aluminum, most of which will be in a state of mechanical mixture with the carbon; and further, that we have produced specimens of aluminum 99 per cent pure in at least three different methods by the electric furnace, and that notwithstanding all this we have not made much of an effort in this direction, the majority of you will agree that the great problem of producing pure and cheap aluminum is practically solved. How cheap this method will be you may judge from the fact that, at our Lockport works, which will have a capacity of only two or three tons per day, we expect to produce the aluminum in bronze with the little silicon contained in it at a cost not to exceed 40 c. per lb., or with copper at 12 c. per lb., the bronze will really cost but about 15 c. per lb.

"In truth, 'The Cowles Electric Smelting and Aluminum Company' is founded upon the faith that ere long we shall be marketing pure aluminum at a cost not exceeding 50 or 60 c. per lb. An appreciation of how cheap this would be, can be had from the fact that one lb. of aluminum would go about as far as three and one-half of copper, it being that much more bulky, and in reality it would be about as cheap as copper at 18 c. per lb., without counting its vast superiority over copper for many purposes on account of its greater lightness and resistance to corrosive influence."

[NOTE—Since the above paper was filed with the Secretary of the Institute, it was found possible to prolong the length of the "heat" of the furnace for five hours, and increase the charges to over 100 pounds in weight, and during the same week a button of cast aluminum, five ounces in weight, was separated from the matrix of carbon, in which it was reduced by a process so simple and economical, that the production of pure aluminum from its oxide by the agency of heat and carbon only, is now demonstrated beyond all question.—E. H. C.]

Cowles at this time was working on aluminum from alumina.

If you are interested in the history of the Cowles, Cole and Hall controversy which took so many years in the courts, and concerning which I believe I talked with you personally (as I was called in from time to time on it and therefore interested), I would refer you to my brother, Cecil L. Saunders, Ithaca, N. Y., who has a large number of letters from Hall to Cole, written during these early years, the contents of which will clear the matter for all time.

Romaine Cole was my brother's brother-in-law, and these letters came to my brother upon Romaine's death, and it is a pity that they were not produced many years before to have settled that tedious heart breaking litigation. I hope the letters will be used.

The above is simply an attempt to set the records straight.

PHILADELPHIA

February 14, 1916

WM. E. SAUNDERS

## ON THE HISTORY OF ALUMINUM

*Editor of The Journal of Industrial and Engineering Chemistry:*

The correct history of the production of aluminum will be interesting to your readers, and a portion of this correct history is found in the excellent translation by Dr. Leonard Waldo, of New York, of the volume entitled "The Production of Aluminum, Etc.," by Adolphe Minet (Officer of public instruction, and Editor of "L'Electrochimie," Paris), in the chapter by Dr. Waldo on "Aluminum in the United States" wherein Dr. Waldo, referring to those "Masters of Fire" the Cowles brothers (Alfred and Eugene) states as follows:

"The testimony of these gentlemen in the long continued patent litigation forms the most important source of history in this connection. A sketch in the notebook of Mr. Eugene H. Cowles dated June, 1883, and bearing the title 'Proposed Electric Furnace for Working Pecos Ores,' contains the essentials of the later patented forms for the smelting of aluminum alloys. The mass of mixed ores for reduction by incandescent heat, the posing inclined carbon terminals, the vents at the top of the furnace, and the tap hole for withdrawing the molten charge, all are present."

Here then was the invention of the incandescent electric furnace and the process of internal heating used therewith whereby aluminum and all high heat products are made.

In fact early in 1886, The Franklin Institute, of Philadelphia, in a long and exhaustive report, awarded the Cowles brothers two gold medals and the Scott legacy premium for their inventions relating to aluminum and among other things set forth, this extended report states as follows:

"This process is applicable to the reduction of all kinds of ores but particularly to those unreducible by other means. "The committee is of the opinion that the Messrs. Cowles and their associates deserve the highest commendation for their inventions, furnishing, as they do, a distinctly new and important metallurgical process."

On presentation of this report to the session of the Franklin Institute the following was adopted.

"Amended to incorporate a recommendation for the award of the John Scott Legacy Premium and Medal to the inventors for their electric smelting furnace; and of the Elliott Cresson Medal, for the invention of a new process in the metallurgical arts for the reduction of refractory substances: and as so amended, adopted."

H. R. HEYL, *Chairman*

Philadelphia, April 7, 1886."

The advance by the Cowles brothers in the production of aluminum, as far back as 1885, is shown by Dr. T. Sterry Hunt of Montreal, Canada, in a paper read by him at the Halifax meeting in 1885 of The American Institute of Mining Engineers as follows:

"But it was reserved to Eugene and Alfred H. Cowles, of Cleveland, Ohio, to take a new step in the metallurgic art by making the (internal) heat thus produced a means of reducing the oxides not only the alkaline metals, but of calcium, magnesium, manganese, aluminum, silicon and boron, with an ease that permits the production of these elements, and their alloys with copper and other metals on a commercial scale."

Dr. T. Sterry Hunt in the same paper stated that he had just spent a number of days in the Cowles brothers' works in Cleveland, in investigations, and in actual direction of one of their furnaces (see pp. 101 to 104 of Exhibits in the aluminum litigation).

In the spring of 1887, Charles M. Hall applied to the Cowles Electric Smelting and Aluminum Company for a position in said company's works, he claiming to have an electric process for the production of aluminum which he wished to develop, and on his representations he was employed in July, 1887, and remained with said company until July 27, 1888, and was given the freedom of the Cowles Company's plant in his experiments and work. At the very beginning of his connection with the Cowles Company in July, 1887, and frequently thereafter the Cowles Company notified Hall that in the Cowles original applications for patents the reduction of alumina with cryolite was mentioned, using therewith an *internally* heated furnace and that they had used that process long before they ever knew of or met the said Hall, and that if Hall proposed to use the alumina-cryolite-*internally* heated process, he would be trespassing on what the Cowles Company claimed as its own. Hall thereupon disclaimed any such use, claiming that his (Hall's) process was by the use of other substances in an *externally* heated crucible. Hall worked with his stated method a full year at the Cowles Company's plant and never in all that time was he able to, nor did he, produce one ounce of aluminum.

At the expiration of Hall's employment, July 27, 1888, Hall went to Pittsburgh, Pa., and organized a company to perfect a process and manufacture aluminum.

Hall continued his external heating process in Pittsburgh for months, and all without success, and until the officers and stockholders of his company bitterly complained at his failure and thereupon Hall changed to the Cowles process of *internal* heating, as shown in Hall's letter to Romaine C. Cole, dated *Pittsburgh, January 8, 1889*, wherein he states he had trouble and that "The electrolyte hardened at the bottom of the pot because it was not hot enough to keep it from hardening." Hall then changed to *internal* heating and states "that has been almost overcome by using carbon sticks which are up in the bath and very hot, for negative electrodes instead of the pot, is avoided entirely."

Also in Hall's letters to Cole dated *January 13, 1889*, and *June 30, 1889*, Hall shows his said change in his method of heating (see complainant's Exhibits of Hall's letters to Cole in the aluminum litigation referred to herein).

When Hall started his company at Pittsburgh and failed to produce aluminum, he secretly hired the said Romaine C. Cole (who was then a metallurgical expert in the employ of the Cowles Company) and also several other employees, heads of departments of the Cowles Company, away from the Cowles Company.

Hall had written the said Cole as follows: "Simple cryolite plus alumina, quickly spoils and is no good."

Hall also later wrote Cole<sup>1</sup> as follows:

"Bradley has recently had a patent issued on 'Fusing and Electrolyzing by the Electric Current.' He has broad claims in the office which may or may not be rejected *which would cover our commercial method of working, and his applications date back to 1883.*

"What makes it more important is that we know that some of Bradley's claims still in the office are allowed."

"Yours hastily,

CHARLES M. HALL"

But Hall, on being shown by the said experts he had hired away from the Cowles Company, the proper way to use said process of alumina and cryolite in conjunction with *internal* heating, as stated to Hall, by the Cowles Company as said Company's process, under patent owned by said Cowles Company and so stated while Hall was in the employ of said Cowles Company in 1887 and 1888. Thereupon, in 1889 Hall adopted said process bodily and it was for the use of *this identical process* that Hall's Company (The Pittsburg Reduction Company, now the Aluminum Company of America) was defeated and enjoined from further manufacturing aluminum, by the U. S. Circuit Court of Appeals, sitting in the City of New York, in the suit of The (Cowles) Electric Smelting and Aluminum Company, against said Hall's Company, in which case the Court held as follows:

"The process patented to Hall adopts *external* heat to produce fusion" (125 Federal Reporter, 934).

As to the patent owned by the Cowles Company, the Court held:

"Its process is not confined to cryolite or aluminum: it relates to all ores or compounds of aluminum and all other refractory ores of like type. Cryolite is mentioned as an illustration in the specification but it might as well have mentioned alumina or any other similar ore. That there is nothing in the patent or out of the patent, requiring the limitation to cryolite seems too plain for debate. The process may be used with cryolite alone or alumina alone or *both together* whether applied synchronically or successively. *In either case the essential features of the process are appropriated*" (125 Federal Reporter, 935).

On the issuing of said injunction there was done what is stated on page 1081 of the December (1915) number of THIS JOURNAL, namely:

"A settlement was arrived at between the two companies wherein the Hall Company paid the Cowles Company a large sum for past infringement and a royalty on all aluminum to be produced up to the end of the life of the Bradley (Cowles Company's) patent. The Bradley patent being held to dominate the Hall patent and process, made it impossible for the Hall Company to continue in business without coming to an agreement with the Cowles Company."

All of the foregoing are matters of record, and clearly show that Hall was *not* the inventor of the "process for extracting aluminum from alumina," and laymen, who are not familiar with the full facts fall into the error of believing and stating that Hall was the inventor of the process for so producing aluminum, as did Dr. C. F. Chandler who is quoted in the February, 1916, numbers of several technical journals as using the following language in a presentation address of the Perkin Medal to Dr. Baekeland before the Society of Chemical Industry, to wit:

<sup>1</sup> See complainant's "Exhibits in the Aluminum Litigation"



"Charles M. Hall, a Perkin Medalist, had brought out his beautiful and simple process for extracting aluminum from alumina, in 1886, and had given a practically new metal to the world to replace copper, tin and zinc in many arts."

Simple justice demands that such errors should be corrected. For *above it is shown that Hall never made an ounce of aluminum before 1889*, for in a letter to Leonard Waldo, Esq., dated "Oberlin, O., August 20, 1888," set forth in the exhibits in said litigation, Hall states as follows:

"I am not doing anything at present regarding the production of pure aluminum, but am waiting mainly to get my patent matters in better shape. My patents are not yet issued and are, if I may use the expression 'in the woods.'"

As shown heretofore by Hall's letter to Cole, Hall admitted that the Bradley patent dominated his process, and the U. S. Circuit Court of Appeals also so found and held, as quoted from the Court's opinion above, and it is therefore clear and unanswerable that Dr. Chandler's erroneous and unsupported statement is to be held as naught; and should any further proofs be desired reference is also hereby made to Charles M. Hall's admissions in his cross-examination, between pages 724 and 753 of defendant's testimony in the aforesaid case, and also to all the admissions by Hall in all the letters set forth as exhibited in said case.

FRANCIS C. McMILLIN

General Counsel for the (Cowles) Electric Smelting and Aluminum Company

111 BROADWAY, NEW YORK CITY  
March, 1916

#### NOTE ON THE DETECTION OF FAULTY SIZING IN HIGH-GRADE PAPERS

*Editor of the Journal of Industrial and Engineering Chemistry:*

Reference is made by Herzberg<sup>1</sup> to the test for the detection of faulty sizing in high-grade papers,<sup>2</sup> in which he states that the method is not new and is similar to that of Klemm.<sup>3</sup>

Herzberg has apparently overlooked the actual principle upon which the method is based.

In the proposed method the paper is carefully drawn over the surface of an iron tannate ink and allowed to drain and dry. This procedure differs considerably from that of Klemm, in which the paper is allowed to float for a longer period of time and the excess ink subsequently blotted off. The inked as well as the reverse side of the paper is judged for uniformity of color, the time it takes should the ink strike through, and whether it has come through uniformly. From this appearance it is possible with experience, to judge the sizing quality.

Should it be desired to test a paper for its writing quality only, Klemm claims that ten minutes' floating on the ink, examining both the wire and top side, is sufficient. The appearance of the inked and reverse sides is noted for the characteristics above mentioned, and if the ink does not penetrate the sheet, it is considered properly sized for all practical purposes.

Should it be desired to make further distinctive tests Klemm says it is only necessary to float the paper for intervals of 2, 5, 10, 20, 30 and 60 mins. and examine as before, from which most instructive results can be obtained.

In the proposed method the new and distinctive feature is in the examination of the individual fibers under a magnifying glass to observe the absorbed ink. It is upon the absorption of the ink by the fibers and not upon the appearance of the surface as a whole that the accuracy of this test depends and upon which claim for its originality and superiority is based.

The possible results which Klemm may obtain by his procedure do not approach the refined distinctions in sizing quality between two well-sized papers that the proposed method will

bring out. Uniformity of color is not the best criterion for distinguishing the sizing quality. The depth of color of the inked surface is far more differentiating, as has been mentioned in *Circular 107*. Furthermore, in the procedure of Klemm there are many factors which may influence the results, such as the amount of ink, the evaporation, the formation of the sheet, the moisture in the paper, its weight, loading, and thickness. The proposed method is largely independent of the variations which may be caused by these factors as it deals entirely with the appearance of the fibers on the surface of the paper, and as has been stated, "Upon examining the inked surface with a magnifying glass it will be found that a well-sized paper will show no indication of the fiber having absorbed the ink, \* \* \*

The experiences of many who have used this method properly have shown it to give distinctions in the quality of sizing where other methods have failed.

LEATHER AND PAPER LABORATORY  
BUREAU OF CHEMISTRY, WASHINGTON  
March 14, 1916

C. FRANK SAMMET

#### METHOD FOR DETERMINATION OF HARDNESS

*Editor of the Journal of Industrial and Engineering Chemistry:*

Referring to the note "Method for Determination of Hardness," THIS JOURNAL, 8 (1916), 281, the writer begs to state that the method described is not a French invention, but is the product of American brains. It is covered by U. S. Patent No. 1,125,912, issued January 19, 1915, to Messrs. Albert Ringland and Frank H. Schoenfuss, of Philadelphia. This patent covers "The method of ascertaining the Brinell hardness of a piece to be tested, which consists in placing a ball between said piece and a standard piece of known Brinell hardness, applying a force to the assemblage to produce a ball depression in each piece and then comparing the depressions and thereby ascertaining the Brinell hardness of the piece to be tested."

It will readily be seen that this method is a very clever scheme to extend the application of the accurate Brinell method to metal pieces which cannot be placed into the Brinell machine; it permits accurate Brinell hardness determinations of metal masses of practically any size or shape, and in any place or structure. The proportion of the two ball indentations used for comparative measurements is an absolutely direct one, independent of the pressure applied. It is varying directly as the spherical areas of the two impressions, consequently varying directly as the squares of the diameters of each impression. On basis of this proportion, a table can be easily worked out, which will give the Brinell hardness for any readings.

HERMAN A. HOLZ

50 CHURCH STREET, NEW YORK  
March 15, 1916

#### COPIES OF JANUARY AND FEBRUARY ISSUES OF OUR JOURNALS WANTED

*Editor of the Journal of Industrial and Engineering Chemistry:*

Owing to the rapid increase in membership of the American Chemical Society, the early issues of the 1916 journals are already practically exhausted. Two hundred and seventy (270) more members have been elected in the early months of this year than in 1915; accordingly, the plans for publication were underestimated and the Secretary is now advertising for these numbers.

Members not binding their journals will convey a great favor by returning to the Secretary's office any January and February issues of any of the Society's publications that they can spare. The numbers especially wanted are the January and February issues of both the *Journal of the American Chemical Society* and *Journal of Industrial and Engineering Chemistry*, and the January 20, 1916, issue of *Chemical Abstracts*.

CHARLES L. PARSONS, Secretary

BOX 505, WASHINGTON, D. C.  
March 24, 1916

<sup>1</sup> Mitt. kgl. Material-prüfungsamts, 11 (1915), 130.

<sup>2</sup> Bureau of Chemistry, Circ. 107.

<sup>3</sup> Handbuch der Papierkunde, 1910, 312.

## PERSONAL NOTES

Harry Clary Jones, professor of physical chemistry at Johns Hopkins University, died suddenly at his residence in Baltimore on April 9th, aged 51 years. Professor Jones received his Ph.D. degree from Johns Hopkins in 1892 and later studied in Leipzig, Amsterdam and Stockholm. He returned to Johns Hopkins in 1895 as an instructor in physical chemistry and in 1904 he became a professor. Prof. Jones was a member of the American Chemical Society, the American Physical Society, the American Philosophical Society, and the Washington Academy of Sciences. He was Langstreth medalist of Franklin Institute in 1913.

The Willard Gibbs Medal, founded by William A. Converse, of Chicago, was been awarded to Dr. Willis Rodney Whitney, director of research laboratories of the General Electric Company, Schenectady, N. Y. The presentation will be made on May 19th, in connection with the meeting of the Chicago Section of the American Chemical Society, when Dr. Whitney will make an address on "Incidents of Applied Research."

Arthur D. Little, of Boston, has been retained by the Canadian Pacific Railway to establish a central organization for research work to carry out Lord Shaughnessy's proposal for a scientific investigation of Canada's mineral, metal, hydro-electric and chemical resources, and to stop waste in forests, mines and mills. The new organization will be known as the Canadian Research Bureau.

The United States Civil Service Commission announces the following open competitive examinations: *Assistant petroleum chemist*, for men only, salary \$1,800 per annum, on May 16, 1916; *assistant alloy chemist*, for men only, salary \$1,620 per annum, on May 17 and 19, 1916; *laboratory aid in chemistry and physics*, for men and women, salary \$600 to \$900 per annum, on May 3 and 4, 1916; *chemist*, for men only, salary \$1,200 a year, on June 7, 1916. Further information may be had from the United States Civil Service Commission, Washington, D. C.

Dr. Charles Holmes Herty, president of the American Chemical Society, delivered an address on "Chemistry as an Aid to the Efficiency of Democracy," before the Indiana Section of the A. C. S., on April 21st.

Columbia University will hereafter confer the degree of Master of Science upon graduate engineering students who satisfactorily complete the graduate course in Highway Engineering. From 1911 to 1915, the graduate engineering students who have specialized in Highway Engineering have been candidates for the degree of Master of Arts.

Mr. Walter E. Lummus, distillation engineer, of Boston, has recently incorporated his company which is now known as The Walter E. Lummus Company, and has moved from 88 Broad Street to 173 Milk Street, Boston, where he has taken more than twice the space formerly occupied and has added to his staff in order to properly handle the increasing business. Mr. Lummus provided increased manufacturing facilities last year.

The Dorr Company, with offices in New York, Denver and London, is successor to The Dorr Cyanide Machinery Company, taking over the patents and commercial business of its predecessor. John V. N. Dorr is president of The Dorr Company.

Arthur Lowenstein has resigned his position as technical director of Morris & Company, and is now engaged in practice as a consulting chemical engineer at 1723 First National Bank Building, Chicago.

Alfred W. Bosworth, associate chemist at the New York Agricultural Experiment Station, has been appointed biological chemist for the Boston Floating Hospital.

A fire on March 24th, believed to have been due to a blazing burner, damaged the Harrison Chemical Laboratory building at the University of Pennsylvania to the extent of \$1,000.

Horace Bowker, of Boston, has been elected a director of the American Agricultural Chemical Company, succeeding the late W. H. Bowker.

The Franklin Institute has awarded the Elliott Cresson Medal to Dr. Robt. Gans, of Germany, for his Permutit.

Grinnell Jones has been appointed assistant professor of chemistry in Harvard University.

Dr. Otto Diels, of Berlin, has been called to the chair of chemistry at Kiel.

Dr. R. Willstätter, professor of chemistry at Berlin, has been elected a foreign member of the Swedish Academy of Sciences.

Sir Thomas H. Holland, F.R.S., professor of geology in the University of Manchester, has been appointed chairman of a commission which the British Government is forming to survey the economic resources and industrial possibilities of India, with a view to promoting business after the war.

Mr. C. S. Gibson, of Sidney Sussex College, England, has been appointed assistant to the professor of chemistry at the University of Cambridge.

The authorities of Oxford University, England, intend shortly to change the system of examination for an honors degree in chemistry. It is proposed that research be introduced as an essential towards the obtaining of a degree.

Mr. Ivan Levenstein, of the well-known Manchester firm of aniline dye manufacturers, died on March 15th at his residence in Cheshire, England, at the age of 70 years.

Mr. A. V. Hill, Humphrey Owen Jones lecturer in physical chemistry at the University of Cambridge, has been elected a fellow of King's College.

The eighth semi-annual meeting of the American Institute of Chemical Engineers will be held in Cleveland, Ohio, June 14-17, 1916.

The plant of the Carcolite Chemical Company, at Copper Hill, Tenn., which is controlled by the Tennessee Copper Company, is to be rebuilt. It was recently destroyed by fire, the loss exceeding \$250,000.

Dr. E. C. Bingham, who for the past few years has been professor of chemistry in Richmond College, Richmond, Va., is spending the year 1915-16 in the Bureau of Standards, Washington, D. C.

Dr. Garrett Ryland has been made professor of chemistry at Richmond College, Richmond, Va.

Mr. M. F. Lindsley spoke on "The History, Characteristics and Methods of Manufacture of Modern Explosives," before the regular meeting of the Cincinnati Section of the A. C. S., on April 12th.

Dr. Frederick H. Wagner, of the Bartlett, Hayward Company, gave an illustrated lecture on "Coal Gas Residuals," at the 13th regular meeting of the Maryland Section of the A. C. S., on April 15th.



# GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

## GEOLOGICAL SURVEY

**Ground Water in Lasalle and McMullen Counties, Texas.** ALEXANDER DEUSSEN AND R. B. DOLE. Water Supply Paper 375-G, from Contributions to the Hydrology of the United States, 1915, pp. 141-73; published February 17, 1916. This report includes a discussion of the general characteristics of water and the relation of the quality to geologic strata and the geographic position. The desirable characteristics of water for domestic use, for irrigation, and for boiler use are discussed and a tabulation of analyses of water from these districts is included.

## DEPARTMENT OF AGRICULTURE

**Milling and Baking Tests of Wheat Containing Admixtures of Rye, Corn Cackle, Kinghead and Vetch.** R. C. MILLER. Department Bulletin 328. 24 pp. Paper, 10 cents. "The results of these tests show that the presence of more than 2 per cent of any of these impurities in wheat as milled has detrimental effects on the milling and baking qualities."

**Utilization of American Flax Straw in the Paper and Fiberboard Industry.** JASON L. MERRILL. Department Bulletin 322. 24 pp. Paper, 5 cents. This report gives an account of recent work regarding utilization of straw from American seed-flax. It is of interest to chemists and manufacturers as well as to flax farmers.

**Fermented Milks.** L. A. ROGERS. Department Bulletin 319. 31 pp. Paper, 5 cents. This bulletin describes the various forms of fermented milks, discusses their food value and gives a bibliography on the subject.

**The Milling of Rice and Its Mechanical and Chemical Effect upon the Grain.** F. B. WISE AND A. W. BROOMELL. Department Bulletin 330. 31 pp. Paper, 10 cents.

**The Present Status of the Pasteurization of Milk.** S. HENRY AYERS. Department Bulletin 342. 16 pp. Paper, 5 cents.

**The Utilization of Cherry By-Products.** F. RABAK. Department Bulletin 350. 24 pp. This article describes investigation made to determine methods for the application of materials now waste products in the cherry industry. Applications for fixed and volatile oil, meal and juice are discussed.

**Boron: Its Absorption and Distribution in Plants and Its Effect on Growth.** F. C. COOK. Journal of Agricultural Research, 5 (Feb. 7), 877-90.

**Relation between the Properties of Hardness and Toughness of Road-Building Rock.** PREVOST HUBBARD AND F. H. JACKSON, JR. Journal of Agricultural Research, 5 (Feb. 7), 903-7.

**Nitrogen Content of the Humus of Arid Soils.** FREDERICK J. ALWAY AND EARL S. BISHOP. Journal of Agricultural Research, 5 (Feb. 14), 909-16.

**Some Factors Influencing the Longevity of Soil Microorganisms Subjected to Desiccation, with Special Reference to Soil Solution.** WARD GILTNER AND H. VIRGINIA LANGWORTHY. Journal of Agricultural Research, 5 (Feb. 14), 927-42.

**Apparatus for Measuring the Wear of Concrete Roads.** A. T. GOLDBECK. Journal of Agricultural Research, 5 (Feb. 14), 951-4.

**A Method of Correcting for Soil Heterogeneity in Variety Tests.** FRANK M. SURFACE AND RAYMOND PEARL. Journal of Agricultural Research, 5 (Feb. 28), 1039-50.

**Chemical Testing of Milk and Cream.** ROSCOE H. SHAW. Unnumbered publication from the Bureau of Animal Industry; issued February 17, 1916. 38 pp. This report gives complete simple laboratory instructions for determination of fat, total solids, specific gravity and acidity of milk and cream and gives directions for calculating total solids by formula and for the detection of preservatives. A list of chemicals and apparatus necessary for this analytical work is given. The whole constitutes a virtually primer of milk-testing methods.

## BUREAU OF MINES

**Economic Methods of Utilizing Western Lignites.** E. J. BABCOCK. Bulletin 89. 67 pp. Paper, 15 cents. "The purpose of this bulletin is to present a summary of the results thus far obtained in the work done at the college of mining engineering and at the mining substation of North Dakota, and to indicate the prospects that the results hold out for the future development of the lignite fields of the West.

"In this work special attention has been paid to the production of gas and its utility and economy for heating, lighting, and power purposes and the manufacture of briquets. In addition, many other improvements in methods of burning and utilizing lignite have been attempted. As the Federal Government controls great tracts of land underlain with lignite, it has a direct interest in the utilization of this fuel, and the Bureau of Mines, in its investigations of fuels belonging to or for the use of the Government, has cooperated in the study of lignite.

"What has been accomplished in this experimental work leads to the belief that great improvements can be made in the methods of utilizing lignite and in the manufacture of cheap gas for power and other purposes, and that the making of high-grade fuel briquets can be put on a commercially satisfactory basis. The result will be that not only will lignite be much more serviceable and much more generally used, but an immense quantity of slack and coal that would otherwise be wasted will be saved.

"Furthermore, by the process described in this bulletin, large quantities of gas, especially valuable for power purposes, may be obtained at a low cost, as the work thus far carried on indicates that this gas can be used successfully with an internal combustion engine for the production of electricity so as greatly to reduce the cost of power production and thus make possible a wide utilization of cheap electricity for industrial purposes."

The methods of handling lignite and of briquet manufacture and testing which have been found most desirable are described, including the machinery and commercial equipment needed for this work.

**Manufacture of Gasoline and Benzene-Toluene from Petroleum and Other Hydrocarbons.** W. F. RITTMAN, C. B. DUTTON AND W. E. DEAN. Bulletin 114. 268 pp. Paper, 35 cents. (The free supply of this publication is exhausted, copies can be secured only through the Superintendent of Documents

at the price named.) For an extended abstract of this Bulletin see *THIS JOURNAL*, 8 (1916), 351-61.

The full paper includes an extended bibliography of the subject which has been compiled by M. S. Howard.

#### BUREAU OF STANDARDS

**Value of the High-Pressure Steam Test of Portland Cements.** R. J. WIG AND H. A. DAVIS. Technologic Paper 47. 34 pp. Paper, 15 cents. "The investigation reported in this paper was made to establish, if possible, a relationship between the behavior of Portland cements in high-pressure steam and their physical properties under normal conditions of use and exposure, and to determine what value, if any, the high-pressure steam test has as a means of detecting unsoundness which might cause a weakening or disintegration of the cement or concrete.

"For practical work under normal conditions of construction, the results of this investigation fail to show that the high-pressure steam test is of value as a means of determining the ultimate soundness of concrete."

**Standard Test Specimens of Zinc Bronze. Part I. Preparation and Specifications.** C. P. KARR. Technologic Paper 59. Pp. 1-45. Paper, 25 cents. "For the present investigation the following tests were finally decided upon to be carried out in connection with the methods of preparing the alloy:

"1—Experiments to determine the best form of test block and test piece.

"2—Tests to determine the best casting temperature, to be made after the best form of test block and test piece have been determined.

"3—Tests of the following sorts on all the bars cast for the tests Nos. 1 and 2 above: (1) Tensile test, including the determination of elongation, reduction of area, and tensile strength, and recording of the stress-strain curve; (2) compression test; (3) study of microstructure; (4) thermal analysis.

"With the exception of the compression tests, this program has been carried out as planned.

"The operations of casting and molding, etc., as well as the experiments on the variations in foundry practice, are described in considerable detail, so that the exact bearing of the results obtained may be the more readily appreciated, and for the reason, well known to practical foundrymen, that minute variations in seemingly insignificant details are often crucial in determining the resulting properties of the cast metal."

Appendix A gives complete set of suggested specifications for preparation of standard zinc bronze test bars.

**Part II. Microstructure.** HENRY S. RAWDON. Technologic Paper 59. Pp. 47-67. Included with above publication, in paper, 25 cents. "The general conclusion from the study of the microstructure is that the presence of oxides is a much more potent source of mechanical weakness of the alloy in its cast condition than any of the other causes enumerated. From the standpoint of microstructure, the variations in methods of casting, pouring temperature, etc., are to be regarded primarily as means for the production of sound oxide-free material and to confer no mysterious properties upon the alloy. The frequent occurrence of oxides in this series, prepared under careful supervision and using precautions for avoiding such contaminations, suggests the abundance of such inclusions in similar alloys as prepared commercially. The failure of such cast alloys for many purposes is most probably to be ascribed to the presence of oxide films rather than to any other cause."

From this investigation the following conclusions are drawn:

"(a) The addition of the small percentage of zinc does not affect the theoretical microstructure of the alloy.

"(b) The method of casting, pouring temperature, etc., affect the structure only indirectly by influencing the rate of cooling, amount and distribution of inclusions, etc.

"(c) The microstructure offers an explanation for the characteristic appearance of the tensile bars after testing.

"(d) Of the various microstructural features affecting the physical properties, oxide films must be considered to exert the greatest influence, by far.

"(e) The changes of microstructure accompanying annealing are explained and illustrated."

**Determination of Carbon in Steels and Irons by Direct Combustion in Oxygen at High Temperatures.** J. R. CAIN AND H. E. CLEAVES. Technologic Paper 69. 10 pp. Paper, 5 cents. Published practically in full, *THIS JOURNAL*, 8 (1916), 321-4.

#### PUBLIC HEALTH SERVICE

**Vitamines and Nutritional Diseases.** A. SEIDELL. Public Health Reports, 31 (Feb. 18, 1916), pp. 364-9. Available also as a reprint. This article reports on a stable form of vitamine, which is efficient in the prevention and cure of certain nutritional deficiency diseases. The source of the material is the waste brewers' yeast which appears to be rich in the valuable constituents.

**Publicity of Formulas of Package Medicines.** MARTIN I. WILBERT. Public Health Reports, 31 (March 17, 1916), pp. 711-14. This is a discussion of recent legislation and the nature of requirements which are effective in affording reasonable publicity as to the exact composition of proprietary drugs. It is argued that the value of published formulas is so great as to fully justify this publicity.

#### SANITARY LEGISLATION

**Poisons and Habit-Forming Drugs.** MARTIN I. WILBERT. Public Health Reports, 31 (Feb. 25, March 3 and 10, 1916), pp. 468-511, 551-610, and 651-703. This is a long report which consists of a digest of laws and regulations, which have been enacted during 1914 and 1915 in the United States, regulating the possession, use, sale, and manufacture of poisons and habit-forming drugs. The material is presented as a third supplement to Public Health Bulletin 56. The preceding supplements are available as reprints of the Public Health Service Nos. 146 and 240.

**Selling Foodstuffs Containing Arsenic.** Public Health Reports, 31 (March 3, 1916), p. 550. This is a report on the case of *Weeks v. United States*, 224 Fed. Rep. 69, in which the United States Circuit Court of Appeals decided that a conviction was justified for selling shellac varnish for use in glazing cheap candies even though it appeared improbable to the person selling the material that the quantity of arsenic was sufficient to be injurious to the health. The sales company claimed that the quantity was not sufficient to be deleterious to health under any ordinary conditions but the findings of the jury as to this question were of the opposite import. It was held that the jury should properly determine this question.

**Regulation of Industries in which Poisonous Fumes or Dusts May Be Produced.** Illinois Legislature Act, June 29, 1915. Public Health Reports, 31 (March 17, 1916), pp. 746-51. This regulation makes certain provisions as to the prevention of industrial diseases which result in factories and elsewhere because of the fumes and dust produced. The requirements are of interest to chemical works affected.

**Efficacy of Antiseptic Dressing for Floors.** Louisiana Board of Health Regulation, January 18, 1915. Public Health Reports 31 (March 17, 1916), p. 759. This regulation specifies that manufacturers and dealers submitting floor dressing for



use in schools must give to the State Board of Health satisfactory evidence from reputable bacteriologists and must submit a guarantee that the materials are efficient for the purposes for which they are sold.

**Production, Care, and Sale of Milk and Milk Products.** Revised Regulations of Louisiana Board of Health, June 15, 1915. Public Health Reports, 31 (Mar. 17, 1916), pp. 755-8.

**Standards for Viruses, Serums, Toxins, and Analogous Products.** Regulation 104, Minnesota Board of Health, adopted November 14, 1915. Public Health Reports, 31 (March 24, 1916), p. 793. This regulation forbids the use of any of these products for therapeutic purposes, if their efficacy has been disapproved by the United States Public Health Service.

**Labelling Articles Containing Wood Alcohol.** Act of the Rhode Island Legislature, adopted March 12, 1915, Chap. 1183. Public Health Reports, 31 (March 24, 1916), p. 814. The conditions under which methyl alcohol can be used in articles sold for external or internal use are prescribed.

#### COMMERCE REPORTS—MARCH, 1916

A plant for the production of **soda ash** and by-products is to be established in Holland. (P. 833.)

**Manganese ore** is now being shipped from Colon, Panama, to the United States. (P. 839.)

The provisions of the recent Japanese law for the subsidizing of companies for manufacturing **dyes** and **drugs** are given. (P. 874.)

Efforts are being made to develop, under government supervision, the mining resources of Hupeh Province, China, especially **iron**, **coal**, **lead** and **copper**. (P. 887.)

In a recent British process, wool is being **dyed** various shades of yellow and khaki color, by treatment with nitric acid (about 5 percent  $\text{HNO}_3$ ) at a temperature of  $180^\circ \text{F.}$ , and subsequent immersion in alkali, or alkaline mordants. (P. 898.)

Among the native drugs exported from Siam are **gum**, **benzoin**, **gamboge**, **cutch**, **cardamoms**, **licorice**, **turmeric**, and **sesame**. (P. 916.)

The Chilean **nitrate** industry continues to improve. (P. 918.)

The saving and collection of rags and old paper are urged in order to relieve the present shortage of **paper stock**. (P. 929.)

Efforts are being made to develop the production of **tanning extract** from Brazilian **mangrove**. (P. 935.)

An experimental **electric copper smelter** with a capacity of 12 tons of ore per day is being tried out in Newfoundland. (P. 950.)

Owing to the demand for **natural dyes**, the production of **cutch**, used for both dyeing and tanning, is increasing in Borneo. (P. 958.)

The price of **camphor** in Japan shows a marked increase. (P. 979.)

A serious shortage of **wood pulp** exists in Spain. (P. 981.)

Barrels for the shipment of **sugar** are being made in Hawaii from fiber board produced from bagasse. (P. 984.)

A proposal is made to **cast sewer pipes** and **bricks** directly from molten lava in Hawaii. (P. 994.)

Conditions in the **cement industry** of Silesia are distinctly unfavorable. (P. 998.)

Recommendations of a committee of the British Board of Trade include protective tariff upon **paper**, **silverware**, **cutlery**, **glass** and **earthenware**. (P. 1000.)

The new **mining law** of Chosen (Korea) restricts new claims

to Japanese subjects, and foreigners acquiring old claims must have their head office in Chosen. (P. 1003.)

It is predicted by the U. S. Geological Survey that the **oil shales** of Colorado, Utah, and Wyoming will provide a large part of the gasoline and other oils for this country. (P. 1007.)

Abundant quantities of **rock-crystal** are available in Brazil. (P. 1070.)

The Bureau of Standards is investigating the danger involved in the **filtration of gasoline** through chamois, etc., due to the production of an electrical charge, which may give rise to a spark. (P. 1125.)

A decrease in the output and consumption of **coal** in British Columbia is attributed to the increasing use of imported **fuel oil**. (P. 1126.)

**Calcium carbonate** made in this country has been found to be a satisfactory substitute for English **whiting** for use in **ceramic glazes** and **bodies**. New domestic sources for glass pot and crucible **clays** have been discovered. (P. 1131.)

The U. S. Geological Survey will have this year twelve parties studying the **mineral** and **water power resources** of Alaska. (P. 1133.)

The **mineral production** of Canada in 1915 shows an increase for all metals except silver; and a decrease in building materials. (P. 1136.)

In stating the opportunities for labor-saving machinery in the Chilean **nitrate** beds, the present methods of operation are desired. (P. 1144.)

A new English method for recovery of **grease** and **potash** from **wool scouring liquors** involves separation of the free grease by centrifuging and repeated use of the liquor till it contains 6-8 per cent of potash, when it is evaporated for recovery of the potash. (P. 1172.)

The German Government is taking measures to increase the **sugar beet** cultivation in that country. (P. 1187.)

In order to provide a supply of **tungsten**, the British Government has taken over all stocks of tungsten ores in British colonies. (P. 1191.)

The new edition of the U. S. Pharmacopoeia will make use of the **metric system** exclusively. (P. 1208.)

The greatly increased production and export of **porcelain**, etc., from Japan has necessitated the introduction of improved methods and machinery. (P. 1218.)

Normally most of the **platinum** output of Colombia is exported to England, but in 1915 over 11,000 ounces were exported to the United States. (P. 1219.)

Recent observations of the Bureau of Standards upon concrete roads confirm their previous conclusion, that **concrete** expands in winter and spring owing to increase of moisture content, and contracts in summer due to loss of moisture. (P. 1223.)

Large quantities of **dyewoods** are available in Santo Domingo, especially fustic and logwood. (P. 1254.)

**Supplements** issued in March are 5a France, 23b British Columbia.

#### STATISTICS OF EXPORTS TO THE UNITED STATES. (Pp.)

FRANCE	Sup 5a	BRITISH COLUMBIA— Sup. 23b	STRAITS SETTLEMENTS —1175
Albumen		Gold	Benzine
Aluminum		Cascara	Gambier
Bones		Fertilizer	Gum copal
Chemicals		Fire-brick	Gum damar
Pottery		Drugs	Gutta jelutong
Drugs		Glassware	Gutta-percha
Glue		Hides	Mangrove bark
Glycerine		Rubber	Rubber
Hides		Lime	Tin
Soap		Copper ore	
Platinum, etc		Potash	
Saffron		Whale oil	

## BOOK REVIEWS

**Transactions of the American Institute of Chemical Engineers.** Vol. VII (1914). Office of the Secretary, Cooper Union, New York, N. Y. Published by the Institute through D. Van Nostrand Company, New York, 1915. 8vo. iii + 308 pp.

The seventh volume of these Transactions is somewhat larger than its predecessor. This is because of the greater average length of the papers published and because an unusual number of illustrations are included in the volume. Many of these have never been previously published elsewhere and cover operations hitherto unpictured. The volume is printed on a better surfaced paper than customary with the series and, therefore, does justice to the illustrations. In other respects it is built and arranged like the preceding one except that some committee reports are included, for the first time in three years. In this case they are the previously omitted reports of progress of the Institute's Committee on Chemical Engineering Education.

The following addresses, reports and papers read before the Institute are contained in the publication:

- "Some Professional Obligations," M. C. Whitaker.
- "Distribution of Industrial Opportunities," G. O. Smith.
- "Report of the Committee on Chemical Engineering Education."
- "The Present Status of the Chemical Engineering Work of the American Institute of Chemical Engineers."
- "Report of the Committee on Chemical Engineering Education."
- "The Need of Revised Chemical Statistics," B. C. Hesse.
- "The Application of Physical Chemistry to Industrial Processes," W. F. Rittman.
- "The Use of Hydrometallurgical Apparatus in Chemical Engineering," J. V. N. Dorr.
- "Studies on Filtration," J. W. Bain and A. E. Wigle.
- "Scrubber for Chemical Laboratory Vacuum System," C. Baskerville.
- "Shoddy and Carbonized Waste," L. J. Matos.
- "Chemistry of the Bleaching of Cotton Cloth," J. C. Hebden.
- "Ozone in Ventilation," J. C. Olsen and Wm. H. Ulrich.
- "The Present Patent Situation," M. Toch.
- "The Development of the Rotary Kilm and Its Application to Various Chemical and Metallurgical Processes," R. K. Meade.
- "A Combination Water Softener and Storage Tank," L. M. Booth.
- "Feldspar as a Possible Source of American Potash," A. S. Cushman and G. W. Coggeshall.
- "The Hardwood Distillation Industry in America," E. H. French and J. R. Withrow.
- "Painting Defects, Their Causes and Prevention," G. W. Thompson.
- "Code of Ethics."

This volume illustrates like its predecessors the Institute's varied interests. The address of the retiring president, Mr. Whitaker, on "Some Professional Obligations," bears much food for thought and should be read by every chemist as well as chemical engineer. The need of revised chemical statistics, greatly accentuated by present conditions, is clearly emphasized by Dr. Hesse and it is to be regretted that the Institute was unable to secure the services of Dr. Hesse as chairman of its committee to assist in ameliorating the present condition of chemical statistics. The paper by Dorr on the possibilities in the use of his well-known hydrometallurgical apparatus in chemical engineering will mark a new epoch in chemical engineering progress. This will take time and patient development but bids so fair that we have wondered for years why chemical engineers in certain lines did not give these devices more attention. The paper by Thompson is in his well-known thorough style. A distinct contribution to the bleaching problem is made by Hebden. The other papers in the list are enrichments of the literature and should encourage others to open their hearts and tell the details of their industries in turn for the benefit of general development.

JAMES R. WITHROW

**The Metallography and Heat Treatment of Iron and Steel.** By ALBERT SAUVEUR. Second Edition. 486 pp., 438 illustrations. Sauveur & Boylston, Cambridge, Mass.: Price, \$6.00.

This second edition of Sauveur's "Metallography of Iron and Steel" is a complete revision, some fifty pages of text and

about 100 new illustrations having been added. The first 85 pages deal with apparatus for the metallographic laboratory and their manipulation, the methods of preparation and of etching specimens, etc.

Chapter IV, on pure metals, takes up their structure, the effect of strain and of annealing, and explains very clearly the amorphous cement theory of Beilby and Rosenhain, Twinning, Neumann lines. Next the structure of pure iron is explained, followed by chapters on wrought iron, low-carbon, medium, and high-carbon steel. Of very great interest is the chapter on the impurities in steel. Some 50 pages discuss the critical points of iron and steel, their causes and effects. Next comes the structure of cast steel, the effect of hot and cold work, the annealing and hardening and the tempering of steel with a short, clear presentation of the various theories of hardening. Cementation and case-hardening are followed by an excellent discussion of alloy steels. Cast iron, its impurities and their effects on structure; malleable cast iron and its course of changes are then dealt with. On page 396, in discussing the proximate chemical analysis of cast iron of 2 per cent Si, the whole of this is set down as FeSi, instead of Fe<sub>3</sub>Si. All of the manganese is taken as combining with the S and the carbon to form MnS and Mn<sub>3</sub>C: some of it finds its way into the ferrite of the pearlite, we believe.

Chapter XXV—the constitution of metallic alloys—is very elementary, dealing only with the copper-nickel (or Pt-Au) and the silver-copper type curves. The Sb-Pb curve is given with the eutectic at 228° C. instead of 247° C.

The chapter on the equilibrium diagram of the iron-carbon alloys is brief and to the point. One obvious error occurs in explaining the freezing of a hypo-eutectic cast iron, Fig. 411, by saying that it begins to solidify at 1230° C., when crystals of iron containing 1.7 per cent C (saturated austenite) begin to form! Again, the statement that the eutectic is composed of minute crystals of saturated austenite and minute crystals of cementite, is hardly acceptable—a mechanical mixture, of course, with a typical eutectic structure, but not of minute crystals surely.

Taken as a whole the book is a good one, and gives a broad presentation of the metallography of iron and steel in a simple, straightforward manner. With such a book at hand, no one interested in iron and steel, their properties and treatment, can excuse his ignorance of metallography by saying it is too abstruse for anyone outside of a college. It is a book for the practical man just as much as for the worker in the college laboratory. Taken in sections, there is but one criticism of any weight, and that deals with the chapter on the constitution of metallic alloys. This is too short for a book of the size. The main type diagrams could easily be explained, with examples such as Fe-Mn : Fe-Ni : Fe-Cu : Fe-Si : Fe-Phos; and lastly Fe-FeS. In fact, a page on the simplest case of ternary alloys used to explain the phosphide eutectic in high phosphorus cast iron could also be added.

Professor Sauveur is to be congratulated on giving us a book that is interesting, practical and useful.

WILLIAM CAMPBELL

**Nahrungsmittel chemie in Vorträgen.** Herausgegeben von Dr. W. KERF. Leipzig: Akademische Verlagsgesellschaft, 1914. Price in paper, M. 26.50; bound, 28 M.

This volume of 579 pages reports the lectures delivered in the first *Fortbildungskursus* for German food chemists (March,



1912. The topic, author, and distribution of space are as follows:

General outline of food legislation and control in Germany (Kerp), 32 pages; Application of modern physicochemical theory to food chemistry (Paul), 78 pages; Recent studies of cell metabolism by chemical methods (Abderhalden), 14 pages; Biological differentiation of the proteins with special reference to forensic blood and flesh investigation (Uhlenhuth), 48 pages; Problems of the day in food chemistry (Kerp), 32 pages; Recent developments in the legal aspects of food chemistry (Juckenack), 30 pages; Customs and impost-problems for the food chemist (Fritzweiler), 20 pages; Control of the milk industry (Mai), 16 pages; Biology of milk (Weigmann), 32 pages; Recent methods for the investigation of edible fats and oils (Heiduschka), 19 pages; Wine problems (Kulisch and Gunther), 112 pages; Brandy (von Buchka), 8 pages; Recent methods for the examination of honey (Friche), 33 pages; Water and sewage (Grinhut), 93 pages; Forensic chemistry and microscopy (Popp), 27 pages.

Kerp points out that the latest of the laws controlling commerce in commodities of popular consumption in Germany, the wine law of 1909, was enacted just 30 years later than the fundamental food law of 1879. He then proceeds to review the development of the food industry in Germany during that period (with statistics for the year 1909-10) and to outline the food laws and the functions of the food chemist. Under problems of the day in food chemistry he discusses the use of preservatives in food, the renovation of butter, refined vegetable fats, the coating of rice, the bleaching of flour, the greening of vegetables by means of copper salts, the glazing of coffee and the problem of substitutes in foods and beverages. Paul reviews the ionization theory, especially in its application to analytical methods and the interpretation and expression of results, beginning with Arrhenius and ending with such problems as the selection of indicators, the determination of "free" and "bound" sulfurous acids in foods, and the method of stating results of a mineral water analysis.

The scope of the other chapters is sufficiently indicated by their titles.

General criticisms of the volume are scarcely feasible because of the diversity of topics upon which it touches and the differences of method and style among the numerous authors who have independently written the separate chapters which compose the book. The fact that these were originally prepared especially as lectures to be delivered by and to official German food chemists adds interest and weight to the work as a presentation of the German viewpoint. It remains to be seen in what way and to what fact this viewpoint will be permanently modified as the result of the friendly attitude toward the *Ersatz* made necessary by war conditions in Germany.

As a means of comparing the problems of the German food chemist with our own, and as indicating the judgment of the German committee in charge as to the subject matter most needed in a *Fortbildungskursus* for food chemists, as well as for its summaries of recent advances in certain lines of food analysis, the work should be of distinct interest to chemists engaged in the food industries or in food control.

H. C. SHERMAN

#### Explosives, Their Manufacture, Properties, Tests and History.

By ARTHUR MARSHALL, A.C.G.I., F.I.C., F.C.S., Chemical Inspector, Indian Ordnance Department, Naini Tal, India, 1915. P. Blakiston's Son & Co., Philadelphia. 624 pages, 137 illustrations. Price, \$7.00 net.

This book is probably the most comprehensive general work on the subject of explosives that has been published in English, and contains much of interest and value to the manufacturer

or chemist in the explosive industry, as well as to the student. It is largely a collection of well-chosen facts from the best literature on the subject, including most of the best material published in the journals in recent years. The author's general treatment of the subject shows excellent insight into the many topics discussed, and indicates both a practical knowledge of the industry and a thorough familiarity with the literature on the subject. References to original articles are liberally supplied—a fact which greatly increases the value of the book—and it is gratifying to note the numerous references to American work.

A thorough review of this book would cover many pages, and it is therefore impossible to enter into any great detail in this review. The author has given his attention chiefly to subjects which have not been already fully discussed in other books. Thus, he has considered only briefly the details of manufacture and practical use of explosives, but has elaborated on such subjects of present-day interest as the stability of nitrocellulose, developments in physical and chemical testing of explosives, improvements in means of initiating explosive reactions, etc. A review of the early history of explosives and their development up to the present time occupies 39 pages. The manufacture of black powder (34 pp.) and its raw materials, and the manufacture of nitric and sulfuric acids (20 pp.) are discussed only briefly. Of interest to explosives manufacturers is the unfortunately too brief discussion of mixed and waste acids, their handling and recovery. The usual processes of nitrating cellulose and nitrocellulose, including the displacement process, are described in detail, and the most recent knowledge of stabilization well presented. Nitroglycerin, its raw materials, properties and manufacture (40 pp.), and smokeless powders, their composition, manufacture and requirements, including shot-gun powders (34 pp.), are given due consideration. Under Solvents special attention is given to the subject of acetone, its manufacture, impurities and recovery from cordite, presenting facts not available in the literature. The discussion of blasting explosives (34 pp.) includes nitroglycerin explosives, chlorate explosives and ammonium nitrate explosives. The suitability of various explosives for purposes of peace and war is briefly treated in 15 pages. Under Properties of Explosives (82 pp.) is found a summary of the latest work on the thermochemistry of explosives, a very good discussion of the rate of detonation of explosives, and a description of recent investigations of detonating compositions. All of the important physical tests for explosives are described. Special explosives (40 pp.) treats of safety and detonating fuses, detonators, and "safety explosives" for coal mining, describing the tests made at all of the U. S. and European testing stations; 22 pages are devoted to the proper construction and protection of factory buildings, magazines, etc.

Under Stability and Stability Tests (27 pp.) is a good discussion of the decomposition of smokeless powders, its retardation by the use of various stabilizers, and the more commonly used stability tests. In the section devoted to Materials and their Analysis, the author has attempted to discuss in 53 pages the general methods for testing most of the materials used in the manufacture of explosives, and the preparation and properties of many of them. The list includes acids, solvents, glycerin, cotton, nitroglycerin, nitrocellulose, azides, fulminates, and nitrosubstitution compounds. Many important points are necessarily treated only briefly. An appendix contains the Imperial German Railway Commission's regulations regarding tests of explosives for safety in transportation, and also some excellent thermochemical tables.

The entire book is exceptionally free from typographical errors and is excellently illustrated.

C. G. STORM

# NEW PUBLICATIONS

By IRENE DEMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

- CORRECTION:** The Metallurgy and Heat Treatment of Iron and Steel. ALBERT SAUVREUR. The price of \$4.00 quoted in THIS JOURNAL, 8 (1916), 393, should read \$6.00. The publishers are Sauvreur & Boylston, Cambridge, Mass., and not the McGraw-Hill Book Co.
- Ammonia:** The Thermodynamic Properties of Ammonia. F. G. KEYES and R. B. BROWNLEE. 4to. 73 pp. Price, \$1.00. John Wiley & Sons, New York.
- Analysis:** Outline of the Methods of Qualitative Chemical Analysis. R. J. CARNEY. 6th Ed. 8vo. 37 pp. Price, \$0.20. G. Wahr, Ann Arbor.
- Atom:** The Universe and the Atom; the Ether Constitution, Creation and Structure of Atoms. MARION ERWIN. 12mo. 314 pp. Price, \$2.00. D. Van Nostrand Co., New York.
- Coal and Coke.** F. H. WAGNER. 8vo. 413 pp. Price, \$4.00. McGraw-Hill Book Co., New York.
- Concrete and Reinforced Concrete.** W. L. WEBB and W. H. GIBSON. 12mo. Price, \$1.50. American Technical Society, Chicago
- Explosives:** Manual on Explosives. A. F. J. RAMSEY and H. C. WESTON. 8vo. 123 pp. Price, \$0.25. George Routledge & Sons, London.
- Galvanizing and Tinning.** W. T. FLANDERS and OTHERS. 8vo. 350 pp. Price, \$3.00. D. Williams Co., New York.
- Gas:** Das Gas als Warmequelle und Triebkraft. F. SCHAEFER and OTHERS. 8vo. 249 pp. Price, \$3.00. R. Oldenbourg, Munich.
- Iron:** Die physikalische und chemische Grundlagen d. Eisenhuettenwesens. WALTHER MATHESIUS. 8vo. Price, \$5.20. O. Spamer, Leipzig.
- Lathe Design, Construction and Operation.** C. O. E. PERRIGO. 8vo. 469 pp. Price, \$2.50. Norman W. Henley Publishing Co., New York.
- Machine Design, Questions and Problems in.** F. D. FURMAN. 8vo. 68 pp. Price, \$0.80. The Author, Hoboken, N. J.
- Metallurgists' and Chemists' Handbook.** D. M. LIDDELL. 16mo. 603 pp. Price, \$4.00. McGraw-Hill Book Co., New York.
- Organic Chemistry:** Grundriss der Organischen Chemie. CARL OFFENHEIMER. 9th Ed. 8vo. 168 pp. Price, \$0.75. C. Thieme, Leipzig.
- Oxy-Acetylene Welding and Cutting.** H. P. MANLY. 8vo. 215 pp. Price, \$1.00. Fred. J. Drake & Co., Chicago.
- Packing House and Cold Storage Construction.** H. P. HENSCHEN. 8vo. 310 pp. Price, \$5.00. Nickerson & Collins Co., Chicago.
- Physiological Chemistry.** A. P. MATTHEWS. 8vo. Price, \$5.25. Baillière, Tindall & Cox, London.
- Potassium Salts:** Die Kaliohsalze, ihre Gewinnung und Verarbeitung. W. MICHELS and C. PRZYBYLLA. 8vo. Price, \$4.60. O. Spamer, Leipzig.
- Power Plant Design.** E. F. MILLER. 4to. 178 pp. Price, \$1.50. Suffolk Engraving & Electrotyping Co., Boston.
- Rubber:** Its Sources, Cultivation and Preparation. HAROLD BROWN. 12mo. 245 pp. Price, \$2.00. D. Van Nostrand Co., New York.
- Rubber Industry of the Amazon.** J. F. WOODRUFFE. 8vo. 435 pp. Price, \$5.50. G. E. Stechert & Co., New York.
- Salt and Alkali Industry, Including Potassium Salts and the Stassfurt Industry.** GEOFFREY MARTIN and OTHERS. 8vo. 108 pp. Price, \$1.90. Crosby Lockwood & Son, London.
- Steel:** The Metallurgy of Steel and Cast Iron. H. M. HOWE. 8vo. 641 pp. Price, \$10.00. McGraw-Hill Book Co., New York.
- Steel and Its Heat Treatment.** D. K. BULLEN. 8vo. 431 pp. Price, \$3.75. John Wiley & Sons, New York.
- Sulfuric Acid and Sulfur Products.** GEOFFREY MARTIN and J. L. FOUCAR. 8vo. 93 pp. Price, \$1.90. Crosby Lockwood & Son, London.
- Technical and Scientific German.** E. V. GREENFIELD. 8vo. 284 pp. Price, \$1.00. D. C. Heath & Co., New York.
- Thermodynamics:** Les theories statistiques en thermodynamique. H. A. LORENTZ. 8vo. 120 pp. Price, \$1.50. B. G. Teubner, Leipzig.
- Thermodynamics:** Text Book of Mechanics. Vol. 6. L. A. MARTIN, JR. 12mo. 313 pp. Price, \$1.75. John Wiley & Sons, New York.
- Water:** Harper's Hydraulic Tables for the Flow of Water. J. H. HARPER. 192 pp. Price, \$2.00. D. Van Nostrand Co., New York.
- Blast Furnace:** The Raw Materials of the Blast Furnace. J. E. JOHNSON, JR. *Metallurgical and Chemical Engineering*, Vol. 14 (1916), No. 6, pp. 318-323.
- Ceramics:** Der Weltmarkt in keramischen Waren im Jahre 1915. L. W. SCHMIDT. *Sprechsaal*, Vol. 49 (1916), No. 8, pp. 55-57.
- Chemical Testing in Sulfite Pulp Work.** R. B. WOLF. *Paper*, Vol. 18 (1916), No. 1, pp. 11-14.
- Coking and Caking Coal.** S. H. VIALI. *Power*, Vol. 43 (1916), No. 13, pp. 432-434.
- Colors:** Das absolute System der Farben. WILHELM OSTWALD. *Zeitschrift fuer physikalische Chemie*, Vol. 101 (1916), No. 2, pp. 129-142.
- Copper:** Some Sources of Errors in the Iodometric Determination of Copper. C. E. SMITH. *Metallurgical and Chemical Engineering*, Vol. 14 (1916), No. 7, pp. 379-380.
- Electrolytic Zinc.** H. A. B. MOTHERWELL. *Mining and Scientific Press*, Vol. 112 (1916), No. 12, pp. 401-403.
- Electrostatics of Flotation.** F. A. FAHRENWALD. *Mining and Scientific Press*, Vol. 112 (1916), No. 11, pp. 375-378.
- Flotation:** Interfacial Tension in Flotation. H. J. STANDER. *Engineering and Mining Journal*, Vol. 101 (1916), No. 13, pp. 576-578.
- Furnace Slag, Uses of.** HERBERT LANG. *Mining and Scientific Press*, Vol. 112 (1916), No. 13, pp. 443-445.
- Gas Producers, Operating Characteristics of.** FRANZ DENK. *Blast Furnace and Steel Plant*, Vol. 50 (1916), No. 4, pp. 177-178.
- Hydrogen:** The Technical Production of Hydrogen and Its Industrial Application. H. L. BARNITZ. *Metallurgical and Chemical Engineering*, Vol. 14 (1916), No. 7, pp. 391-395.
- Inorganic Chemistry:** Experimentelle anorganische Chemie und Elektrochemie im Jahre 1915. A. GUTBIER. *Zeitschrift fuer angewandte Chemie*, Vol. 29 (1916), No. 17, pp. 69-76.
- Internal Combustion Engines, Influence of Compression in.** R. E. MATHOT. *Power*, Vol. 43 (1916), No. 15, pp. 512-514.
- Leather:** Neuere Kunstleder und Ersatzstoffe fuer Leder. R. LAUFFMANN. *Kunststoffe*, Vol. 6 (1916), No. 4, pp. 41-43.
- Mineral Industry of Chile.** L. W. STRAUSS. *Mining and Scientific Press*, Vol. 112 (1916), No. 14, pp. 475-478.
- Natural Gas in Ohio.** J. A. BOWNOCKER. *Journal of the Cleveland Engineering Society*, Vol. 8 (1916), No. 5, pp. 313-332.
- Poli-Oil, a New Adulterant of Ghee-Indian Clarified Butter-Fat.** J. H. BARNES. *The Analyst*, Vol. 41 (1916), No. 480, pp. 72-73.
- Resins:** Synthetische Harze. ROBERT ELLER. *Kunststoffe*, Vol. 6 (1916), No. 4, pp. 45-47.
- Rubber Waste, The Reclaiming of.** A. H. KING. *Metallurgical and Chemical Engineering*, Vol. 14 (1916), No. 6, pp. 309-311.
- Sedimentation and Flocculation.** E. E. FREE. *Engineering and Mining Journal*, Vol. 101 (1916), No. 12, pp. 509-513.
- Selby Lead Smelter.** T. A. RICKARD. *Mining and Scientific Press*, Vol. 112 (1916), No. 15, pp. 505-510.
- Spelter Statistics for 1915.** W. R. INGALLS. *Engineering and Mining Journal*, Vol. 101 (1916), No. 14, pp. 606-611.
- Steel:** Some Recent Developments in Tool-Steel Testing. E. G. HERBERT. *American Machinist*, Vol. 44 (1916), No. 10, pp. 419-421.
- Steel Rails:** Nick and Break Steel Rail Test. R. W. HUNT and C. W. GENNETT, JR. *Iron Trade Review*, Vol. 58 (1916), No. 13, pp. 709-719.
- Sulfur:** Die Bestimmung des Schwefels in der Zinkblende. H. KOELSCH. *Chemiker-Zeitung*, Vol. 40 (1916), No. 24, p. 174.
- Surface Condensers.** A. B. CLARE. *Power*, Vol. 43 (1916), No. 13, pp. 437-439.
- Tannin:** Kunstgerbestoffe. R. LAUFFMANN. *Kunststoffe*, Vol. 6 (1916), No. 1, pp. 1-4.
- Tungsten Ores:** Recent Practice in Concentrating Colorado Tungsten Ores. H. C. PARMELEE. *Metallurgical and Chemical Engineering*, Vol. 14 (1916), No. 6, pp. 301-304.
- Ultraviolet:** Apparatus for Producing Ultraviolet Radiation. W. S. ANDREWS. *General Electric Review*, Vol. 19 (1916), No. 4, pp. 317-319.
- Welding:** Some Brief Descriptions of Welding Processes. M. W. WARD. *Power*, Vol. 43 (1916), No. 14, pp. 478-479.
- Wood Flour.** F. W. KRESSMANN. *Metallurgical and Chemical Engineering*, Vol. 14 (1916), No. 7, pp. 372-374.
- Wool Fat, Recovery of.** E. E. AYRES, JR. *Metallurgical and Chemical Engineering*, Vol. 14 (1916), No. 6, pp. 317-318.

## RECENT JOURNAL ARTICLES

- Analysis:** Methods of Rapid Analysis. L. B. PRINGLE. *Engineering and Mining Journal*, Vol. 101 (1916), No. 15, p. 650.
- Antimony in China.** F. L. COLE. *Mining and Scientific Press*, Vol. 112 (1916), No. 11, pp. 369-373.



## INORGANIC CHEMICALS

Acetate of Lime, gray	100 Lbs.	7.00	@	7.05
Alum, lump	100 Lbs.	4.25	@	4.75
Aluminum Sulfate, high grade	100 Lbs.	5.00	@	6.00
Ammonium carbonate, domestic	Lb.	9 1/2	@	10
Ammonium chloride, gray	Lb.	8	@	9
Ammonium Phosphate, commercial, 98-100%	Lb.		@	
Aqua Ammonium 16% drums	Lb.	2 1/4	@	2 1/2
Arsenic, white	Lb.	6 1/2	@	
Barium Chloride	Ton	115.00	@	110.60
Barium Nitrate	Lb.	15	@	16
Barytes, prime white, foreign	Ton	24.00	@	26.00
Bleaching Powder, 85 per cent	100 Lbs.	6.75	@	8.00
Blue Vitriol	Lb.	17	@	20
Borax, crystals, in bags	Lb.	6 1/4	@	7
Boric Acid, powdered crystals	Lb.	11 1/4	@	15
Burnstone, crude, domestic	Long Ton	29.00	@	30.00
Bromine, technical, bulk	Lb.	4.5	@	5.25
Calcium Chloride, lump	Ton	11.75	@	12.00
Calcium Chloride, granulated	Ton	14.78	@	15.00
Caustic Soda, 74 per cent	Lb.	5 1/4	@	6
Chalk, light precipitated	Lb.	4 1/2	@	5 1/4
China Clay, imported	Ton	15.00	@	18.00
Feldspar	Ton	8.00	@	12.00
Fuller's Earth, foreign, powdered	100 Lbs.	80	@	1.05
Glauber's Salt, in bbls.	100 Lbs.	70	@	85
Green Vitriol, bulk	100 Lbs.	1.25	@	1.50
Hydrochloric Acid, commercial, 18%	100 Lbs.	2.50	@	3.00
Hydrochloric Acid, C. P., conc., 22%	100 Lbs.	3.00	@	3.50
Iodine, resublimed	Lb.	5.00	@	6.00
Lead Acetate, white crystals	Lb.	15 1/2	@	16
Lead Nitrate	Lb.	17 1/2	@	18
Litharge, American	Lb.	9 1/4	@	
Lithium Carbonate	Lb.	90	@	1.00
Magnesium Carbonate	Lb.	10	@	11
Magnesite, "Calcined"	Ton	—	@	—
Nitric Acid, 36%	Lb.	6 1/4	@	7
Nitric Acid 42%	Lb.	8 1/2	@	9 1/4
Phosphoric Acid, sp. gr. 1.750	Lb.	28 1/2	@	30
Phosphorus	Lb.	35	@	1.00
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bichromate, casks	Lb.	56	@	60
Potassium Bromide	Lb.	—	@	—
Potassium Carbonate, calcined, 80 @ 85%	Lb.	85	@	90
Potassium Chlorate, crystals, spot	Lb.	72	@	—
Potassium Cyanide, bulk, 98-99 per cent	Lb.	—	@	—
Potassium Hydroxide	Lb.	90	@	92
Potassium Iodide, bulk	Lb.	4.30	@	4.35
Potassium Nitrate	Lb.	—	@	—
Potassium Permanganate, bulk	Lb.	1.80	@	1.90
Quicksilver, flask, 75 lbs.	Lb.	125.00	@	—
Red Lead, American, dry	Lb.	9 3/4	@	—
Salt Cake, glass makers'	Ton	13.00	@	—
Silver Nitrate	Oz.	40 3/4	@	—
Soapstone in bags	Ton	12.00	@	—
Soda Ash, 48 per cent	100 Lbs.	3.00	@	4.00
Sodium Acetate	Lb.	13 1/2	@	14.00
Sodium Bicarbonate, domestic	100 Lbs.	1.75	@	2.00
Sodium Bicarbonate, English	Lb.	3 1/2	@	3 3/4
Sodium Bichromate	Lb.	60	@	70
Sodium Carbonate, dry	100 Lbs.	4.00	@	4.25
Sodium Chlorate	Lb.	45	@	55
Sodium Fluoride, commercial	Lb.	18	@	20
Sodium Hyposulfite	100 Lbs.	2.25	@	2.50
Sodium Nitrate, 95 per cent, spot	100 Lbs.	3.40	@	3.50
Sodium Silicate, liquid	100 Lbs.	1.25	@	1.75
Sodium Sulfide, 30%, crystals, in bbls.	Lb.	2	@	2 1/2
Sodium Sulfite, crystals	Lb.	7	@	8
Strontium Nitrate	Lb.	22	@	24
Sulfur, flowers, sublimed	100 Lbs.	2.30	@	2.70
Sulfur, roll	100 Lbs.	1.95	@	2.25
Sulfuric Acid, chamber, 60%	Ton	65.00	@	70.00
Sulfuric Acid, conc., sp. gr. 1.842	100 Lbs.	2.50	@	3.00
Sulfuric Acid, oleum (fuming)	100 Lbs.	2.50	@	3.00
Talc, American white	Ton	15.00	@	17.00
Terra Alba, American, No. 1	100 Lbs.	75	@	80
Tin Bichloride, 50%	Lb.	16	@	16 1/4
Tin Oxide	Lb.	60	@	62
White Lead, American, dry	Lb.	8 3/4	@	—
Zinc Carbonate	Lb.	20	@	24
Zinc Chloride, commercial	Lb.	14	@	15
Zinc Oxide, American process	Lb.	8 3/4	@	8 7/8
Zinc Sulfate	Lb.	6 1/2	@	7 1/4

## ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.	Lb.	2.50	@	2.55
Acetic Acid, 28 per cent, in bbls.	Lb.	7 1/2	@	8
Acetic Acid, glacial, 99 1/2%, in carboys	Lb.	50	@	—
Acetone, drums	100 @	50	@	50
Alcohol, denatured, 180 proof	Gal.	50	@	61

Alcohol, grain, 188 proof	Gal.	2.68	@	2.70
Alcohol, wood, 98 per cent, refined	Gal.	65	@	68
Amyl Acetate	Gal.	4.25	@	5.00
Aniline Oil	Lb.	80	@	—
Benzene Acid, ex. toluol	Lb.	6.50	@	7.00
Benzol, 90 per cent	Gal.	85	@	90
Camphor, refined in bulk, bbls.	Lb.	52	@	—
Carbolic Acid, U. S. P., crystals, drums	Lb.	90	@	—
Carbon Bisulfide	Lb.	8	@	—
Carbon Tetrachloride, drums, 100 gals.	Lb.	20	@	—
Chloroform	Lb.	80	@	—
Citric Acid, domestic, crystals	Lb.	65	@	70
Cresol, U. S. P.	Gal.	1.15	@	1.25
Dextrine, corn (carloads, bags)	100 Lbs.	3.20	@	3.26
Dextrine, imported potato	Lb.	—	@	—
Ether, U. S. P., 1900	Lb.	15	@	20
Formaldehyde, 40 per cent	Lb.	11	@	12 1/4
Glycerine, dynamite, drums included	Lb.	63	@	—
Oxalic Acid, in casks	Lb.	73	@	—
Pyrogallol Acid, resublimed bulk	Lb.	2.50	@	—
Salicylic Acid	Lb.	4.25	@	—
Starch, cassava	Lb.	3 1/4	@	4 1/2
Starch, corn (carloads, bags)	100 Lbs.	2.25	@	2.36
Starch, potato	Lb.	12	@	—
Starch, rice	Lb.	8	@	10
Starch, sago	Lb.	3 1/2	@	4
Starch, wheat	Lb.	5	@	6
Tannic Acid, commercial	Lb.	60	@	64
Tartaric Acid, crystals	Lb.	66	@	68

## OILS, WAXES, ETC.

Beeswax, pure, white	Lb.	47	@	55
Black Mineral Oil, 29 gravity	Gal.	12 1/2	@	13
Castor Oil, No. 3	Lb.	20	@	28
Ceresin, yellow	Lb.	10	@	14
Corn Oil, crude	100 Lbs.	9.75	@	10.00
Cottonseed Oil, crude, f. o. b. mill	Gal.	71	@	74
Cottonseed Oil, p. s. y.	Lb.	10 1/2	@	11
Cresote, beechwood	Lb.	9.00	@	10.00
Cylinder Oil, light, filtered	Gal.	20	@	25
Fusel Oil, crude	Lb.	3.75	@	4.50
Japan Wax	Lb.	17	@	20
Lard Oil, prime winter	Gal.	97	@	99
Linseed Oil, raw (car lots)	Gal.	76	@	—
Menhaden Oil, crude (southern)	Gal.	—	@	—
Naphtha, 68 @ 72	Gal.	38	@	—
Neat's-foot Oil, 20%	Gal.	98	@	99
Paraffine, crude, 118 & 120 m. p.	Lb.	5	@	—
Paraffine Oil, high viscosity	Gal.	26	@	28
Rosin, "F" Grade, 280 lbs.	Bbl.	5.05	@	—
Rosin Oil, first run	Gal.	32	@	—
Shellac, T. N.	Lb.	23	@	24
Spermaceti, cake	Lb.	25	@	26
Spinel Oil, bleached winter, 38%	Gal.	78	@	79
Spindle Oil, No. 200	Gal.	19	@	19 1/2
Stearic Acid, double-pressed	Lb.	14	@	14 1/2
Tallow, acidless	Gal.	86	@	70
Tar Oil, distilled	Gal.	30	@	31
Turpentine, spirits of	Gal.	49 1/2	@	50

## METALS

Aluminum, No. 1, ingots	Lb.	58	@	60
Antimony, ordinary	Lb.	40	@	41
Bismuth, N. Y.	Lb.	3.15	@	3.25
Copper, electrolytic	Lb.	29 1/2	@	—
Copper, lake	Lb.	29 1/2	@	—
Lead, N. Y.	100 Lbs.	7.50	@	—
Nickel, electrolytic	Lb.	50	@	—
Nickel, shot and ingots	Lb.	45	@	—
Platinum, refined	Oz.	90.00	@	—
Silver	Oz.	65 5/8	@	—
Tin	100 Lbs.	50.50	@	—
Zinc, N. Y.	Lb.	19	@	—

## FERTILIZER MATERIALS

Ammonium Sulfate	100 Lbs.	3.55	@	—
Blood, dried	Unit	2.80	@	—
Bone, 4 1/2 and 50, ground, raw	Ton	29.00	@	—
Calcium Cyanamid	Unit of Ammonia	2.55	@	—
Calcium Nitrate, Norwegian	100 Lbs.	—	@	—
Castor Meal	Unit	—	@	—
Fish Scrap, domestic, dried, f. o. b. works	Unit	—	@	—
Phosphate, acid	Unit	80	@	85
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent	Ton	2.75	@	3.00
Tennessee, 78-80 per cent	Ton	5.00	@	5.50
Potassium "muriate," basis 80 per cent	Ton	400.00	@	—
Pyrites, furnace size, imported	Unit	15	@	15 1/2
Tankage, high-grade; f. o. b. Chicago	Unit	2.85	@	10

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## EDITORIALS

### CHEMICAL ABSTRACTS—DECENNIAL INDEX PLANS

The work of compiling the collective index to *Chemical Abstracts* has been in progress since publication was authorized (April 19th). It seems probable that many who have expressed their willingness to pay \$10 for a copy want to know a bit about what is being done and what our plans are. Various types of index could be prepared. An index could be built with comparative ease and at low compiling cost with the annual indexes as a basis. The collective author index will be so prepared. However, a combination of the ten annual subject indexes would not produce the best index possible, both because the annual indexes lack uniformity and because the entries are not made nor arranged in the most convenient form. A change in form is contemplated both for the collective index and for future annual indexes. The fundamental properties which we shall strive to give the index are accuracy, thoroughness and convenience in use.

In the interest of accuracy and thoroughness the annual author indexes are being checked against the printed abstracts and in some cases against the original papers in order to eliminate errors and to detect omissions. Other checking schemes will be applied at various stages of the work. The collective subject index will be compiled directly from the abstracts. Each of the 190,000 abstracts will be examined twice; *first*, to select and indicate the subjects to be indexed, and *second*, to verify or correct the index cards written on the basis of the marked text. Special attention will be given to the modifying phrases.

To increase convenience in use it is planned to print the subject index in entry-a-line form with an alphabetic order of modifications when feasible. This scheme will save much time in many cases; it has disadvantages, but none that the old method does not have also, except that it is more expensive. In the hope of improving the method used in past indexes, a study is being made of the problem of indexing organic compounds in order to reduce as much as possible the number of places where the name of any compound might be indexed. It may be that indexing under parent compounds with a systematic order of radicals will prove most feasible. All new compounds and all those specially studied will be entered in the index.

Our object will be the best index possible without consideration of the time element, rather than the best index that can be prepared in a given time. Nevertheless every effort will be made to issue the index as promptly as is consistent with quality and with the fact that there are many phases of the index work and of our regular work which cannot well be turned over to assistants.

E. J. CRANE

OHIO STATE UNIVERSITY  
COLUMBUS, OHIO

### LET'S ABOLISH OUR UNNECESSARY WASTE OF POTASSIUM COMPOUNDS

The extent of the present use of potassium salts is unnecessary. Sodium salts will serve just as well for many of the uses to which potassium salts are put. With the use of the latter where they are superior to sodium compounds, for the purpose in hand, we have no quarrel, and are grateful for the availability of the more satisfactory material.

The use, however, of the more costly potassium salts whenever sodium salts will do just as well, should be discouraged in every case, be it ever so insignificant, for the aggregate effect is a waste of greater importance than one imagines. The fact that the nation is not self-contained with reference to potash and that we have expended large sums in the attempt by chemical and geologic exploration to make ourselves potash-independent, serves the more to insist on the early abolition of this form of waste. The aggregate amount of this waste can be only a small per cent of the total potash used, but this is no measure of its importance or of the annoyance which can arise in industry by an unexpected curtailment of supply, for in such emergencies the development of substitutes consumes time and effort which should be directed to matters which are not the result of our own thoughtless and unnecessary waste.

Let us get at the root of the evil at once. We do not set a good example in the laboratories of our schools and colleges in avoiding wasteful and unnecessary use of potassium compounds. Our texts and laboratory manuals in the various branches of chemistry prescribe or suggest the use of potassium compounds time after time where sodium compounds would do just as well. Text after text adopts from its predecessors experiments or at least general procedures unnecessarily requiring the use of potassium salts which inculcate the error that slight extravagance in cost is a minor matter when the driving home of a principle is concerned. Even this excuse is often not available. We use for instance literally tons of "cleaning mixture" made from bichromate of potash and sulfuric acid, when the sodium salt is better.

Is it any wonder then after such precept and example that our factory laboratories, and particularly our whole list of manufactures and numerous miscellaneous material-consuming operations, in every department of life, are also saturated with unnecessary potash requirements?

It is particularly these later cases which demand our protection as chemists. The business man and petty consumer who does not or cannot employ chemical assistance is the great sufferer by the bad example in our unnecessary use and specification of potassium salts even if apparently for inconsequential things. It is these same classes also who suffer most if our imports of potash should be suddenly withheld for they cannot help themselves, and when they suffer, we all suffer. The experience of the last two

years warns us of the importance of a prior elimination of unnecessary dependence on potash as well as other foreign supplies, so that in the event of any unexpected cessation of supply we can confine ourselves to the problems arising from the crippling of industries or operations unavoidably hampered by such curtailment. We should plan to be annoyed as little as possible by these minor troubles in a national emergency. This is preparedness in which all chemists can take part.

We chemists can be of national help in this matter by eliminating as soon as possible all unnecessary use of potash and permitting our soda industries to grow gradually to the higher demands instead of expecting them to do so in time of stress. Recent high prices might be expected to solve this problem for us, but they will not do so without our concerted efforts. Even chemists do not readily forsake wasteful habits and if they did, not every one who uses potash has the advantage of chemical advice.

Many chemists already have information on potash elimination which their judgment or economic situation has caused them to work up. We perhaps cannot always make this information public when it is the property of a manufacturer but in all other cases, and these too if we can secure permission, let us make this contribution to the public welfare. I can well remember, when we had our first intimation, nearly fifteen years ago, of the importance coal tar derivatives were to have in future warfare, and began in this country our investigations on synthetic phenol, that we labored under the delusion that potassium

hydroxide was a necessity for the proper fusion of the sodium benzene-sulfonate. Now we manufacture thousands of pounds per day without a pound of potassium hydroxide. It takes little imagination to see other cases where a similar revolution should be possible. For instance, one Ohio machinery manufacturing concern has saved \$8,000 per year by replacing with sodium compounds the potassium compounds formerly used in incidental operations, such as cleaning. This was a result of the efficiency of their chemists and was accomplished sometime before the war. Since the war others have been forced to do the same to avoid complete elimination, and many have been surprised to find sodium salts not only more economical but at times apparently better.

Let us resolve to-day, therefore, to do away with all unnecessary use of potassium compounds. Let us do away with such use of potassium compounds in our schools and universities, and in our technical laboratories and attack it vigorously at every opportunity in its strongholds of manufacturing and every-day use. Let every teacher of laboratory chemistry, therefore, and every director of any kind of chemical work look up his potash consumption and have sodium tried where they have been using potassium if sodium is available. Let students be taught the results and give them publicity for the benefit of other chemists, teachers and the general public.

JAMES R. WITHROW

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## ORIGINAL PAPERS

### FURTHER EXPERIMENTS ON THE VOLATILIZATION OF PLATINUM

By C. K. BURGESS AND R. G. WALTEMBERG

Received April 17, 1916

The experiments here described are an extension of those of Burgess and Sale,<sup>1</sup> undertaken at the suggestion of Dr. W. F. Hillebrand, Chairman of the Committee on "Quality of Platinum Utensils" of the American Chemical Society. In the earlier papers are described a convenient thermoelectric method of testing platinum purity and observations on loss of weight of crucibles subjected to heating at 1200° C. and subsequent acid treatment, together with certain magnetic and photomicrographic observations.

The present investigation consists of a series of observations on change in weight of several platinum crucibles of various degrees of purity when subjected to heating at 700°, 1000°, and 1200° C. Determination of the loss of iron content after successive heatings and of other materials soluble in hydrochloric acid have also been made as well as a few observations by treatment with hydrofluoric acid to detect the presence of silica, which may come largely if not entirely from the marquardt porcelain portions of the furnace described in previous papers, to which papers

reference should also be made for the details of apparatus and methods.

The choice of heating temperatures of 700°, 1000° and 1200° C. proved a fortunate one in that it not only covers the temperature range to which platinum crucibles are ordinarily subjected in practice, but besides it so happens that there also occurs within this temperature interval a reversal from a loss to a gain in weight of all grades of platinum ware observed in this investigation.

The observations and the numerical inferences from them are recorded in Tables I and II for the seven crucibles of this investigation, ranging from the purest thermoelement and "tiegel platin" ware of Heraeus to crucibles containing up to 2.7 per cent iridium and 8 per cent rhodium and with divers amounts of iron and other unknown soluble materials (including probably Pt itself, which in presence of Fe is slightly soluble in HCl) also as impurity. Five of these crucibles—all except 1 and 2 which are practically new—had been used in the previous investigation at 1200° C.

The crucibles which had been previously heated at 1200° C. were heated at 1000° C. and then at 700° C.; the others were heated in the reverse order: 700°, 1000° and 1200° C. When crucibles have been prepared for use by strong ignition and treatment

<sup>1</sup> THIS JOURNAL, 6 (1914), 452; 7 (1915), 561; Bureau of Standards, Scientific Paper, 254 (1915).



TABLE I—OBSERVATIONS ON PLATINUM CRUCIBLES

Source or Maker	Crucible Weight reference Grams	Area of Surface Cm <sup>2</sup>	E. m. f. mv.	Iridium %	Rhodium %
Heraeus, Normal Thermoelment Pt.	17.2	27	77	0.1	0.05
Heraeus, Tiegel Platin.	18.0	26	82	2.6	0.8
Johnson Matthey Co., Best Crucible Ware.	26.2	33	106	0.5	0.2
Baker & Company, Commercial Ware.	23.9	34	79	6.5	2.4
Baker & Company, Commercial Ware	39.6	56	108	6.9	2.7
Baker & Company, Special Rh Ware.	19.9	24	79	9.7	8.0
Quennessen, De Belmont, Legendre et Cie.	15.4	22	78	2.7	0.9

TABLE II—SUMMARY OF HEATING AND ACID TESTS

Crucible reference	a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p	q	r	s	t	u	v	w	x	y	z
E. m. f. against Pt. mv.	0.1	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Equivalent alloy	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Temperature of heating, ° C.	700	1000	1200	700	1000	1200	700	1000	1200	700	1000	1200	700	1000	1200	700	1000	1200	700	1000	1200	700	1000	1200	700	1000
Heat treatment loss, mg. 100 cm <sup>2</sup> /hr.	+0.004	0.007	0.812	+0.004	0.007	0.812	+0.004	0.007	0.812	+0.004	0.007	0.812	+0.004	0.007	0.812	+0.004	0.007	0.812	+0.004	0.007	0.812	+0.004	0.007	0.812	+0.004	0.007
Iron recovered as FeO <sub>2</sub> , mg. 100 cm <sup>2</sup> /hr.	0.014	0.008	0.068	0.014	0.008	0.068	0.014	0.008	0.068	0.014	0.008	0.068	0.014	0.008	0.068	0.014	0.008	0.068	0.014	0.008	0.068	0.014	0.008	0.068	0.014	
Heat treatment loss, mg. 100 cm <sup>2</sup> /hr.	0.010	0.008	0.880	0.010	0.008	0.880	0.010	0.008	0.880	0.010	0.008	0.880	0.010	0.008	0.880	0.010	0.008	0.880	0.010	0.008	0.880	0.010	0.008	0.880	0.010	
Total loss, heat + acid, mg. 100 cm <sup>2</sup> /hr.	0.020	0.016	0.948	0.020	0.016	0.948	0.020	0.016	0.948	0.020	0.016	0.948	0.020	0.016	0.948	0.020	0.016	0.948	0.020	0.016	0.948	0.020	0.016	0.948	0.020	
Iron compared to total loss per cent.	160	140	9	160	140	9	160	140	9	160	140	9	160	140	9	160	140	9	160	140	9	160	140	9	160	
Acid compared to total loss per cent.	140	150	115	140	150	115	140	150	115	140	150	115	140	150	115	140	150	115	140	150	115	140	150	115	140	

with acid there is apparently no difference in the loss in weight due to reversing the order of heating. This would be expected from the previous work at the Bureau. The experimental operations were, in brief, as follows:

Before heating, each crucible was cleaned and weighed. The furnace was brought to the temperature desired, then the crucible was placed in it and allowed to remain for four hours. (In the work of Burgess and Sale at 1200° C. the crucibles were heated for two-hour periods.) The crucibles were then taken out of the furnace, cooled in a desiccator and weighed. A treatment for 5 min. with boiling hydrochloric acid (1 acid to 4 water) followed. They were again weighed after washing, followed by a slight ignition over a Bunsen burner. The iron in the hydrochloric acid solution was weighed as ferric oxide after precipitating with ammonium hydroxide; slight discrepancies appear in some of the results, due to the ash uncertainty on ignition of the filter paper. The crucibles were usually heated three times at each temperature with similar treatment after each heating.

Table I shows the results of each treatment in milligrams per 100 cm<sup>2</sup>. of platinum surface. Crucibles *b* and *n* are alloys containing about 0.19 and 7.95 per cent rhodium respectively; the others contain iridium: *n* was made up specially and *b* is presumed to contain rhodium from its behavior.

For several crucibles the first treatment results in a loss appreciably greater than the succeeding ones. This illustrates the necessity of proper preparation of the crucibles before using for accurate determinations.

Table II gives a summary of the results. The change in weight on heating at 700° C. was very small and in most cases was an increase (0.005 to 0.028 mg./100 cm<sup>2</sup>/hr.), but the loss with acid treatment was greater than the gain on heating in all but one case. The 8 per cent rhodium alloy, crucible *n*, gained a little more weight on heating than it lost with acid. This is due possibly to a small amount of silica deposited on the crucible from the furnace tube. On treating these crucibles with strong hydrofluoric acid, after the hydrochloric acid treatment, there was a loss, which for crucible *n* amounted to 0.24 mg./100 cm<sup>2</sup>. There was no additional loss on repeating the treatment with hydrofluoric acid.

The curves showing the relation between loss at 1200° C. and the e. m. f. against pure platinum at 1100° C., including observations of Burgess and Sale, are reproduced in Fig. I and similar diagrams could be constructed for 700° and 1000° C. The loss on heating plus the loss with acid treatment is termed total loss and it is also shown in the plot for several crucibles. It is evident that crucibles containing iron lose less on heating than those which contain no iron, but their loss after the acid treatment is correspondingly greater. On some crucibles a surface film of iron oxide may be detected after heating and the decreased loss on heating and increased loss with acid treatment is probably due to this iron oxide, as previously explained.

The relation between temperature and loss on heat-

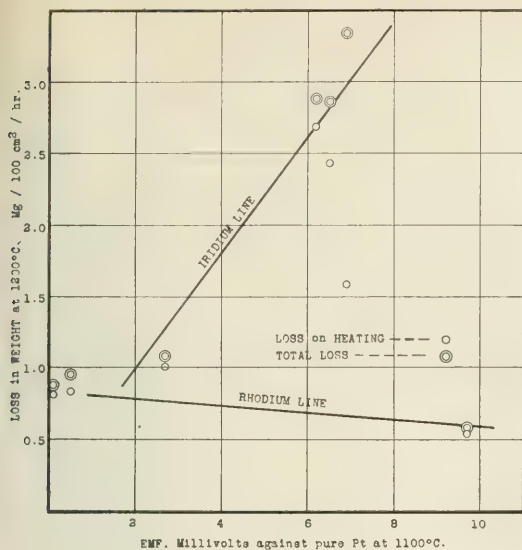


FIG. I

ing for several crucibles is shown in Fig. II. These curves are typical of certain classes of laboratory ware, i. e., pure platinum, platinum containing rhodium, and platinum containing iridium.

The loss in weight of platinum laboratory ware is here shown to be negligible below 900° C., but for all crucibles tested the loss at 1000° C. is appreciable and rapidly increased with temperature.

The presence of rhodium, iridium, and iron in platinum produces similar results on heating at 1000° and at 1200° C. Rhodium decreases and iridium increases the loss of weight. Iron is objectionable because of the surface film of oxide which forms on heating the platinum containing it.

It is possible to predict the loss in weight of an iridium or rhodium alloy crucible on heating below 1200° C. provided the ware contains little iron.

In Table III are given the approximate changes in weight to be expected in mg. per 100 cm<sup>2</sup>. of surface and per hour of heating of platinum nearly free from iron. The presence of iron in appreciable quantities renders the prediction uncertain but it always acts in the direction of lowering the volatilization loss; silica, if taken up from the furnace, will also tend to lower the results slightly.

TABLE III—APPROXIMATE LOSS IN WEIGHT, MG./100 CM<sup>2</sup> HOUR, AT TEMPERATURES INDICATED, FOR PLATINUM NEARLY FREE FROM IRON

Platinum containing:	Pure Pt	1% Ir	2.5% Ir	8% Rh
900° C. or less	0	0	0	0
1000	0.08	0.30	0.57	0.07
1200	0.81	1.2	2.5	0.54

Other metals, such as osmium, alloyed with platinum may further decrease the loss on heating and it is hoped to try some of them in the near future.

It was hoped to be possible, in this investigation, to carry out experiments with platinum crucibles alloyed with small quantities of osmium, but this was found to be impossible on account of the condition of the platinum market.

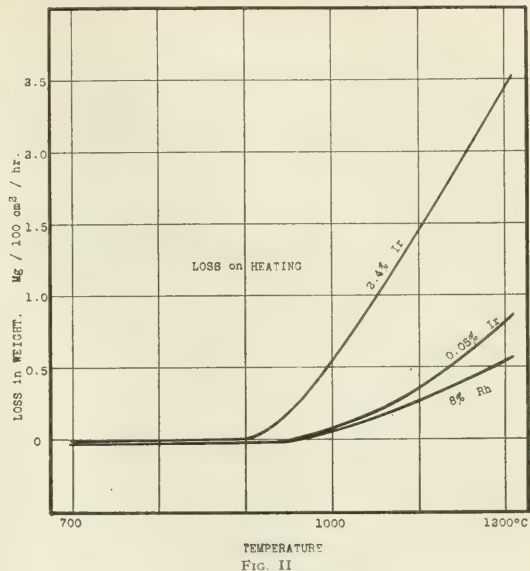


FIG. II

Experiments by other observers have recently been made which contribute data to this problem of the loss or gain in weight of heated platinum ware. Thus Vinal and Bovard<sup>1</sup> find on heating to about 600° C. platinum voltameter dishes of 38 and 80 g. weight freed from silver "very little change if any in the weight of the empty cups due to heating them to redness."

Sosman and Hostetter,<sup>2</sup> investigating the reduction of iron oxides by platinum, show, as would be expected from a consideration of phase relations, that: "if the existing pressure of oxygen is less than this equilibrium pressure, the oxide will dissociate and metallic iron will be absorbed by the platinum. If the pressure of oxygen be greater, on the other hand, iron from the platinum solution will be oxidized, the oxide will separate on the surface of the metal, and the concentration of the iron in the platinum will be reduced." In the experiments listed in the above tables we are, of course, working at a pressure high enough and at temperatures low enough for the second operation, oxidation of the iron.

#### SUMMARY AND CONCLUSIONS

In addition to the conclusions from the previous work of Burgess and Sale,<sup>3</sup> there may be noted the following:

1—Platinum ware in the form of crucibles of whatever degree of purity, behaves, with respect to gain or loss of weight, on heating in air at ordinary atmospheric pressure, in a manner characteristic only of the temperature of heating.

2—Each impurity (as iridium, rhodium, or iron) appears to exert its effect on the volatilization of platinum independently.

3—For platinum crucibles of all degrees of purity containing Ir, Rh, Fe, Si (up to a content of at least

<sup>1</sup> Bureau of Standards, *Scientific Paper* 271, 1916.

<sup>2</sup> *J. Wash. Acad. Sci.*, 6 (1915), 293.

<sup>3</sup> *Loc. cit.*



50 per cent Ir. The loss on heating is negligible below about 600° C.

4—Below this temperature there may even be a slight gain in weight on heating platinum, owing to the iron content diffusing to the surface and oxidizing. At higher temperatures the presence of iron will lower the volatilization loss by amounts depending on the quantity of iron present. There appears to be no platinum made which does not contain some iron.

5—The volatilization of platinum containing rhodium is less than that of pure platinum at all temperatures above 600° C.

6—The volatilization of platinum containing iridium is, above 900° C., very much greater than that of pure platinum, and increases with the Ir content and with temperature.

7—It appears to make no material difference in the volatilization results, in the range 700° to 1200°, what is the order of heating, ascending or descending temperatures.

8—In an oxidizing atmosphere at temperatures of the order of 1000° C., platinum, in the presence of (but not in contact with) silica, will apparently take up small quantities of this substance.

9—The loss in crucible weight due to the solution of soluble matter in HCl, after heating, is variable, depending on the crucible, and may be large. This loss is relatively greater at low than at high temperatures.

10—All of the above losses, caused by heating, acid treatment, and iron diffusion, apparently continue with undiminished magnitude after the first treatment, which is usually erratic; although, eventually, of course, the concentration of iron, etc., must become appreciably diminished.

BUREAU OF STANDARDS, WASHINGTON

## VARNISH ANALYSIS AND VARNISH CONTROL I—MOLECULAR WEIGHTS OF VEGETABLE OILS

By MAX Y. SEATON AND G. B. SAWYER

Received February 23, 1916

Modern methods of analysis and control have only recently been applied to the products of the varnish-making industry. Physical chemistry has, in particular, been the last branch of the science to find application in this field. Although physical constants of varnishes have been determined as a matter of routine testing for a great many years, investigation has in general stopped with the determination of such constants as viscosity or gravity and the relation which variations of these constants bear to variations in the treatment in the varnish kettle has but recently been appreciated.

Considerable work in the determination of physical constants of varnishes and the causes for the variations in these constants has been done in this laboratory, together with much work on the chemical properties of the products produced. It is planned to issue a series of papers covering as much of this work as is available for publication. The first paper, which follows, will deal with the determination of molecular weights of the vegetable oils used in the varnish-

making industry and will indicate the molecular weights of some of the resulting products.

The literature pertaining to the composition and reactions of the oils commonly used abounds in references to the molecular weights of both the raw and the heat treated oils. The inter-molecular changes which occur during treatment of the oil in varnish-making processes are admittedly very complex. Determination of molecular weights has recently been found valuable for their study and has been widely used by various authors.

In the attempt to apply the usual methods for the determination of molecular weights of substances in solution to oils and varnishes, so many difficulties have arisen that it has been necessary to investigate the use of a number of solvents, until finally one was found in which consistent molecular weights could be obtained. This paper, then, will cover the investigation of methods for the determination of molecular weights of oil and varnish products, together with a description of a suitable and accurate method.

The observed molecular weight of a vegetable oil or of a varnish mixture is in every case merely a mean or average molecular weight of the several substances which may be present. Thus, the most simple substance which will generally be investigated, linseed oil, will contain the glycerides of a number of different fatty acids together with small amounts of alcohols and traces of other substances. Under no circumstances can the molecular weight be looked at as being as definite a constant as it is in case of a pure material, but it can, nevertheless, give much information as to the composition and properties of the material investigated.

The literature in which most complete record of molecular weight determinations in this field appears refers to the mechanism of the polymerization reactions both of linseed and China wood oils. In this connection Maquenne,<sup>1</sup> Lewkowitsch,<sup>2</sup> Genthe,<sup>3</sup> Morrell,<sup>4</sup> Normann,<sup>5</sup> and others, have reported determinations using the boiling point method in ether and in benzol, and the freezing point method in benzol and glacial acetic acid.

In general, results of previous investigators show a comparatively wide variation in the values obtained. Some difference is naturally to be expected on account of the different sources and accordingly different composition of the oils studied, but the values reported differ too widely for the difficulty to be ascribed to this source. There is a dearth of information as to the exact details of the methods used, so that in most cases critical examination is impossible. Of extreme interest, however, is the observation of Normann,<sup>5</sup> who shows that varying values are obtained in different concentrations of solution. Normann obtained these results in an investigation of the molecular weight of raw and polymerized oils and although

<sup>1</sup> *Compt. rend.*, **1902**, 686-688.

<sup>2</sup> "Chem. Tech. and Oils, Fats and Waxes," Vol. III, pp. 98-100.

<sup>3</sup> *Z. angew. Chem.* **19** (1906), 2098.

<sup>4</sup> *Trans. Chem. Soc. London*, **101** (1912), 2082-2089.

<sup>5</sup> *Chem.-Ztg.*, **1907**, 188.

he details in full the results of his experiments he does not suggest a remedy for the trouble indicated. As far as the literature available to the writers indicates, his observation is the only one of this type which has been reported on such molecular weight work.

In a number of cases various authors have reported molecular weights of the acids prepared by saponification of the oils. It is probable that such a device has been used, owing to the greater solubility of the acids in most solvents, and also to the fact that by the use of the acids, solvents of the type of glacial acetic acid are made available. Such solvents cannot be used on the original oils on account of low solubility. In many instances where the molecular weights of the acids are obtained, simple molecular weights are not obtained. Morrell,<sup>1</sup> for example, shows that the molecular weight of oleic acid in benzol is double the simple molecular weight, which latter however is obtained in glacial acetic acid.

An examination of the literature shows that there appears to be a conflict of evidence as to whether the molecular weights of oil-acids paralleled those of the oils from which they are prepared; *i. e.*, whether in polymerized oils the molecular weight of the fatty acid increases in the same ratio as that of the oil. Until this question can be cleared up, methods dealing with the molecular weights of the acids must be considered as useful only when no satisfactory methods for determination of the molecular weights of the oils themselves are available. The determinations on the acids necessitate, in addition, lengthy saponification, separating and drying processes and from the standpoint of speed of working are not attractive.

In the determinations attempted in this laboratory, the freezing point method using benzol as a solvent was first tried. The method is attractive on account of its rapidity and sharpness of freezing point. Benzol is a good solvent for most oils and polymerized oils and might be expected to give satisfactory results. The apparatus used was the familiar freezing point apparatus. In all determinations benzol of a boiling point range of less than one-tenth degree was used. In Table I are given the results obtained on a number of substances by use of this method.

It is seen at once that the molecular weight of the oils in solution varies widely with the concentration. Especially in the case of polymerized oils the variations are very great. The determinations on oil acids indicate that the method does not give correct results even on these substances. When the acids are obtained from raw linseed oil the molecular weight remains approximately constant over a wide variation of concentration, the value obtained being about double the simple molecular weight, but when the acids are obtained by saponifying and acidifying a polymerized oil a constant molecular weight cannot be obtained, the variations becoming more pronounced as polymerization increases.

In every case a lowering of the molecular weight with increase in concentration is observed. This is rather surprising as the reverse result might perhaps be expected. It is known, for example, that solutions of polymerized oils in many solvents show all of the characteristics of colloidal solutions. In such

TABLE I MOLECULAR WEIGHTS BY FREEZING POINT METHODS

Substance	BENZOL SOLVENT		NITROBENZOL SOLVENT	
	Per cent Concentration	Mol. Wt.	Per cent Concentration	Mol. Wt.
Naphthalene	0.80	126	0.61	130
(true molecular weight = 128)	1.93	125	1.38	129
Benzoic Acid	0.38	202	0.54	200
(true molecular weight = 122)	1.26	217	1.41	222
	2.78	223	2.29	224
	2.78	223		
Raw Linseed Oil	0.593	930	1.37	825
	1.32	890	3.48	845
	2.46	874	7.09	895
	3.46	864	9.75	905
	5.55	803		
	8.45	740		
Raw China Wood Oil	10.00	728		
	1.5	765		
	3.5	760		
	6.5	740		
	10.0	715		
	19.5	590		
Polymerized Wood Oil.	12.2	1290		
heated 45 minutes at 450° F.	22.1	1025		
	31.0	890		
Oil Acids from Refined Linseed Oil	8.6	500		
	17.2	490		
	19.3	480		
Oil Acids from Refined Linseed Oil	15.1	580		
heated 1 hour at 600° F.	22.3	555		
	33.0	520		
Oil Acids from Refined Linseed Oil	6.3	780		
heated 3 hours at 600° F.	13.5	755		
	31.0	690		

solutions and in solutions in which association of the solute occurs molecular weight rises as concentration is increased. A lowering such as is indicated in Table I is generally ascribed to combination between the solvent and the solute, and until some better explanation appears this must be accepted as the cause of the phenomenon noted here.

It is possible that association does play some part in the changes observed, although it is apparently overbalanced in this case by the influence of combination. Solvents which generally possess markedly different associating powers from benzol might be expected to give interesting results. Benzol is generally accepted as an associating solvent; nitrobenzol behaves as a neutral solvent and chloroform as a dissociating solvent in ordinary molecular weight determinations. The two latter materials were therefore chosen for further investigation.

Determinations of molecular weight by the freezing point method using nitrobenzol as the solvent were made in the ordinary apparatus and although slight difficulty was found with excessive undercooling fairly accurate results could be obtained. Some of the observations in this solvent appear in Table I. In this case the characteristics usually ascribed to association in solution appear, that is, increase of molecular weight with increase in concentration. It is interesting to note, however, that benzoic acid increases in exactly the same ratio in this solvent as it did in benzol, while the behavior of linseed oil is exactly the opposite.

Boiling point determinations were made by suspending the boiling point tube in a Dewar bulb to insure insulation from external temperature changes, and heating the solvent to boiling by means of an

<sup>1</sup> *J. Soc. Chem. Ind.*, **34**, 105.



immersed coil of wire heated electrically. This method has been widely applied recently and has been found to give results comparable with those obtained in the older style boiling point apparatus.

TABLE II—MOLECULAR WEIGHTS BY BOILING POINT METHODS  
CHLOROFORM SOLVENT

	% Conc.	Mol. Wt.
Naphthalene (a)	0.8	129
	2.7	133
Benzene Acid (b)	0.2	211
	0.63	222
	1.75	228
	5.70	220
Alkali Refined Linseed Oil.....	0.87	(c)
	2.00	1400
	3.00	865
	4.6	700
	6.0	655
	7.4	580
	9.3	472
Raw Linseed Oil...	1.3	(d)
	2.9	845
	4.3	700
	5.75	625
	7.2	605
	9.3	512
Polymerized Linseed Oil.....	1.8	(e)
	3.6	3380
	5.5	1800
	7.9	1192
	9.8	960

(a) True Mol. Wt. = 128. (b) True Mol. Wt. = 122. (c) Lowered Boiling Point 0.01°. (d) Lowered Boiling Point 0.033°. (e) Lowered Boiling Point 0.07°.

The results of determinations in chloroform by this method (see Table II) indicate lowering of molecular weight with increase in concentration, although benzoic acid still behaves as though associated. The variations are even greater in chloroform than in the other solvents previously tried. The remarkable lowering of the boiling point which has been observed by Firth and Myers<sup>1</sup> appears here when low concentrations are used. In one instance, for example, it has as high a value as 0.07°. That this phenomenon occurs explains to some extent the abnormally high molecular weights observed in low concentrations.

Using benzol as a solvent, different results as regards association might be expected at boiling temperature from those observed at freezing temperature. Accordingly, determinations were made by the boiling point method in benzol. Here again (see Table II) molecular weight varies widely with concentration and the results cannot be accepted as satisfactory. It should be noted that the value of the constant used in calculating the results was somewhat in error as is shown by the high molecular weight of naphthalene observed.

It is seen from the preceding results that all the methods so far tried have given unsatisfactory results. In the search for a solvent which would give normal molecular weights, stearic acid was suggested. Stearic acid has been recommended by Biltz,<sup>2</sup> who finds it a satisfactory solvent for many determinations. It is especially desirable in an investigation of the molecular weights of oils as it possesses remarkable solvent powers for the highly polymerized and highly oxidized oils which are but sparingly soluble in other solvents. It was accordingly tried as a solvent in the usual freezing point method.

It developed at once that the ordinary apparatus

is not suitable as the stearic acid tends to crawl up the side of the tube and up the stirrer, giving considerable trouble. Such difficulty was readily remedied, however, by covering with asbestos paper a piece of brass tubing of such size as to fit over the top of the freezing point tube, and winding on a resistance coil of nichrome wire. By passage of a suitable current the tubing was maintained at about 60° C. By the use of this simple heater the top of the freezing point tube remains clean and free from acid throughout many determinations.

Stearic acid of commercial purity, preferably the triple pressed grade, will be found suitable for the determinations. The melting point is not quite as sharp as in the case of benzol, but it is sharp enough to give concordant results as the data quoted later will show. It is necessary first to dry the acid by heating it for some time below 100° C. in an oven or on a steam-heated hot plate. The acid thus dried does not readily absorb moisture from the air and can be filled directly into the freezing point tube. The constant of the acid used was found to be 42.5, a figure in concordance with the results reported by Biltz.<sup>1</sup>

Table III indicates the results of the determinations of molecular weights of a large number of substances by this method. In this method no uni-

TABLE III—MOLECULAR WEIGHTS BY STEARIC ACID METHOD

Substance	Per cent Concentration	Molecular Weight
Naphthalene.....	3.2	126
(true molecular weight 128)	9.1	127.5
Benzoic Acid.....	2.2	120
(true molecular weight 122)	6.1	121
	10.8	123.1
Raw Linseed Oil.....	3.8	740
(chemically refined)	7.4	735
	10.2	760
Refined Linseed Oil.....	4.3	735
heated to 600° F.	7.7	770
	11.8	765
Refined Linseed Oil.....	4.1	1000
heated 1 hr. at 600° F.	8.4	1000
	12.0	1020
Refined Linseed Oil.....	3.84	1250
heated 2 hrs. at 600° F.	7.5	1220
	18.8	1240
Refined Linseed Oil.....	6.2	1510
heated 3 hrs. at 600° F.	11.3	1500
	17.1	1530
Acids from Refined Linseed Oil.....	5.3	274
	14.0	300
	19.0	316
Acids from Refined Linseed Oil.....	5.9	310
heated 1 hr. at 600° F.	10.0	325
	21.8	342
Acids from Refined Linseed Oil.....	5.1	335
heated 3 hrs. at 600° F.	12.1	354
	19.2	380
Raw China Wood Oil.....	7.0	840
	13.5	825
	28.2	855
Polymerized China Wood Oil.....	6.5	1700
heated 45 mins. at 450° F.	14.8	1760
	21.1	1740
Soya Bean Oil.....	5.6	719
	8.1	735
	10.2	750
Polymerized Soya Bean Oil.....	15.0	1250
heated 2 hrs. at 600° F.	30.0	1230
W. G. Rosin.....	5.9	282
	6.5	288

form variation of molecular weight with concentration is shown. In the determination of the molecular weights of oil acids slight variation does appear, it is true, but this is not as pronounced as in the case of molecular weights of oils in other solvents. It should also be noted in this connection that the molec-

<sup>1</sup> Chem. Soc. Trans., 105, 2887-2892.

<sup>2</sup> Z. physik. Chem., 19, 385.

<sup>1</sup> Loc. cit.

ular weights of the acids obtained are fairly close to the simple molecular weight as calculated from the combining numbers. With the possible exception noted, then, the method can be applied to routine determinations without the necessity of laboriously plotting curves showing the concentration effect for each oil used.

Owing to the great solubility in stearic acid of the various oils likely to be encountered, the method is widely applicable and, in fact, there will be but very few oils found that cannot be dissolved completely in the quantities required for a determination. The method is simple and easy to operate. No correction for loss of solvent by evaporation need be applied. The solvent is non-hygroscopic and the precautions which must be taken with nitrobenzol and, to some extent, with benzol, can therefore be omitted.

Some difficulties with the method have, of course, developed during its investigation in this laboratory; these in general, however, admit of satisfactory solution. For example, to obtain concordant results it is necessary to keep the bath in which the freezing point tube is immersed at approximately 40° C. Variation of more than one degree in the temperature of the bath will cause slight variation in the observed freezing point. If an automatically regulated thermostat is available that factor will cause no trouble. It is necessary to stir somewhat more vigorously than when benzol is used, in order to prevent undue supercooling. Under no circumstances are the observed freezing points sharper than one one-hundredth of a degree. On this account the accuracy of the method is not as great as the freezing point method in benzol but it compares very favorably with any of the boiling point methods.

The method as outlined clears up a number of difficulties which have been found with the determinations of molecular weights of oils and varnishes in the past and opens up the field for further investigations of this type. It has been found in this laboratory, for example, that determinations of molecular weights are of great importance in varnish control work and of even greater value in varnish analysis, for in many cases the treatment of an oil or varnish will be more accurately represented by its molecular weight than by any other of the common constants. For such application it is, of course, necessary to have at hand methods for determining the molecular weight of the various substances which make up the mixture of which the mean molecular weight has been determined by the methods indicated.

The process of determining such individual molecular weights in substances as simple as oils and polymerized oils is comparatively easy and will be outlined in full in a subsequent paper on polymerized linseed oil. Much greater difficulties arise when the molecular weight of the oil portion of a rosin-China wood oil varnish needs to be determined, but considerable progress has been made in the development of satisfactory methods. This will also be reported on later.

#### SUMMARY

The question of the determinations of molecular weights of oils, treated oils and varnishes has been outlined and the value of such investigations brought out.

The most usual solvents used in molecular weight determinations have been investigated and their inadaptability to the present problem pointed out.

A method for determinations of molecular weights of these products by use of stearic acid as a solvent has been outlined and the conditions surrounding its use developed.

Determinations by this method have been made on a large number of oil and varnish products.

The applicability and value of such a method have been indicated.

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#### GILSONITE AND GRAHAMITE: THE RESULT OF THE METAMORPHISM OF PETROLEUM UNDER A PARTICULAR ENVIRONMENT

By CLIFFORD RICHARDSON

Received December 29, 1915

Gilsonite and grahamite are two forms of solid native bitumen which are not widely distributed in nature, gilsonite being the rarer, and are the result of metamorphism of petroleum under a particular environment. They are found in fissure veins which approach the vertical and afford conditions which are favorable for the metamorphosis of petroleum into those materials. This change has gone on, under a varying time factor, to an extent that has resulted in substances presenting various degrees of condensation, from one which flows slowly in the sun, as in the case of the softest gilsonite, to one of the hardness of the brittlest grahamite, which does not melt even at high temperatures. Between these extremes is to be found materials of varying consistency, both in the gilsonite and grahamite series, showing that these bitumens are the products of metamorphism, to a varying extent, under the environment to which they have been subjected, of some more or less liquid bitumen.

The indication of these changes or metamorphism is to be explained in the gradual decrease, as the metamorphism goes on, of the hydrocarbons and their derivatives which are soluble in naphtha, from the amount present in the softest gilsonite to that found in the hardest grahamite, with a corresponding increase in the residual coke which they yield on ignition. The following data for typical gilsonites and grahamites demonstrate this very plainly.

The gradual decrease from the softer to the harder form in the percentage of bitumen soluble in naphtha and increase in the yield of residual coke is striking. At the same time there is a corresponding increase, as the metamorphism increases in degree, in the melting point and in the specific gravity. These results



demonstrate very plainly the changes which go on in nature under a certain environment, in particular types of petroleum. The environment is a governing condition. Under a different one true asphalt would be formed, such as is widely distributed in nature. The question arises as to what these conditions are, especially in view of the fact that both forms of solid bitumen must be looked upon as originating in petroleum and are sharply differentiated from each other. The asphalts consist, to a very considerable extent,

keep from the fact that in one instance in the strata in which gilsonite occurs there is a fault extending a quarter of a mile without any disturbance of the enclosed bitumen, showing that the gilsonite must have been introduced into the vein before the displacement.

WOODWORTH BUILDING  
NEW YORK CITY

## THE GALACTAN OF *LARIX OCCIDENTALIS*

By A. W. SCHORGER AND D. F. SMITH

Received March 1, 1916

SOURCE	Flow F	Specific Gravity	Per cent Soluble in Naphtha	Per cent Residual Coke
RESIDUAL Texas Residual Petro- leum		0.9524	88.0	6.5
GILSONITES				
1 Utah (softest).....	285	1.011	55.5	10.0
2 Utah.....		1.037	46.9	12.3
3 Utah.....	260		47.2	12.8
4 Utah.....	345	1.037	46.1	13.9
5 Utah (hardest).....	Intumesces	1.057	24.5	16.7
GRAHAMITES				
Cuba, Bahia.....	Intumesces	1.157	38.8	40.0
Trinidad.....	Intumesces	1.156	14.8	40.0
West Va.....	Intumesces	1.130	9.4	36.8
Colorado.....	Intumesces	1.160	0.8	47.4
Oklahoma.....	Intumesces	1.184	0.4	51.4

of hydrocarbons not acted upon by sulfuric acid; *i. e.*, of saturated hydrocarbons. Gilsonite, on the other hand, contains but a very small amount of such components. They may both have a common origin in petroleum but the environment to which this has been subjected has been so dissimilar in each case as to result in quite a different product. In the case of the gilsonite, the bitumen in which it has originated has been confined in relatively narrow veins. In that of the asphalts it has been spread out horizontally and subjected to quite different conditions, with a resulting product of entirely different character, the one consisting of more than 20 per cent of saturated hydrocarbons and the gilsonites and grahamites containing but a relatively small amount, as appears from the following data:

	Specific Gravity	Per cent Soluble in Naphtha	Per cent Saturated Hydrocarbons
Petroleum Flux (Texas).....	0.956	97.5	72.8
Residual Pitch.....	1.089	65.0	33.1
Bermudez Asphalt.....	1.082	62.2	24.4
Gilsonite (Utah).....	1.044	47.7	5.5
Grahamite (Okla.).....	1.171	0.4	0.3

These differences in character may be accounted for by the fact that gilsonite and grahamite originate in veins which are vertical or nearly so while the asphalts occur under entirely different conditions.

A material intermediate between an asphalt and gilsonite is found in shales of Tertiary age in the Central Valley of California at Asphalto, in vertical fissures, which confirms the idea that the character of a solid bitumen originating in petroleum is dependent on the environment to which it is exposed.

It is of interest to observe that the veins of gilsonite and grahamite end rather abruptly at certain depths and do not thin out gradually, and also that the material near the vein walls and also the surface consists of a harder form of bitumen than the mass of the deposit.

Grahamite is the result of metamorphic changes in gilsonite and gilsonite of similar changes in petroleum brought about by its environment. That they are of considerable geological age as to origin can be

The western larch (*Larix occidentalis*, Nuttall) is found in extensive stand in the Pacific Northwest. It is a magnificent tree sometimes reaching a height of 200 feet and a diameter of 5 to 8 ft. In the course of some experiments it was found that a considerable portion of the wood was soluble in water. Further investigations led to the interesting discovery that the soluble matter consisted almost entirely of a galactan  $(C_6H_{10}O_5)_n$  (specific rotation  $[\alpha]_D^{20} + 12.11^\circ$ ) yielding only galactose on hydrolysis. The water-soluble content of the wood varied from 8 to 17 per cent in the individual trees examined.

A large number of galactans have been found in nature but only a few have been well characterized. Many of the galactans yield other sugars than galactose on hydrolysis so that the terms galacto-mannan, galacto-araban, etc., are applied, depending upon the sugars obtained. The galactan from western larch has been called  $\epsilon$ -galactan. The  $\delta$ -galactan isolated by Müntz<sup>1</sup> from the seeds of lucerne, by Maxwell<sup>2</sup> from beans, and by Lindet<sup>3</sup> from barley has the rotation  $a_j + 84.6^\circ$  and is precipitated from aqueous solution with lead acetate:  $\epsilon$ -galactan has the rotation  $[\alpha]_D^{20} + 12.11^\circ$  and it is not precipitated from aqueous solution with lead acetate.

The  $\beta$ -galactan of Winter<sup>4</sup> and Prinsen-Geerligs<sup>5</sup> has a yellow color and when dried is insoluble in water:  $\epsilon$ -galactan is white and is readily soluble in water after drying.

The  $\gamma$ -galactan of Lippman<sup>6</sup> and others is *originally* insoluble in cold water and is precipitated from concentrated solutions by lead acetate:  $\gamma$ -galactan differs also from  $\epsilon$ -galactan in having a very high rotation,  $[\alpha]_D = +238^\circ$ . The  $\delta$ -galactan of Payen<sup>7</sup> and Bauer<sup>8</sup> obtained from agar-agar and other sources is insoluble in cold water and when dissolved in 500 parts of boiling water a gelatinous mass is formed on cooling:  $\epsilon$ -galactan shows no inclination to gelatinize.

The unusual occurrence of  $\epsilon$ -galactan was of such interest as to warrant a careful examination of the literature with respect to the occurrence in woods of carbohydrates yielding galactose. It was found that Trimble<sup>9</sup> had examined an *excrecence* of *Larix occidentalis* that contained 19.4 per cent of reducing sugar and

<sup>1</sup> *Compt. rend.*, **94**, 453.

<sup>2</sup> *Am. Chem. J.*, **12**, 26.

<sup>3</sup> *Bull. B. A. Chem.*, **20**, 1225.

<sup>4</sup> *Deut. Zuckerind.*, **15**, 538.

<sup>5</sup> *Chem. Ztg.*, **21**, Rep. 150.

<sup>6</sup> *Ber.*, **20** (1887), 1001; *Z. Ver. Zuckerind.*, **36**, 259; **37**, 468; **38**, 1252.

<sup>7</sup> *Compt. rend.*, **49**, 521.

<sup>8</sup> *Jour. prakt. Chem.*, **30**, II, 283.

<sup>9</sup> *Am. J. Pharm.*, **70** (1898), 15.

68.7 per cent of non-reducing sugar. The reducing sugar was stated to resemble dextrose but none of the carbohydrates were actually identified. In the specimens of wood examined no indication of exudations was observed. We have found that galactan itself has a slight reducing action on Fehling's solution. In the purification of the galactan all the alcoholic solutions were saved and examined for the occurrence of free sugar. The concentrated extract deposited a small amount of impure crystals having a sweetish taste. The phenylosazone was prepared but the amount was too small to be sufficiently freed from impurities to give a melting point of value. Apparently the only authentic occurrence of galactose in nature is that found by Lippman.<sup>1</sup> Ivy berries after a frost were found to have a crystalline efflorescence of galactose. It is possible that the free sugar in the larch is galactose that has been formed in a similar manner.

Galactans have been indirectly found in small amounts in wood by oxidation to mucic acid, but in no case apparently has the source of the mucic acid been actually isolated or determined. Tollens,<sup>2</sup> Krause<sup>3</sup> and recently Hägglund<sup>4</sup> have detected galactose in sulfite liquor. The galactose found by Hägglund amounted to only 0.27 per cent of the weight of the wood of *Pinus sylvestris*. Klason<sup>5</sup> also obtained traces of mucic acid from *P. sylvestris* and Fromherz<sup>6</sup> from the lignocellulose of the aspen (*Populus tremula*).

We have found galactans to be characteristic of the coniferae, using the mucic acid method of identification.

#### EXPERIMENTAL

**ISOLATION OF  $\epsilon$ -GALACTAN**—The following method of isolation was adopted, after considerable experimentation:

Approximately 500 g. of sawdust are placed in a flask with 2 liters of water and allowed to digest on the steam bath for 24 hours, with frequent shaking. The amber-colored extract is filtered off and the extraction repeated with additional quantities of water. The extract is decolorized by addition of 15 to 20 cc. of a saturated solution of tannic acid followed by a slight excess of a solution of lead acetate. The tannic acid-lead acetate compound that occludes all the coloring matter is allowed to settle and the supernatant solution decanted and filtered. The excess of lead acetate is removed by treating the filtrate with hydrogen sulfide and filtering. After neutralizing the free acetic acid with sodium carbonate and evaporating the extract to a thin syrup under reduced pressure to minimize charring, the galactan is precipitated by allowing the syrup to flow slowly into a large excess of 95 per cent alcohol with constant stirring.

Under proper conditions the galactan precipitates as a white gummy mass that becomes hard and granular as dehydration proceeds. In some cases the galactan

forms a milky colloidal solution when poured into alcohol. Under these conditions precipitation can be effected by the addition of a small amount of an electrolyte such as hydrochloric acid. Products of hydrolysis, if formed, will be removed in the subsequent purification. The galactan is then filtered. In order to obtain a pure product it is necessary to resort to fractional precipitation with the aid of a centrifuge. The galactan is dissolved in sufficient water to form a thin syrup and then 50 per cent alcohol is added with rapid stirring until permanent turbidity is produced. The solution is then quickly placed in the centrifuge and whirled until the supernatant liquid is perfectly clear. The solution is then decanted and the same operation repeated as often as necessary. The galactan is finally purified by repeated solution in water and precipitation with alcohol. It is finally triturated with absolute alcohol, washed with ether and dried at 105° C.

**PROPERTIES OF  $\epsilon$ -GALACTAN**—The purified galactan forms a white, amorphous, granular powder, readily forming a clear solution in cold and hot water without gelatinization, and is slightly soluble in acetic acid and 95 per cent alcohol. It had no definite melting point but decomposes around 250°. One gram of a very pure preparation gave only a trace of ash. A 10 per cent solution of the galactan in water had the specific rotation  $[\alpha]_D^{20} + 12.11^\circ$ .

Twenty-five cc. of a solution containing 2.5 g. of galactan reduced 0.1554 g. of Cu by Allihn's method. When distilled with 12 per cent hydrochloric acid the galactan gave 6.18 per cent of furfural equivalent to 10.54 per cent of pentosan. Pure galactose under similar conditions gave a precipitate with phloroglucine equivalent to 0.55 per cent furfural. The furfural phloroglucide from the galactan was only slightly soluble in 95 per cent alcohol showing the absence of methyl furfural in the distillate. Analysis of the galactan gave the following results:

	Found	C <sub>6</sub> H <sub>12</sub> O <sub>5</sub>	Calculated for 89.5 C <sub>6</sub> H <sub>12</sub> O <sub>5</sub> + 10.5 C <sub>6</sub> H <sub>8</sub> O <sub>4</sub>
C.....	44.63	44.44	44.53
H.....	6.20	6.17	6.16
O.....	49.17	49.39	50.31

The yield of furfural indicates the presence of 10.5 per cent pentosan but no pentose could be isolated from the sugars formed by hydrolysis of the galactan. The differences between the figures found by analysis and those calculated are insufficient to establish the presence of a pentosan. The mother liquor remaining after the removal of the greater portion of the galactose by crystallization gave on acetylation only galactose pentacetate; the osazone obtained was that of galactose; and on oxidation with nitric acid, mucic and oxalic acids were formed but no trihydroxyglutaric acid. It is believed that the formation of furfural is due to the peculiar structure of the galactan molecule and not to the presence of a pentosan residue. A parallel case is found in the celluloses isolated from various woods. The cellulose from western larch gave 5.5 per cent of furfural and that from yellow birch about 17.0 per cent of furfural on distillation with 12 per cent hydrochloric acid.

<sup>1</sup> *Irr.*, **43** (1910), 3611.

<sup>2</sup> *Ber.*, **23** (1890), 2990.

*Chem. Ind.*, **29** (1906), 217.

<sup>4</sup> *Biochem. Z.*, **70** (1915), 416.

*Arkiv. Kemi, Min. Geol.*, [6] **3** (1908), 1.

<sup>6</sup> *Z. physiol. Chem.*, **50** (1906), 238.



The difficulty of purifying the galactan is due to its colloidal nature. When examined in an ultra-microscope of the Zsigmondy-Sedentopt type a fine Tyndall effect was obtained. In determining the molecular weight by the freezing point method 3.875 g. of galactan dissolved in 30.88 g. of water lowered the freezing point  $0.055^{\circ}$ . These data indicate a molecular weight of 3,386 or an empirical formula  $(C_6H_{10}O_5)_{20}$ . Since the galactan was of questionable purity the lowering of the freezing point observed may have been due to the presence of foreign matter.

**HYDROLYSIS OF THE GALACTAN** The galactan was hydrolyzed by dissolving in 2.5 per cent sulfuric acid in a round bottom flask, provided with a reflux condenser, and boiling in an oil bath maintained at  $105-110^{\circ}$ . The time necessary for complete hydrolysis varied considerably with the concentration of the solution in galactan. In one experiment 57 g. of galactan dissolved in 1.5 liters of 2.5 per cent  $H_2SO_4$  required 40 hrs. boiling for complete hydrolysis. During this period the contents had charred somewhat. The sulfuric acid was then neutralized with  $BaCO_3$ , filtered, the filtrate decolorized by boiling with blood charcoal and again filtered. Concentration of the filtrate under diminished pressure gave a syrup only slightly colored. The syrup was then taken up in hot 95 per cent ethyl alcohol and allowed to stand over night for the precipitation of a small amount of gummy matter invariably present. The clear alcoholic solution was decanted, evaporated to a syrup and the syrup treated with a small amount of absolute methyl alcohol. On cooling in a freezing mixture and stirring with a glass rod crystallization of the sugar takes place at once. The crystals were then filtered off, washed with methyl alcohol, redissolved in a small amount of water, and again crystallized with methyl alcohol as before.

This method gives excellent results, perfectly white crystals being readily obtained. Glacial acetic acid and hot methyl alcohol containing about 0.25 per cent of HCl gas were also employed. The syrup obtained from the 57 g. of galactan hydrolyzed as outlined above was then taken up in about 200 cc. of hot methyl alcohol containing hydrochloric acid. By seeding with galactose crystals and scratching with a rod, 35 g. of sugar crystallized out after standing in the ice box over night. The mother liquor from these crystals gave an additional 2 g. of sugar after 24 hours, making a total yield of 65 per cent crystalline sugar. On concentrating the mother liquor to a syrup, adding phenylhydrazine and glacial acetic acid and heating on the water bath, only a small amount of osazone was obtained.

Another experiment was carried out in which the course of the hydrolysis was followed by Fehling's solution. Galactan amounting to 9.4278 g. was dissolved in one liter of 2.5 per cent sulfuric acid and hydrolyzed in the manner previously mentioned. By means of a syphon through the stopper of the flask portions of the solution were removed at regular intervals. After cooling, 25 cc. of the solution were

transferred to a 100 cc. flask, the acid being neutralized with sodium carbonate and the solution made up to the mark. Twenty-five cc. of the solution so prepared were used for determining the reducing power by Allihn's method. The copper was obtained electrolytically. The factor 0.898 given by Brown<sup>1</sup> was used in reducing to galactose the percentages of sugar obtained in terms of dextrose. Theoretically, 9.4278 g. of galactan should yield on hydrolysis 10.475 g. of galactose and the 25 cc. sample employed would contain 0.06547 g. of galactose. The following results were obtained:

No. hours Boiled	Mg. of Cu Found	Mg. Galactose Found	Theoretical Amount of Galactose	Per cent of Theoretical
3	77.1	43.82	65.47 g.	66.93
5	110.1	62.47	65.47 g.	95.42
7	111.1	62.97	65.47 g.	96.19
8	114.4	64.85	65.47 g.	99.06
12	130.4	62.58	65.47 g.	95.59
18	106.5	60.41	65.47 g.	92.17
20	105.6	59.91	65.47 g.	91.51
28	105.1	59.63	65.47 g.	91.08

The results obtained show that under the conditions of the experiment, maximum hydrolysis, that is 99 per cent, is obtained by eight hours' heating.

The ease with which the galactose can be obtained and the high yields recommend  $\epsilon$ -galactan as a source of galactose. Ordinarily galactose is obtained by hydrolysis of lactose and elimination of the glucose by fermentation. This is but a troublesome method and the yields obtained are not good.

#### EXAMINATION OF SUGAR

**GALACTOSE**—The repeatedly crystallized sugar melted at  $155-157^{\circ}$ , by rapid heating at  $159-160^{\circ}$ . The melting point of galactose is ordinarily  $163-165^{\circ}$ . The sugar in aqueous solution had an initial rotation  $[\alpha]_D^{20} = +124^{\circ}$ , changing to  $[\alpha]_D^{20} = +83.54^{\circ}$ , where it remained constant. The sugar is accordingly mutarotatory. The following results were obtained on ultimate analysis:

	C	H	O
FOUND.....	39.93	6.65	53.42
Calculated for $C_6H_{10}O_5$ .....	40.00	6.66	53.34

**GALACTOSE HYDRAZONE**—Five grams of the sugar in 10 cc. of water were added to a solution of 20 cc. of water containing 5 g. of freshly distilled phenylhydrazine and 5 g. of glacial acetic acid. By rubbing the side of the beaker with a glass rod, the hydrazone began to form in 10 min. and after about 15 min. almost a solid mass was obtained. The yield was 3.5 g. After three crystallizations from 95 per cent alcohol by addition of water, the snow-white hydrazone obtained melted at  $155-156^{\circ}$ . When mixed with the hydrazone of galactose obtained from lactose the melting point was not changed.

**GALACTOSE PHENYLOSAZONE**—Osazones were prepared from the galactose from  $\epsilon$ -galactan and from lactose. The galactose phenylosazone from western larch melted at  $189^{\circ}$ . The galactose phenylosazone prepared from lactose melted at  $189-190^{\circ}$ . When mixed with the first preparation the melting point was not changed.

**GALACTOSE PENTACETATE**—The pentacetate<sup>1</sup> prepared by the method of Erwig and Konig<sup>2</sup> melted at 141°. Ten grams of the sugar yielded 4.5 g. of the pentacetate.

**FERMENTATION**—Attempts to ferment the hydrolyzed sugar with *Saccharomyces cerevisiae* gave negative results, but with *S. Carlsberg* I about 40 per cent of alcohol was obtained. The fermentation experiments are being continued.

#### OXIDATION OF THE SUGAR

The sugar as oxidized with nitric acid (sp. gr. 1.15) by the method of Tollens and about 75 per cent of its weight of mucic acid was obtained. Using the factor 1.33 the yields of mucic acid obtained showed the sugar to consist of 98.61 to 99.98 per cent galactose.

#### OXIDATION OF THE GALACTAN

The galactan as well as the crystalline sugar yields considerable quantities of mucic acid on oxidation with nitric acid. The mucic acid after solution in a large volume of hot water deposited, on cooling, fine crystals that melted at 215° after washing with alcohol and ether. The ammonium salt decomposed at 222–223° and gave the pyrrol reaction.

The mucic acid was further oxidized to tartaric and oxalic acid by Fischer's<sup>3</sup> method using alkaline potassium permanganate. After removal of MnO<sub>2</sub>, acidification with HCl and addition of NH<sub>4</sub>Cl and CaCl<sub>2</sub> at boiling temperature, a precipitate of calcium oxalate was obtained which was decomposed with sulfuric acid. The filtrate from the CaSO<sub>4</sub> yielded crystals of oxalic acid. These crystals were identified by heating with *p*-toluidine, the oxal-*p*-toluidine obtained melting at 268°.

The tartaric acid remaining in the filtrate from the calcium oxalate was obtained as the calcium salt by concentration of the solution. On digestion with K<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub> was formed and filtered off. Acidification of the filtrate with acetic acid yielded the insoluble acid potassium tartrate. After recrystallization from water and drying the potassium was determined as K<sub>2</sub>SO<sub>4</sub>.

0.2898 g. of KH.C<sub>4</sub>H<sub>4</sub>O<sub>6</sub> gave 0.1324 g. K<sub>2</sub>SO<sub>4</sub>  
0.1324 g. K<sub>2</sub>SO<sub>4</sub> = 0.08941 g. K<sub>2</sub> = 20.50 per cent found  
K<sub>2</sub> calculated for KH.C<sub>4</sub>H<sub>4</sub>O<sub>6</sub> = 20.74 per cent

#### QUANTITATIVE DETERMINATION OF GALACTAN BY OXIDATION TO MUCIC ACID

A method for the quantitative determination of galactose and galactans, depending on oxidation by means of nitric acid to the difficultly soluble mucic acid, has been employed for a long time, especially by agricultural chemists. Even pure galactose seldom yields more than 75 per cent of its weight of mucic acid so that it is necessary to employ a factor according to the material oxidized. The method first developed by Tollens is essentially as follows:<sup>4</sup>

<sup>1</sup> Acknowledgment is made to Mr. H. C. Howard for preparation of the galactose pentacetate.

<sup>2</sup> *Ber.*, **22** (1889), 2207.

<sup>3</sup> *Ibid.*, **27** (1894), 1, 397.

<sup>4</sup> Bureau of Chemistry, *Bull.*, **107**, 55; see also Miyake, *J. Coll. Agr. Japan*, **4**, Pt. 8.

Place in a beaker 5.5 cm. in diameter and 7 cm. deep, 1 to 5 g. of galactose (or galactan) together with 60 cc. of nitric acid (sp. gr. 1.15) and evaporate the solution to exactly one-third of its volume in a water bath at 94–96° C. After standing 24 hrs., add 10 cc. of water, and allow to stand an additional 24 hrs. The mucic acid is then filtered off, washed with water, alcohol, and ether in succession, dried and weighed. The weight of mucic acid multiplied by 1.33 gives galactose while multiplying the weight of mucic acid by 1.20 gives galactan. If the galactan occurs in plant or similar material, extraction with ether is made previous to oxidation. The mucic acid obtained is dissolved out with ammonium carbonate and subsequently liberated with nitric acid.

Since but 65 per cent of crystalline galactose was obtained from the galactan, proof was lacking that the galactan as isolated consisted entirely of the anhydride of galactose. It was hoped that this point could be settled by oxidation to mucic acid but curiously conflicting results were obtained. In the majority of our experiments direct oxidation could be employed since we were using the isolated galactan.

The first case of the unreliability of the method was found in oxidizing the extract from the wood. Only 6 to 9 per cent of the galactan could be accounted for in this way while by precipitation of the galactan from the clarified solution with alcohol and weighing the galactan directly a yield of 17 per cent of galactan was obtained from one sample of wood.

Samples of galactan were prepared by repeated precipitation from the aqueous solution with alcohol, washing with ether, and drying finally at 105°. A large number of oxidations were carried out by the usual method. Some of the results obtained are given in the following table:

Sample	Exp. No.	Grams Galactan Employed	Grams Mucic Acid Obtained	Per cent Galactan By factor 1.20
A	1	3.7419	1.6615	53.28
	2	2.7647	1.2532	54.39
B	3	1.3324	0.4869	43.85
	4	0.9038	0.6120	81.26
	5	1.3075	0.8914	81.81
C	7	0.3603	0.2815	93.77
	8	0.3306	0.1400	50.82
	9	3.8350	1.4242	44.56
	12	0.8886	0.5835	78.80

The above data show clearly that the method does not yield accurate or consistent results regardless of the weight of sample employed.

The method was then tried for galactose. A carefully purified sugar prepared from lactose and melting at 162–163° was oxidized with the following results:

Gram Galactose	Gram Mucic Acid Obtained	Per cent Galactose By Factor 1.33
0.5285	0.3968	99.86
0.3538	0.2606	92.96
0.5732	0.4194	97.31

Oxidation of galactose from the galactan in the same manner gave results equivalent to 99.98 to 98.61 per cent galactose. Considering the character of



the method the results obtained with galactan are very satisfactory.)

It was thought that better results might be obtained if the galactan were hydrolyzed previous to oxidation. Accordingly known amounts of galactan were hydrolyzed with 3 per cent  $H_2SO_4$ , the acid was removed with  $Na_2CO_3$  and the sugar in the form of a thick syrup oxidized with 60 cc. of the nitric acid.

TABLE III

Grams Galactan	Gram Mucic Acid	Per cent Galactan By Factor 1.20
1.0628	0.7074	65.68
1.6928	0.3948	27.92
0.5953	0.4775	88.15
1.7	0.6138	68.85

The results are no more satisfactory than those obtained by direct oxidation of the galactan.

A series of experiments were conducted in which the strength of the nitric acid was varied while other conditions remained the same. A series of eight acids were employed in which the sp. gr. at 18° as determined by a Westphal balance ranged from 1.124 to 1.356. The per cent of galactan as determined from the weights of mucic acid using nitric acid of sp. gr. 1.124, 1.130 and 1.174 were 87.57, 80.95 and 89.52 per cent, respectively. When the sp. gr. of the acid exceeded 1.174 there was a marked decrease in the yield of mucic acid.

A considerable number of additional experiments were carried out employing nitric acids of sp. gr. 1.124, 1.150, and 1.174, in which the evaporation temperature and amount of acid were varied. However, no conditions were found by which consistent results could be obtained. Since in some cases (experiment No. 7, Table I) at least 94 per cent of the galactan could be accounted for as galactose anhydride, it is not probable that any sugar other than galactose is formed on hydrolysis; at least, if an additional sugar is formed, it is present in small amount.

Our experiments have shown that the method of determining galactans by oxidation to mucic acid is entirely unreliable even when the isolated galactan is used. If the method is unreliable for apparently pure galactans it must be even less reliable where the plant material containing the galactan is oxidized directly. It is well known that the presence of foreign organic bodies<sup>2</sup> hinder and in some cases entirely prevent the separation of the mucic acid. The unreliability of the method has recently been pointed out also by Dore.<sup>3</sup>

<sup>1</sup> The work on the oxidation of galactose and galactan was completed before the note by Dore, *THIS JOURNAL*, 7 (1915), 721, on the determination of galactan appeared. According to Dore when 2 g. of galactose were oxidized 90 per cent was recovered as mucic acid while when 0.2 g. was used the recovery was 54 to 74 per cent. The oxidations were accordingly repeated on small samples of galactose from western larch. The beakers were immersed in a water bath, the temperature of which did not exceed 87°. The following results were obtained:

Galactose Gram	Mucic Acid Obtained Gram	Galactose By Factor 1.33 Per cent
0.2843	0.2036	95.25
0.3658	0.2760	100.30
0.2290	0.1578	91.65
0.4642	0.3489	99.97

<sup>2</sup> Lippman, "Chemie der Zuckerarten," 3rd Ed., Vol. I, p. 274.

<sup>3</sup> *Loc. cit.*

#### ACETYL DERIVATIVES OF GALACTAN

An attempt to prepare an acetyl derivative of the galactan with acetic anhydride using zinc chloride as a catalyst was unsuccessful. The material charred badly during heating and no acetyl derivative separated on pouring the solution into water. It was found, however, that acetyl derivatives could be prepared using acetic anhydride with sodium acetate crystals or anhydrous sodium acetate. The derivatives obtained by means of anhydrous and crystalline sodium acetate were found to be entirely different in melting point and ease of hydrolysis with mineral acids.

The anhydrous sodium acetate gave an acetyl derivative that melted between 165 and 173°. This derivative was extremely hard to hydrolyze, using sulfuric acid of approximately  $N/4$  strength.

The crystalline sodium acetate gave a derivative that melted between 185 and 192°, and hydrolyzed readily with the sulfuric acid employed.

The acetyl derivatives were prepared as follows:

(a) *Derivative with Anhydrous Sodium Acetate*—Four grams of anhydrous sodium acetate were added to 50 g. of acetic anhydride and heated to boiling; 7 g. of finely powdered galactan were then added in small amounts at first and the remainder after a lapse of 10 min. The boiling was continued for 20 min. after the last of the galactan had been added. All of the galactan did not go into solution. After cooling to about 50°, the whole was poured into 600 cc. of cold distilled water from which the acetyl derivative separated at first as a heavy viscous oil that became hard and granular after several minutes standing. The acetyl derivative was then filtered off and washed with a large amount of cold water. It was then dissolved in a very small amount of glacial acetic acid solution, being assisted by gentle heating. The solution is poured into a liter of cold water, the precipitated derivative filtered off and well washed with water. This procedure was repeated an additional three times. The derivative was finally dissolved in a small amount of 95 per cent alcohol and poured into a liter of cold water. In this case a milky solution was obtained and it was necessary to add a small amount of an electrolyte ( $NaCl$ ) in order to produce coagulation and precipitation. The derivative was finally well washed with water and dried for 3 hrs. at 105°. The yield was 3 g.

The acetyl derivative was very resistant to hydrolysis. When 0.1912 g. of the material was boiled with 87 cc. of approximately  $N/4$   $H_2SO_4$  for 28 hrs., hydrolysis was still incomplete and considerable charring had resulted. When 0.2614 g. of the derivative was boiled with  $N/4$   $KOH$  for 19 hrs., approximately 20 per cent of the material remained unattacked.

It was found that hydrolysis could be effected under pressure with  $N/4$   $H_2SO_4$ . About 0.5 g. of the derivative was placed in a pressure bottle with 70 cc. of standard acid. The bottle was then placed in an autoclave for 1 $\frac{1}{4}$  hours under a pressure of 40 lbs. per sq. in. The resulting solution was then titrated with standard alkali, using phenolphthalein as the indicator.

0.6788 g. acetyl derivative gave 0.4002 g. acetic acid	
0.3441 g. acetyl derivative gave 0.2061 g. acetic acid	
Per cent Acetic Acid Found	Per cent Calculated for
58.96	$C_6H_5O_2(OC_2CH_3)_2$
59.90	62.5

The results indicate a mixture of triacetyl derivative with a lower derivative.

(b) *Derivative with Hydrated Sodium Acetate*—The procedure followed in this case was identical with that described above except that 4 g. of crystalline sodium acetate and 10 g. of galactan to 50 g. of acetic anhydride were employed. A yield of 3.5 g. of the purified acetyl derivative was obtained.

Approximately 0.3 g. of the derivative was hydrolyzed by boiling with 100 cc. of  $N/4$   $H_2SO_4$  under a reflux condenser for about 4 hrs., complete solution being obtained. The solution was then titrated with standard alkali in the usual manner.

0.2625 g. acetyl derivative gave 0.1297 g. acetic acid	
0.3530 g. acetyl derivative gave 0.1722 g. acetic acid	
Per cent Acetic Acid Found	Calculated for
Duplicates	$C_6H_5O_2(OC_2CH_3)_2$
49.40 49.78	48.78
Mean	
49.09	

The results show that in this case an approximately pure diacetyl derivative of the galactan was obtained.

#### OCCURRENCE OF GALACTANS IN OTHER CONIFERS

A number of species of conifers were examined to determine if galactans were a normal constituent. Approximately 100 g. of the wood in the form of fine sawdust were extracted several times by digestion with hot water on the steam bath, the aqueous extract evaporated nearly to dryness and the residue treated with 60 cc. of nitric acid in the manner previously described. The crystalline residues obtained were filtered off, washed with water, and dissolved in a minimum amount of boiling water. The solution was filtered hot and the filtrate allowed to stand in the cold for 24 hrs. The mucic acid was then filtered off, washed with water, alcohol, and ether and the melting point determined. Owing to the unreliability of the method of determining galactans quantitative results were not attempted and for the same reason a failure to obtain mucic acid in certain samples is not a positive indication of their absence. The results obtained are given in the following table in which the signs + and — indicate the presence or absence of mucic acid:

Sample No.	SPECIES	Mucic Acid Present	Melting Point Mucic Acid
a	Longleaf Pine ( <i>Pinus palustris</i> )	+	214–215°
314-11	Longleaf Pine ( <i>Pinus palustris</i> )	+	215
314-12	Longleaf Pine ( <i>Pinus palustris</i> )	+	215
314-13	Longleaf Pine ( <i>Pinus palustris</i> )	+	210
314-41	Pond Pine ( <i>Pinus serotina</i> )	+	210–211
314-31	Cuban Pine ( <i>Pinus heterophylla</i> )	+	211
314-35	Cuban Pine ( <i>Pinus heterophylla</i> )	+	212
314-21	Loblolly Pine ( <i>Pinus taeda</i> )	—	212
314-22	Loblolly Pine ( <i>Pinus taeda</i> )	—	212
314-30	Loblolly Pine ( <i>Pinus taeda</i> )	—	212
1	Douglas Fir ( <i>Pseudotsuga taxifolia</i> )	+	215

The longleaf and Cuban pines gave apparently the largest amounts of mucic acid.

#### SUMMARY

[—The wood of the western larch (*Larix occidentalis*) has been found to contain approximately 10 per cent of a galactan not previously described and which has been named  $\epsilon$ -galactan.

II—The only sugar obtained on hydrolysis of  $\epsilon$ -galactan is galactose.

III—The determination of galactans by oxidation to mucic acid by the method of Tollens has been shown to be unreliable.

IV—Galactans have been shown to be characteristic of several of the common conifers.

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#### A MODIFICATION OF WHIPPLE'S METHOD FOR ORGANIC NITROGEN IN SEWAGES

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The direct process for total nitrogen in sewage consists in the digestion of a known quantity of sewage in acid solution with or without  $CuSO_4$ , making decidedly alkaline with  $NaOH$ , allowing to settle until clear, and nesslerizing an aliquot portion made up to 50 cc. volume. Several methods embodying these principles have been proposed. Their chief point of difference consists in the reagents used to remove such substances as calcium and magnesium, which cause a turbidity upon nesslerization. They are best adapted to that particular sewage for which they were designed. That another factor of equal importance needs some emphasis was forcibly brought home to us upon trying to apply one of the already proposed methods to Kansas sewage; namely, the effect of time the digestates are alkaline before nesslerized, upon the quantity of nitrogen obtained.

#### HISTORICAL

Rideal<sup>1</sup> was the first to propose a method whereby organic nitrogen could be determined by direct nesslerization. His method is as follows: 10 cc. of a sewage, or 100 cc. of an effluent plus 4 cc. of pure sulfuric acid, are heated in a pear-shaped hard glass flask in a slanting position until the liquid becomes colorless. When about 2 or 3 cc. remain, the flask is cooled and is washed out with small quantities of ammonia-free water into a 100 cc. measuring flask until the volume reaches about 40 cc. An excess, *i. e.*, about 25 cc. of soda solution (25 per cent) free from ammonia is now added, when a flocculent precipitate is thrown down. After cooling, the liquid is made up to 100 cc., transferred to a clean, dry, stoppered bottle, and shaken at intervals until the flocculi subside. A suitable fraction of the clear liquid is then pipetted off into a Nessler glass, diluted to 50 cc., and nesslerized.

McGowan<sup>2</sup> used a similar method, the chief difference being the addition of potassium oxalate to the alkaline solution to precipitate the calcium, and a proviso that the solution be "rendered just alkaline with purified potash."

Phelps<sup>3</sup> used the following method with some success: The sewage is digested with 5 cc. of concentrated  $H_2SO_4$  until colorless, cooled, and diluted to 250 cc. A 2 cc. portion is neutralized with  $NaOH$

<sup>1</sup> See page, 2nd Ed., 1907, 39.

<sup>2</sup> See Rep. Royal Com. on Sew. Dis., 4, 35, Part

<sup>3</sup> J. Infect. Dis., 1 (1904), 3.



15 per cent. made up to 50 cc., and a portion nesslerized at once.

The Columbus Sewage Testing Station<sup>1</sup> published a modification of the Rideal and McGowan methods which is as follows: Measure out an amount of sewage that will contain 0.0005 to 0.001 g. of nitrogen. Add 5 cc. of  $\text{H}_2\text{SO}_4$ , digest until colorless, and rinse the digestate into a 50 cc. flask. Cool and fill to the mark, and pipette 25 cc. into a 100 cc. flask. Add  $\text{NaOH}$  (250 g. per liter) until a precipitate forms, then add 2 cc. of  $\text{Na}_2\text{CO}_3$  (100 g. per liter). Mix and make up to volume and allow to stand 6 hrs. Nesslerize 10 cc. made up to 50 cc. in a Nessler tube, reading after 15 min.

L. Whipple<sup>2</sup> tried to use the Columbus modification on Boston sewage but found that he could not get accurate results, so recommended the following: 50 cc. of the sample are digested with 5 cc. of concentrated sulfuric acid, and a small amount of  $\text{CuSO}_4$  until colorless. The digestion is completed by the addition of a few crystals of permanganate to the hot acid. After cooling, the digestate is diluted to 250 cc., mixed, and a portion (25 cc.) is pipetted out and mixed with an equal portion of 5 per cent  $\text{NaOH}$ , and filtered through a filter paper which has been washed previously with 100 cc. or so of ammonia-free water: 20 cc. of the filtrate are pipetted into a Nessler tube and made up to 50 cc. with water. Mix by pouring one tube into another, and nesslerize. Read after 10 min. A blank should be run on the entire process.

Because of its rapidity, this latter method was tried on Kansas sewages, but with no success, the results obtained always being too low. As we had no trouble due to turbidity in the tubes, we started an investigation to see under what conditions exact results could be secured. For this purpose the effect of large and small amounts of copper sulfate and potassium permanganate were ascertained, as well as the effect of the length of time the samples stood before nesslerizing. The results of our work were finally embodied in the following method which we have found to give accurate results on Kansas sewages at least.

#### METHOD ADOPTED FOR KANSAS SEWAGES

To 100 cc. of sewage add 5 cc. concentrated  $\text{H}_2\text{SO}_4$ , 2 cc.  $\text{CuSO}_4$  (10 per cent) and digest till clear, and then a half hour longer. A small crystal of  $\text{KMnO}_4$  is added, and, after cooling, the whole is made up to 250 cc.: 25 cc. are pipetted out into a 100 cc. Nessler tube, 25 cc. of  $\text{NaOH}$  (5 per cent) added, and the volume made up with ammonia-free water: the tube is then stoppered and allowed to stand 24 hrs.: 10 cc. are nesslerized after making up to 50 cc. The reading on standard  $\times 10$  = parts per million of nitrogen.

#### EXPERIMENTAL

In all the work the following distillation method as recommended by the Standard Methods of Water Analysis was used to check the direct results: To

<sup>1</sup> Public Health, 31, 116, Part 2.

<sup>2</sup> San. Research Lab., 4, 162.

100 cc. of sewage add 5 cc. of concentrated  $\text{H}_2\text{SO}_4$  and 10 cc.  $\text{CuSO}_4$  (10 per cent), digest until clear, and then a half hour longer. Add 0.5 g.  $\text{KMnO}_4$ , make up to 500 cc., and pipette 50 cc. into a steam distillation flask. Add 50 cc.  $\text{Na}_2\text{CO}_3$  (10 per cent) and distil over 250 cc. Make up to 500 cc. and nesslerize 50 cc. Reading  $\times 10$  = parts per million of nitrogen.

**EFFECT OF TIME** In the method at first employed, the samples were nesslerized as soon as they had settled clear, or immediately after filtering. A few typical results are given in Table I. Since the results by direct nesslerization were always too low, it occurred to us that an increase of time for the reaction in alkaline solution might increase the amount of nitrogen found. A series of samples of raw sewage were run, allowing the digestates to stand 24 hrs. before nesslerizing. A shorter period did not give good results. A few of the results are found in Table I.

TABLE I. NITROGEN IN PARTS PER MILLION RAW SEWAGE

IMMEDIATE NESSLERIZATION:															
Distillation	25	25	10	85	35	30	35	50	40	25	35	54	48		
Direct	17	10	15	14	17	10	7	20	20	14	20	52	34		
EFFECT OF TIME:															
Distillation	50	30	40	25	40	35	30	50	30	25	35				
Direct	15	10	20	10	22	18	18	15	14	10	20				
At once	15	10	20	10	22	18	18	15	14	10	20				
After 24 hrs.	50	20	35	20	38	30	25	50	28	22	35				

**EFFECT OF  $\text{KMnO}_4$** —The fact that in the distillation method we added 0.5 g.  $\text{KMnO}_4$  while in the direct we added only a small crystal, suggested to us that in the latter case we might not be adding enough  $\text{KMnO}_4$  in order to bring about an equivalent amount of oxidation. Experiments with varying amounts of  $\text{KMnO}_4$  in both methods showed that the concentration of the  $\text{KMnO}_4$  did not influence the results at all.

**EFFECT OF  $\text{CuSO}_4$** —Varying concentrations of  $\text{CuSO}_4$  were tried, and equally as good results were obtained with 2 cc. as with 10 cc. of 10 per cent solution of  $\text{CuSO}_4$ .

#### CONCLUSIONS

1—The direct method for determining organic nitrogen in sewages proposed by Whipple has been slightly modified.

2—The length of time the digestates are alkaline influences the accuracy of the results. We found that the best results could be obtained by allowing the samples to stand 24 hrs. before nesslerizing.

3—Increase in concentration of potassium permanganate has no influence on the results obtained.

4—Increase in concentration of copper sulfate has no effect.

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#### ON THE VOLUMETRIC DETERMINATION OF TIN BY POTASSIUM IODATE

By GEORGE S. JAMIESON

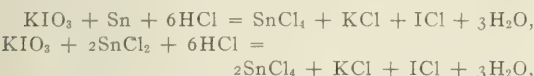
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The iodine and ferric chloride methods are the ones most commonly employed for the volumetric estimation of tin. The iodine method is based upon the titration of stannous chloride in hydrochloric acid solution with iodine, using starch as indicator, while the ferric chloride method in general use is based

upon adding an excess of ferric chloride to a hydrochloric acid solution of stannous chloride and titrating the resultant ferrous chloride with potassium permanganate. The iodine method has by far the widest application, as it can be used to titrate stannous chloride in the presence of ferrous salts as well as metallic antimony, which would react readily with ferric chloride.

The iodate method has the advantage over both of these methods in that the end-point is exceedingly sharp. Furthermore, there is far less danger of over-titrating the solutions. Another advantage is that extreme precautions to prevent outside oxidation of the tin during the titration are not necessary because the potassium iodate may be added very rapidly to the appearance of iodine in the solution, then without further precaution the titration can be completed as slowly as desired. It should be observed that the iodate method cannot be employed to titrate tin or stannous chloride in the presence of cuprous, ferrous, antimonious salts or precipitated metals. However, in the majority of cases, it is a simple matter to avoid or eliminate these interfering substances and apply the method with satisfactory results.

The method to be described is based upon the titration of precipitated tin or stannous chloride with potassium iodate in the presence of strong hydrochloric acid, according to the general method of L. W. Andrews<sup>1</sup> which has not been previously applied to the estimation of tin. In order to test the method, a solution containing 3.567 grams of normal potassium iodate in 1000 cc. was prepared. According to the equations of the reactions,



the equivalents of this solution are respectively 1 cc. = 0.001983 g. Sn and 0.003966 g. Sn. The titrations were carried out in 250 cc. glass stoppered bottles in the presence of a cooled mixture of 30 cc. concentrated hydrochloric acid, 20 cc. of water, and 6 cc. of chloroform. During the first part of the titration, the potassium iodate was added rapidly while shaking the bottle so as to give the contents a gentle circular motion until the iodine color, which gradually appeared, had increased to the maximum amount, then the stopper was inserted and the solution was thoroughly shaken. The titration was continued with thorough shaking of the closed bottle after each addition of potassium iodate until the end-point (the disappearance of the violet color of the chloroform) was obtained.

The first experiments were made using a solution of stannous chloride which was prepared by diluting 50 cc. of the laboratory reagent to a liter. The solution contained 225 cc. of 1 : 1 hydrochloric acid per liter which was sufficient to maintain a perfectly clear solution. This solution was standardized by the iodine method on three different days as indicated in Table I. No precautions were taken to prevent

the oxidation of the stannous chloride solution and it was observed that the more solution removed from the liter flask, the faster the stannous chloride was oxidized by the oxygen of the air admitted to the flask, as would naturally be expected.

TABLE I TITRATION OF STANNOUS CHLORIDE SOLUTION

Expt. No.	Date May	SnCl <sub>2</sub> Solution Cc.	KIO <sub>3</sub> Used Cc.	Sn (As SnCl <sub>2</sub> ) Iodine Method	PRESENT Iodate Method	Error Gram
1.....	14	10.0	16.0	0.0636	0.0635	—0.0001
2.....	17	10.0	14.9	0.0595	0.0591	—0.0004
3.....	17	10.0	15.0	0.0595	0.0595	0.0000
4.....	18	10.0	14.8	0.0587	0.0587	0.0000

From these experiments it will be seen that the iodate titrations checked the iodine titrations closely. The iodate method will be found very convenient to determine the amount of stannous chloride present in solutions. In cases where it is necessary to titrate considerable amounts of stannous chloride, it is recommended that a much stronger solution of potassium iodate be employed, as it is very important to have the solution at the end of the titration contain at least 10 per cent of actual hydrochloric acid to prevent the hydrolysis of the iodine monochloride.

For the next series of experiments, a standard solution was prepared by dissolving exactly 3 grams of pure tin in about 150 cc. of concentrated hydrochloric acid, with enough nitric acid to oxidize the tin to stannic chloride. Three grams of tartaric acid were added and the solution was diluted to one liter. Measured portions of this solution were placed in the titration bottles, in each of which was placed 2 grams of high-grade 30 mesh zinc. After the reaction had proceeded for 20 minutes or longer, 40 cc. of 1 : 2 hydrochloric acid were added. As soon as the zinc had completely dissolved, leaving metallic tin, several cubic centimeters of potassium iodate were added, followed by 10 cc. of concentrated hydrochloric acid and a piece of platinum foil to facilitate the solution of the tin. The titration was continued with very thorough shaking until the tin was practically all dissolved. Then 6 cc. of chloroform were added and the titration finished in the usual manner. It is very important during the titration to add sufficient potassium iodate so that there is free iodine or iodine monochloride present in the solution at all times, otherwise some of the tin might dissolve, forming stannous chloride and hydrogen and thus cause a serious error. A blank determination using 2 g. of zinc and the same amount of hydrochloric acid as in the actual titrations required 0.40 cc. of potassium iodate solution, which has been detected from the amounts of solution (KIO<sub>3</sub> used), given in Table II.

TABLE II—REDUCTION BY ZINC AND TITRATION OF TIN BY IODATE

Expt. No.	KIO <sub>3</sub> used Cc.	Tin present Gram	Tin found Gram	Error Gram
1.....	15.0	0.0300	0.0297	—0.0003
2.....	30.4	0.0600	0.0601	+0.0001
3.....	7.6	0.0150	0.0151	+0.0001
4.....	30.2	0.0600	0.0599	—0.0001
5.....	24.0	0.0476	0.0478	+0.0002
6.....	20.95	0.0420	0.0416	—0.0004
7.....	45.4	0.0900	0.0902	+0.0002

These results show excellent agreement with the amounts present, thus confirming the equation given in the first part of this paper. The solution of tin

<sup>1</sup> J. Am. Chem. Soc., 25 (1903), 675.



each in the presence of platinum was slow and it was found that a titration required from  $\frac{1}{2}$  to  $\frac{3}{4}$  of an hour for completion.

An attempt was made to reduce stannic solutions to the stannous condition with nickel powder which was made by reducing the oxide with hydrogen at a red heat. The nickel powder was found so reactive that unless large amounts were used, it dissolved so quickly that only a partial reduction of the tin was obtained. Since it appeared that nickel would be the most suitable reducing agent for general use with the iodate method, the next series of experiments was made using strips ( $1 \times 5.5 \times 0.1$  cm.) of sheet nickel for the reduction, which was found satisfactory. The reduction was made in 250 cc. Erlenmeyer flasks provided with a 2-hole rubber stopper which carried a glass tube extending to within 1 cm. of the surface of the liquid. The other hole was provided with a short tube which extended a short distance below the stopper. Several experiments were made using measured portions of the stannic chloride solution described above. To each portion of this solution 15 cc. of concentrated hydrochloric acid and 2 nickel strips were added. The stopper was inserted and the flask was heated on the steam bath for 45 minutes to ensure the complete reduction of the tin. Then a current of carbon dioxide gas was passed through the longer tube and the flask was placed in ice water. When the solution had reached approximately the temperature of the bath it was filtered by suction into a titration bottle (containing 6 cc. of chloroform) to remove the finely divided nickel which had separated from the edge of the strips. The filter used was a calcium chloride prolong tube ( $10 \times 1.8$  cm.), provided with a perforated platinum disk upon which was placed a thin layer of absorbent cotton, a layer (2.5 cm.) of purified sea sand, and another thin layer of cotton on top. Other filter mediums were tried but were not found satisfactory. Before pouring the solution into the filter, a moderate stream of carbon dioxide gas was led in by means of a bent glass tube which extended to within 1 cm. of the filter bed for a minute after starting the suction. The flask and filter were washed with small amounts of 1:1 hydrochloric acid and the solution was titrated at once as described above. It was found necessary to make blank determinations under the very same conditions as in the actual experiments with each new lot of sheet nickel and apply the corrections (due to the iron content of the nickel) to the subsequent titrations. The results in Table III

TABLE III—REDUCTION BY SHEET NICKEL AND TITRATION OF STANNOUS SALT

Expt. No.	SnCl <sub>4</sub> taken	KIO <sub>3</sub> used	Tin present	Tin found	Error
	Cc.	Cc.	Gram	Gram	Gram
1.....	30.0	22.77	0.0900	0.0900	0.0000
2.....	21.0	15.80	0.0630	0.0627	-0.0003
3.....	18.0	13.60	0.0540	0.0539	-0.0001
4.....	10.0	7.55	0.0300	0.0299	-0.0001
5.....	9.9	7.40	0.0297	0.0294	-0.0003
6.....	10.0	7.50	0.0300	0.0298	-0.0002
7.....	10.0	7.50	0.0300	0.0298	-0.0002

include this correction, amounting to 0.5 cc. of the potassium iodate solution. Several blank determinations were made upon the nickel used in this investigation with concordant results.

In order to apply this method to the determination

of tin in solder and type metal, a sample of 0.2-0.5 g., depending upon tin content, was heated in a 250 cc. Erlenmeyer flask with 15 cc. of concentrated sulfuric acid. It is very important to boil the solution gently until all the sulfur dioxide is expelled; otherwise, it would be titrated along with the tin.<sup>1</sup> After cooling, 20 cc. of water and 15 cc. of concentrated hydrochloric acid were added, after which the tin was reduced and titrated as described above. The following results were obtained:

TABLE IV ANALYSIS OF TIN ALLOYS

Expt. No.	NAME	Alloy G.	KIO <sub>3</sub> used Cc.	Grav. Det. Per cent	Tin found Per cent
1.....	Type Metal	0.5000	6.30	5.04	4.99
2.....	Type Metal	0.5000	6.25	5.04	4.96
3.....	Type Metal	3.5000	3.90	3.20	3.09
4.....	Type Metal	0.5000	4.00	3.20	3.17
5.....	Solder	0.2000	19.60	38.76(a)	38.86

(a) Iodine method.

It is recommended that an iodate solution containing 8.994 g. of KIO<sub>3</sub> per liter (1 cc. = 0.00900 g. Sn) should be used for the analysis of solders, using 0.5 gram sample.

It should be observed in the analysis of type metals, etc., that when the filter becomes clogged with precipitated antimony, it should be heated with warm nitric and tartaric acids and washed thoroughly with water and hydrochloric acid until all of the antimony is removed. Also it is advisable to keep the nickel strips free from deposited metals by frequent cleaning.

Since bronze contains so much copper it was found best to decompose them in the usual manner with nitric acid and filter the metastannic acid in a Gooch crucible. After washing the precipitate, it was transferred along with the asbestos mat to a 250 cc. Erlenmeyer flask, any metastannic acid adhering to the sides of the crucible being wiped off with a pinch of slightly damp asbestos and added to the main precipitate. About 15 cc. of concentrated sulfuric acid were added and the flask was heated until the acid had boiled gently for 2 or 3 minutes. After cooling thoroughly 20 cc. of water and 15 cc. of concentrated hydrochloric acid were added. The asbestos was filtered off on a Gooch crucible and washed with 1:1 hydrochloric acid, using as little as possible. Then the solution was reduced with nickel and titrated in the usual manner.

TABLE V ANALYSIS OF BRONZE

Alloy G.	KIO <sub>3</sub> used Cc.	Tin by Grav. Det. Per cent	Tin found Per cent
0.5000	10.95	8.75	8.68
0.5000	10.93	8.75	8.66
0.5000	11.05	8.75	8.76

The results of this investigation show that tin may be estimated with accuracy by the iodate method and that it is applicable to the analysis of alloys as well as solutions. With this titration it is important to maintain an acidity of at least 10-12 per cent of actual hydrochloric acid in order to obtain the correct reaction. Furthermore, it should be remembered that cuprous, ferrous, and antimonious salts, as well as any precipitated metal, will react with potassium iodate.

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<sup>1</sup> *Am. J. Sci.*, **38** (1914), 166.

RELATIVE TOXICITY OF SUBSTANCES FOUND IN  
FOODS

By ALFRED N. COOK AND SYLVANNA ELLIOTT  
Received February 7, 1916

This investigation was undertaken with the hope that some useful data might be accumulated that would help solve the question of chemically preserved foods and their effects upon the human system. Since our laws and ethical standards forbid that experiments of the nature to be described should be made upon human beings, the only available method is to experiment upon animals of lower rank and make deductions from the results obtained.

It has been indicated a number of times that there are instances in which the food of one animal is poison for another, for example, copperas is poison for a human being but may be eaten almost with impunity by a hog; saltpeter may be taken into the human system in considerable quantity without deleterious effects but it is poison to a sheep. Notwithstanding these occasional instances, there has been a difference of opinion with regard to the value of such experiments, but many men high in authority have considered them valuable.

Because of the difficulty of caring for many different kinds of animals in the laboratory, our experiments were confined mostly to gold fish and frogs. The frogs averaged about 25 g. in weight and the gold fishes were from 3 to 4 in. long.

The frogs, of fairly uniform size, were kept in shallow pans which were carefully enameled to prevent any chemical action between the substances in solution and the container. The frogs were kept partly immersed in the respective solutions. The gold fishes were of fairly uniform size and were kept in liter beakers. Both frogs and fishes were kept in one liter of the respective solutions which were frequently renewed to prevent any error by concentration or absorption. All solutions were prepared with distilled water.

COMPARATIVE RESULTS	
FROGS	FISHES
Potassium Nitrite.....	0.25 Sodium Chloride.....
Sodium Sulfite.....	0.7 Cane sugar.....
Sodium Benzoate.....	1.0 Rochelle Salts.....
Borax.....	1.0 Glucose.....
Sodium Chloride.....	1.1 Alcohol.....
Sodium Salicylate.....	2.0 Potassium Oxalate.....
Glucose.....	2.0 Sodium Benzoate.....
Alcohol.....	3.0 Caffein.....
Rochelle Salts.....	3.0 Saccharin.....
Potas. Oxalate.....	5.0 Citric Acid.....
Citric Acid.....	6.0 Alum.....
Cane Sugar.....	6.5 Acetic Acid.....
Malic Acid.....	9.0 Carbolic Acid.....
Saccharin.....	10.0 Malic Acid.....
Benzoic Acid.....	13.3 Tartaric Acid.....
Tartaric Acid.....	15.0 Benzoic Acid.....
Alum.....	20.0 <i>p</i> -Cresol.....
Acetic Acid.....	25.0 <i>m</i> -Cresol.....
Caffein.....	42.0 <i>o</i> Cresol.....
Guaiacol.....	150.0
<i>o</i> -Cresol.....	175.0
Carbolic Acid.....	220.0
<i>m</i> -Cresol.....	250.0
<i>p</i> -Cresol.....	300.0

An attempt was made to determine the strength of a given solution in which a frog or a fish would live not less than five nor more than seven days, but the factor of individual resistance, of course, interfered with a high degree of mathematical exactness, and the necessity of using an average of a large number of results is very apparent. Several hundred frogs and

fishes, each, were used in making this investigation and the results recorded here are averages of a very large number of individual experiments.

In order to have some standard, that particular strength of solution of benzoate of soda which would cause the death of a frog or fish in from 5 to 7 days was called "one," and the various solution strengths of the other chemical substances experimented with divided into "one" was taken as the degree of toxicity compared with that of sodium benzoate.

According to the above tabulation (frog standard), sodium benzoate, sodium chloride and borax all have about the same relative toxicity. Sodium chloride is used in foods with impunity, sodium benzoate is allowed in foods if its presence and the per cent thereof is declared on the label, while borax is debarred from use in foods in this country. Sodium salicylate, glucose and alcohol all have about the same relative toxicity, yet sodium salicylate is not allowed in foods on account of its deleterious effects upon the health, while glucose is a common article of food. Under the food laws alcohol is not debarred from foods on account of its toxic effects. Rochelle salts occurring in baking powder residues, potassium oxalate occurring in pie plant,\* citric acid occurring in lemons and other fruits, cane sugar, one of the most common articles of food, malic acid occurring in apples and other fruits, and tartaric acid occurring in grapes are all more toxic to frogs than sodium salicylate which is properly excluded from human foods under the terms of the federal law. It will be noted that sodium sulfite, which is not a legitimate constituent of food, is much less toxic to frogs than many of the most common constituents of our daily food. Cane sugar is about three times as toxic to frogs as glucose, and tartaric and acetic acids are more toxic than saccharine.

In case of fishes, as is well known, sodium chloride is not toxic. Cane sugar, Rochelle salts, glucose, alcohol and potassium oxalate are all less toxic than sodium benzoate. In case of frogs, however, they are all more toxic than sodium benzoate, and some of them much more so. Citric acid, acetic acid, malic acid, and tartaric acid, all of which occur in fruits, some of them in large quantities, are all more toxic to fishes than are either caffeine or saccharine, whereas in case of frogs citric and malic acids are less toxic than saccharine. It is interesting to note that malic, tartaric and benzoic acids are all more toxic to fishes than carbolic acid, whereas in case of frogs the reverse is true. In both cases alum seems to be much more toxic than sodium benzoate or saccharine.

Attention should be called to one point which seems very significant. In case of both frogs and fishes it will be noted that the free benzoic acid is much more toxic than sodium benzoate. This is in accordance with our general knowledge on the subject with regard to the toxicity of the stronger acids and their salts. For example, hydrochloric and nitric acids are very much more toxic than their ordinary metallic salts. It will be observed also that in case of both



frog, and takes tartaric acid is much more toxic than Rochelle salt.

So far as the writer is aware, no series of systematic observations so extensive as those here recorded have ever been made. Only isolated experiments seem to have been conducted with no efforts at comparative results.

Our conclusions from these experiments were far different from our expectations in the beginning, which opinions were based on opinions of some eminent men in the field of investigation. The Referee Board of Consulting Scientific Experts, for example, laid great stress on the fact that sodium benzoate is not toxic to frogs as comparative evidence in drawing conclusions as to its toxicity to men. Such experiments as these in the past have been often relied on as evidence in court as to the poisonous character of substances used in foods, but after studying the data we have accumulated somewhat carefully, the writers have come to the conclusion that experiments of this nature, at least upon animals so distantly related to man, do not furnish conclusive evidence of the effects of such substances upon the human system.

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## THE GRAVIMETRIC DETERMINATION OF REDUCING SUGARS IN CANE PRODUCTS

By GEORGE P. MEADE AND JOSEPH B. HARRIS

Received February 10, 1916

The reference books devoted to sugar analysis all describe the determination of reducing sugars in considerable detail. The detail concerns the method of heating, the time of boiling, the filtration of the cuprous oxide, the determination of the copper by any of several methods, and the calculation of results. On the other hand, the preparation of the solution, the clarification and removal of excess lead are, as a rule, referred to very briefly and in the broadest terms: "Clarified if necessary with a minimum of neutral lead acetate solution—deleading by means of sodium carbonate, sodium sulfate, potassium oxalate or other means."<sup>1</sup> "In case clarification with lead acetate is used, the excess of lead must be removed; this may be done by the addition of a soluble carbonate, sulfate or oxalate."<sup>2</sup>

The present investigation was undertaken at the suggestion of G. L. Spencer, Chief Chemist of The Cuban-American Sugar Company, and carried on under his general direction. The work extended over a period of eighteen months. Failure to obtain concordant figures from several laboratories on exchange samples of final molasses called attention to the necessity for the revision of the routine method. The method of precipitation and the determination of the copper were under strict specifications in all the laboratories to which the exchange sample had been sent, so the indication was that the source of difference lay in the preparation of the solution for analysis.

<sup>1</sup> Browne's "Handbook of Sugar Analysis," p. 443.

<sup>2</sup> Deerr's "Cane Sugar," p. 468.

## GENERAL METHOD

Throughout the investigation the Meissl and Hiller method was employed; 50 cc. of the solution for analysis and 50 cc. of mixed Fehling's solution were heated in a beaker to the boiling point for 4 minutes, and maintained at gentle ebullition exactly 2 minutes. A gasoline burner was the source of heat. At the end of the boiling period 100 cc. of cold, recently boiled distilled water were added and the solution filtered in an alundum crucible or fused silica Gooch crucible. The cuprous oxide was always burned to cupric oxide in an electric muffle at full red heat for at least 30 min. Other methods of determining the copper were employed at times as well, and comparisons are tabulated where this was done.

**LEAD ACETATE SOLUTION**—The lead solution employed was a 56° Brix solution of normal lead acetate, acidified faintly with acetic acid.

**SAMPLE**—For the first part of the work a sample of final molasses of the following analysis was used: Brix 87.2, polarization 36.7, Clerget number 42.43, reducing sugars about 11.00 per cent. This was warmed, mixed thoroughly and stored in an air-tight jar. Weights of this molasses were taken so that 50 cc. of solution contained 1 gram of molasses.

**AMOUNT OF LEAD TO BE USED**—To various portions of solution containing 1 gram of molasses to 50 cc. were added lead acetate solution—0.1, 0.2, 0.3, 0.4, etc., cc., respectively, per gram of molasses. The filtrates were tested with HCl. The filtrate from the portion using 0.5 cc. lead solution showed a slight precipitate. The portion containing 0.1 cc. lead solution filtered slowly, the filtrate showing a precipitate with hydrogen sulfide. This covered the range in which might be included "sufficient lead to clarify," as 0.1 cc. showed an excess of lead in the filtrate (with hydrogen sulfide), and 0.5 cc. was necessary to precipitate everything which could be brought down completely with normal lead acetate. The first series of tests was made using 0.5 cc. lead solution per gram of molasses.

## COMPARISON OF ORDINARY DELEADING AGENTS AND VARYING AMOUNTS OF LEAD

TABLE I—WEIGHTS OF CuO FROM 1 GRAM OF MOLASSES  
0.5 cc. Lead Solution per Gram of Molasses, Deleading with Various Deleading Agents in Solutions, the Amount Indicated Being per Gram of Molasses

Sodium carbonate 2 cc. 10% solution	Potassium oxalate 2 cc. 10% solution	Sodium sulfate 2 cc. saturated solution
0.2547	0.2646	0.2517
0.2547	0.2647	0.2500*
0.2561	0.2649	0.2549
0.2525	0.2644	
0.2515	0.2605	
0.2521	0.2616	
Av., 0.2534	0.2634	0.2522

Spaces separate determinations made on different weighings.

The carbonate and sulfate check, but the oxalate gives weights of CuO 10 mg. higher. As the deleading agents all gave considerable precipitates with 0.5 cc. of lead solution, a second set of tests was made using 0.25 cc. of lead solution per gram, one-half the amount used above. This was about the minimum of lead giving a rapid filtration. As sodium sulfate did not form any precipitate with this smaller

amount of lead, its use was discontinued, and a series with dry sodium oxalate was substituted.

TABLE II—WEIGHTS OF  $\text{CuO}$  FROM 1 GRAM OF MOLASSES  
0.25 cc. of Lead Solution per Gram of Molasses, with Decreased  
Amounts of Deleaching Agents as Shown

Sodium carbonate 1.5 cc. 10% solution	Potassium oxalate 1 cc. 10% solution	Sodium oxalate (dry) 0.1 gram
0.2635	0.2710	0.2703
	0.2704	0.2709
	0.2723	
0.2658	0.2717	
0.2664	0.2732	
0.2689		
0.2638		
Av., 0.2657	0.2715	0.2706

The dry sodium oxalate checks the potassium oxalate in solution, and as before the carbonate figures are much lower than those with oxalates. Comparing the average results with 0.5 cc. of lead solution per gram and with 0.25 cc. lead solution per gram we have:

	Sodium carbonate	Potassium oxalate
0.5 cc. lead solution.....	0.2534	0.2634
0.25 cc. lead solution.....	0.2657	0.2715

The smaller amount of lead gives much higher results with both deleaching agents.

Another comparison of the effect of varying the lead, deleaching with potassium oxalate gave similar results, as here shown.

TABLE III—DIFFERENT AMOUNTS OF LEAD SOLUTION, DELEACHED WITH  
POTASSIUM OXALATE IN SOLUTION

0.5 cc. lead solution per gram molasses	0.25 cc. lead solution per gram molasses
0.2637	0.2748
0.2626	0.2744
Av., 0.2632	0.2746

THE EFFECT OF KIESELGUHR AS AN AID TO FILTRATION, and a comparison of dry reagents with previous figures with reagents in solution was brought out in the following:

TABLE IV—DRY DELEACHING AGENTS, WITH AND WITHOUT KIESELGUHR  
All with 0.25 cc. Lead Solution per Gram of Molasses

0.15 gram sodium carbonate, dry per gram molasses		0.1 gram sodium oxalate, dry per gram molasses	
No Kieselguhr	Kieselguhr	No Kieselguhr	Kieselguhr
0.2670	0.2669	0.2748	0.2743
0.2652	0.2642	0.2740	0.2745
0.2670	0.2672	.....	0.2742
Av., 0.2664	0.2663	0.2744	0.2743
Av. with wet reagent,	0.2657		0.2746

The kieselguhr aids filtration and does not affect the results. Dry reagents give check figures with the same reagents in solution. This tabulation again emphasizes the difference between deleaching with carbonate and with oxalates.

SUMMARY—Considering now the possibilities under the options offered in "sufficient lead to clarify" and "deleaching with carbonate, sulfate or oxalate," the following figures are taken from the foregoing work:

0.5 cc. lead per gram of molasses, deleached with carbonate; average of five check results, weight  $\text{CuO}$  0.2534, per cent glucose 10.64.

0.25 cc. lead per gram of molasses, deleached with oxalate; average of seven check results, weight  $\text{CuO}$  0.2744, per cent glucose 11.54, showing a difference of about 8.5 per cent on the glucose content of the molasses, using methods both of which are permissible under the directions as ordinarily given.

It is evident that concordant results can be obtained only when the amount of lead is accurately measured, and when the deleaching agent is specified. Pending further work, we adopted the use of 0.25 cc. of lead solution per gram of molasses, as this was the minimum amount of lead giving a rapid filtration, and showing an appreciable precipitate with the deleaching agent, removing the excess lead with 1 cc. of 10 per cent potassium oxalate solution, or 0.1 gram of dry sodium oxalate, with kieselguhr added to aid filtration. The oxalates were preferred for several reasons. Boertraeger<sup>1</sup> had raised objections to carbonate, particularly in excess; Sawyer<sup>2</sup> considered the oxalate preferable; solutions deleached with carbonate, on standing a short time, frequently developed a cloud which settles on the glassware; and finally the oxalate gives the higher figures.

WEIGHING AS CUPROUS OXIDE—Before igniting to cupric oxide, in most cases the cuprous oxide was dried at 105° C. and weighed. Several determinations of the copper present in the precipitates were made by Low's modifications of the volumetric iodide method.<sup>3</sup>

TABLE V

$\text{Cu}_2\text{O}$	Cu (calculated)	$\text{CuO}$	Cu (calculated)	Cu by Low's method
0.2532	0.2248	0.2732	0.2183	0.2192
0.2522	0.2240	0.2723	0.2175	0.2176
0.2550	0.2264	0.2742	0.2191	0.2184
0.2449	0.2175	0.2642	0.2111	0.2084
0.2548	0.2263	0.2745	0.2193	0.2187
0.2567	0.2279	0.2740	0.2189	0.2184
Av.,	0.2245		0.2174	0.2168

Weighing as cuprous oxide is evidently worthless. The checks between the copper as calculated from cupric oxide and as determined by Low's titration, show the reliability of the cupric oxide weight.

CLARIFICATION WITH KIESELGUHR ONLY, WITHOUT  
THE USE OF LEAD

With solutions which are free from suspended matter it has long been the practice with many chemists to dispense with the use of lead or other clarifying reagents. This practice has been objected to on the ground that there might be copper-reducing substances, other than sugars, present in the solutions which would be removed by the use of lead. Noel Deerr<sup>4</sup> says: "With the use of no clarifying agent, bodies other than reducing sugars which act on copper may be present. Zerban and Naquin have shown that with cane molasses a little more copper is precipitated with unclarified solutions than with solutions clarified with neutral acetate of lead, and the writer is of the opinion that results closest to the truth are obtained with the use of this material."

In the present investigation we have shown that tests made with neutral lead solution may vary between wide limits depending on the amount of lead and the class of deleaching agent used. It is possible that most of the work comparing the use of lead and no lead has been done using sodium carbonate to de-

<sup>1</sup> *Z. anorg. Chem.*, **1892**, 333.

<sup>2</sup> *J. Am. Chem. Soc.*, **26**, 1631.

<sup>3</sup> Browne's "Handbook," p. 411.

<sup>4</sup> "Cane Sugar," p. 467.



lead, which gives much lower figures than the oxalate, as we have brought out.

The second phase of the work took up the comparison of the lead and oxalate method already developed, as against preparation of the solution without the use of reagents, using kieselguhr for the removal of suspended matter. Experiment showed that the addition of a few teaspoonfuls of kieselguhr to the molasses solution, after making to the mark, gave a solution on filtering which was quite bright and clear. The filtration may also be effected quite as well by adding the kieselguhr to the filter paper before pouring on the solution.

A new sample of molasses was used, polarization 34.24, Clerget number 40.31, reducing sugars about 21.00 per cent. This sample was warmed, mixed and stored as before. Amounts were weighed to give 0.5 g. of molasses per 50 cc. of solution.

TABLE VI—COMPARISON BETWEEN A SET OF TESTS CLARIFIED WITH NORMAL LEAD ACETATE SOLUTION.

0.25 cc. per Gram of Molasses with 1 cc. of 10 Per Cent Potassium Oxalate Solution per Gram of Molasses, and Three Sets of Tests Using Kieselguhr Only, with No Lead or Other Reagent

Lead and potassium oxalate	No lead		
	A	B	C
0.2518	0.2517	0.2478	0.2481
0.2520	0.2517	0.2513	0.2478
0.2538	0.2500	0.2488	0.2505
0.2534	0.2486	0.2509	0.2512
0.2509	0.2491	0.2501	0.2492
..	..	0.2500	0.2496
..	..	0.2494	0.2494
..	..	0.2503	0.2493
..	..	0.2492	..
..	..	0.2510	..
Av., 0.2523	0.2501	0.2499	0.2494

The lead and oxalate gives results higher than the tests where no lead is used. The three sets using no lead agree well with one another and within themselves.

It may be of interest here to note that Series A and B were filtered through alundum crucibles and Series C, through silica Gooch crucibles with porcelain discs. The agreement is good. We found that if alundum crucibles were given a proper treatment the weight remained practically constant through the duration of the test. New crucibles were soaked with nitric acid, washed with hot water, then treated with hot Fehling's solution and again washed thoroughly and finally ignited at red heat in a muffle furnace for at least 30 mins. After use the copper precipitate was removed with nitric acid, the crucible washed thoroughly with very hot water and the ignition carried out as before. Prepared crucibles must be stored in a desiccator to avoid absorption of moisture. The greater part of our work was done with alundum, and in the numerous instances where comparative tests were made using both Gooches and alundum crucibles, the agreement was always very good.

**DETERMINING THE BOILING POINT WITH A THERMOMETER**—In the tabulations given so far it will be seen that, almost without exception, there is a maximum variation of 3 mg. of CuO among tests made on the same solution. The only phase of the precipitation and collection of the copper precipitate which seemed capable of causing this variation was the determination of the beginning of the 2-minute boiling period. The

usual directions read: "Heat the contents of the beaker to the boiling point in 4 minutes and continue the heating for exactly 2 minutes, maintaining gentle ebullition." Some directions define the beginning of boiling as "full ebullition of the solution." Frequently the solution comes to a boil all at once, sometimes it boils locally for a few seconds. To place this part of the operation on a definite basis, so as to limit the variations in check tests, one of us (Harris) suggested the use of a thermometer to determine the beginning of boiling. The thermometer was thrust through a hole in a metal disc which served as a cover for the beaker in place of the usual watch glass. The lower end of the thermometer reached into the liquid to within 4 or 5 mm. of the bottom of the beaker. The solution was heated at such a rate that the thermometer registered 100° C. in four minutes. The heating was continued for exactly two minutes from this point, a gentle ebullition being maintained as usual. We employed this device in all of our succeeding work, and obtained closer checks than with the old method. Not only is the two-minute boiling period made more definite by the use of the thermometer, but it is much easier to regulate the pre-heating to the required 4 minutes. Local boiling frequently takes place before 100° C. is reached, and occasionally full boiling does not begin until after that point is passed. Under any circumstances, the 2-minute period was timed from the 100° point.

Further work with no lead as compared to lead and oxalate was carried out to determine, if possible, the reason for the higher results obtained where lead and oxalate were used.

TABLE VII—CuO PRECIPITATED BY 0.5 GRAM MOLASSES, TESTS WITHOUT LEAD

With 0.25 cc. Lead Solution and 1 cc. 10 Per Cent Potassium Oxalate per Gram of Molasses; and with 0.25 cc. Lead Solution and 1 g. (Large Excess) of Dry Sodium Oxalate per Gram of Molasses

No lead	Lead and potassium oxalate	
	Lead and potassium oxalate	Lead and sodium oxalate
0.2492	0.2498	0.2515
0.2486	0.2500	0.2509
0.2492	0.2497	0.2528
0.2481	0.2506	0.2514
0.2482	0.2515	0.2527
Av., 0.2487	0.2503	0.2519

As in Table VI, the use of lead and oxalate gives higher tests than no lead. The excess of oxalate gives still higher figures. Later work, however, did not bear this out.

(The difference between the no lead and the lead and oxalate methods is so slight that frequently there is a greater maximum difference within a series than between the averages of two series. Our conclusions are justified by the constant tendency of the one method to give higher figures than the other.)

TABLE VIII—TESTS WITHOUT LEAD

With 0.25 cc. Lead Solution and 1 cc. 10 Per Cent Potassium Oxalate Solution per Gram of Molasses; and with No Lead, but 1 cc. 10 Per Cent Potassium Oxalate per Gram of Molasses

No lead	Lead and potassium oxalate	
	Lead and potassium oxalate	Potassium oxalate but no lead
0.2488	0.2512	0.2501
0.2498	0.2497	0.2505
0.2491	0.2503	0.2521
0.2491	0.2492	0.2522
..	..	0.2511
Av., 0.2492	0.2500	0.2512

Again the use of lead and oxalate gives figures higher than the tests in which no lead is used (although in

this particular case the two methods agree more closely than before), but the addition of oxalate alone gives results higher than where no reagent is used. The indication here is that the lead is not the disturbing factor.

The combined precipitates in the second set of tests (lead and oxalate) were dissolved in nitric acid and evaporated with sulfuric acid, but showed no lead.<sup>1</sup>

To 100 cc. portions of a solution to which had been added 0.25 cc. lead solution per gram of molasses, and filtered, were added 0.2, 0.5, 1 and 2 g. of dry sodium oxalate. After standing three hours these were filtered and tested with hydrogen sulfide. The lead was in direct proportion to the amount of oxalate used. In the filtrate from the 0.2 gram of oxalate only a trace of lead was shown, but in the filtrate from 2 grams oxalate the precipitate of lead sulfide was quite appreciable. Treadwell-Hall<sup>2</sup> says, "In an excess of alkali oxalate, many of the insoluble oxalates dissolved, forming double salts."

To determine whether increasing the oxalate with no lead present would increase the results proportionately, a series of tests were made as follows: Four portions of molasses of 5 g. each were made up to 500 cc. with quantities of potassium oxalate in solution as indicated in the tabulation. The lime salts formed a precipitate which was filtered out, using kieselguhr. Tests were run in duplicate. After weighing the ignited cupric oxide, this was reduced to metallic copper in alcohol vapor according to Wedderburn,<sup>3</sup> and this copper in turn was dissolved and determined by Low's volumetric iodide method.

TABLE IX. TESTS USING NO LEAD, BUT WITH INCREASING QUANTITIES OF POTASSIUM OXALATE IN SOLUTION

Grams potassium oxalate per 100 cc.	CuO	Cu (calculated)	Cu reduced by alcohol	Cu Low's titration
None.....	0.2473	0.1975	0.1975	0.1977
None.....	0.2467	0.1970	0.1979	0.1974
0.1.....	0.2501	0.1998	0.1995	0.2018
0.1.....	0.2510	0.2005	0.2011	0.2012
0.4.....	0.2499	0.1996	0.2007	0.2208
0.4.....	0.2487	0.1992	0.1992	0.2005
2.0.....	0.2502	0.1999	0.2008	0.2008
2.0.....	0.2500	0.1997	0.2009	0.2002
With lead and dealed with potassium oxalate.....	0.2500			

The presence of the oxalate gives higher figures than where none is present, but increasing the amount of oxalate does not increase the results. Judging from the volumetric copper, the greater weight where oxalate is present is due to copper actually precipitated and not to some extraneous material precipitated with the copper. The oxalate without lead gives figures corresponding to those where lead is used and the excess removed with oxalate.

From the figures obtained with lead and oxalate, oxalate and no lead, and no lead or other reagent, it seems safe to say that the molasses with which we

<sup>1</sup> The work with no lead covered a period of several months, during which time the molasses sample was not remixed. Stratification and absorption of moisture may account for slight variations between sets of tests by the same method in the different tables. Each table contains all the data for the conclusions drawn from it, and comparisons must not be made between one method as shown in one table and another method as shown in another. Each table should be considered as dealing with a different sample of molasses.

<sup>2</sup> "Analytical Chemistry," Vol. 1, p. 349.

<sup>3</sup> This Journal, July, 1915.

were dealing contained no non-sugar copper-reducing substance removable by lead. Since the oxalate without lead gives just as high figures as the lead and oxalate together, the deleading agent and not the lead is the cause of the difference between the no lead method and the method with lead and deleading agent. As suggested earlier in this article, the probable reason for the conclusion that the use of lead for clarification was necessary because it removed copper-reducing non-sugars, arose from the fact that the comparisons with the no lead method were made using lead and sodium carbonate, which gives low results.

#### SUMMARY

Summarizing the work on final molasses without lead we find that:

Using kieselguhr only, without lead or any other reagent, gives a clear filtrate and consistent results.

The no lead method offers no mechanical difficulties, either in preparing the solution for analysis or in the precipitation and collection of the copper precipitate.<sup>1</sup> It eliminates all chance of the gross errors which we have shown to be possible under the options offered as to the quantity of lead and class of deleading agent. The only objection offered, that there may be present copper-reducing non-sugars which make the use of lead essential, seems to be contradicted by our work with oxalate and lead, and oxalate alone.

Compared with tests made with lead solution and dealed with potassium oxalate, the results without lead are slightly lower, 1.5 to 2 mg. of CuO.

Oxalate alone, without lead, gives figures corresponding to those with lead and oxalate, showing that the oxalate is the disturbing factor, and not the lead.

#### COMPARISON BETWEEN VARIOUS DELEADING AGENTS—

Oxalic acid has been suggested as a deleading agent, as well as phosphoric acid and sodium phosphate. Tests were made with these in comparison with the no lead method. In order to corroborate the earlier work with carbonate and oxalate, these reagents were also included in the comparison.

TABLE X. COMPARISON BETWEEN NO LEAD METHOD AND VARIOUS DELEADING AGENTS. LEAD SOLUTION 0.25 CC. PER GRAM OF MOLASSES

No lead	Lead and 1 cc 10% potassium oxalate	Lead and 1 cc 10% sodium carbonate	Lead and 1 cc 10% oxalic acid
0.2507	0.2532	0.2439	0.2538
0.2508	0.2527	0.2424	0.2531
0.2513	0.2516	0.2447	0.2545
—	0.2516	0.2444	0.2541
—	0.2533	0.2418	0.2540
Average, 0.2508	0.2525	0.2434	0.2540

The carbonate method again gives results much lower than the potassium oxalate, and the relation between the no lead and oxalate is as before. The oxalic acid results are higher than any so far obtained. The high inverting power of oxalic acid (18.7 to 100 for HCl) is sufficient to condemn it for routine work.

The solution dealed with carbonate was slightly alkaline but showed considerable lead when tested with hydrogen sulfide. That from the potassium oxalate showed a trace of lead. The combined precipitates from the tests using potassium oxalate showed no lead when dissolved and evaporated with sulfuric acid.

<sup>1</sup> With some samples of molasses requiring 1 g. for a test it has been found that the filtration of the cuprous oxide is somewhat slower than where lead is used.



TABLE XI.—COMPARISONS BETWEEN NO LEAD METHOD, LEAD AND POTASSIUM OXALATE, LEAD AND PHOSPHORIC ACID, AND LEAD AND SODIUM PHOSPHATE. LEAD SOLUTION 0.25 CC. PER GRAM OF MOLASSES.

	Lead and 1 cc. 10% potassium oxalate	Lead and 0.2 cc. 10% phosphoric acid	Lead and 1 cc. 10% sodium phosphate
No lead			
0.183	0.2501	0.2488	0.2500
0.218	0.2510	0.2479	0.2504
0.211		0.2485	0.2500
		0.2474	0.2491
Average	0.2508	0.2484	0.2498

The agreement between no lead, and lead and phosphoric acid is very close. The sodium phosphate results check those with potassium oxalate. The solutions delead with phosphoric acid and with sodium phosphate were tested with hydrogen sulfide, and neither showed any lead whatever. These are the only cases in which delead solutions were found quite free from lead.

The results using phosphoric acid to delead are so good that the method seems worthy of a more extended investigation than we have been able to give it so far.

Since so many of the deleading agents failed to delead completely, we thought it might be of interest to run a few tests using lead without any deleading agent, *i. e.*, leaving the excess of lead in the solution. The precipitation showed no abnormality and the cuprous oxide was the usual color and filtered without difficulty. Tests were made on two separate weighings of two different molasses samples.

TABLE XII.—TESTS USING LEAD SOLUTION, 0.25 CC. PER GRAM OF MOLASSES, WITHOUT DELEADING REAGENT. NO LEAD AND LEAD AND OXALATE FOR COMPARISON.

Molasses A	No lead	Lead and potassium oxalate	Lead, without removing excess
	0.2483	0.2499	0.2448
	0.2482	0.2502	0.2459
	0.2471		0.2447
Average	0.2479	0.2501	0.2454
Molasses B	0.3282	0.3298	0.3266

The lower figures where lead is not removed are directly opposite to what had been expected. A possible explanation might be that lead salts of reducing sugars are formed, which the oxalate breaks up, but which are not broken up by the boiling with Fehling's solution. Herein also may lie the explanation for the low results obtained with sodium carbonate. The lead salts of reducing sugars may be precipitated by the alkaline carbonate.

#### REDUCING SUGARS IN RAW SUGARS

The percentage of reducing sugars (or "glucose") in raw sugars is so low as a rule that fairly large variations in the weight of the proper precipitate make little apparent difference in the result. On the other hand, the amount of raw sugar handled, both in the factory and the refinery, is so much greater than the amount of molasses produced that small percentage differences in the raw sugar glucose content affect the "glucose balance" perceptibly. The desirability of using the same method for both products is evident. The only difficulty which we thought might be encountered with raw sugar was that of filtering a solution of such density (usually 20 grams to 100 cc.) without defecation. However, we found on experimenting with several sugars, including molasses sugars and raws which had deteriorated, that with

kieselguhr, with solutions of the strength necessary for the glucose test, the filtration was sufficiently rapid for practical purposes, and the resulting filtrate quite clear.

A test was made on a raw sugar with fairly high glucose content, comparing the no lead method with clarification with 0.25 cc. lead solution and 1 cc. 10 per cent potassium oxalate solution per 10 g. of sugar. As it has been claimed that weighing as cuprous oxide is sufficiently accurate for raw sugar determinations, the precipitates were first dried and weighed and then ignited and reweighed, in order to obtain some figures on this point.

TABLE XIII.—5 GRAMS OF RAW SUGAR TO 50 CC. OF SOLUTION.

A. Clarified with 0.25 cc. Lead Solution and 1 cc. of 10 Per Cent Potassium Oxalate per 10 g. of Sugar			
Cu <sub>2</sub> O	(calculated)	CuO	Cu (calculated)
0.2192	0.1947	0.2347	0.1874
0.2189	0.1944	0.2329	0.1863
0.2212	0.1965	0.2361	0.1890
Average	0.1953		0.1876
Per cent glucose	1.79		1.69
B. Clarified with Kieselguhr Only, without Lead or Other Reagent			
Cu <sub>2</sub> O	(calculated)	CuO	Cu (calculated)
0.2174	0.1932	0.2328	0.1862
0.2179	0.1936	0.2337	0.1870
0.2195	0.1950	0.2353	0.1882
Average	0.1939		0.1871
Per cent glucose	1.79		1.68

The difference between the no lead method and the lead and oxalate method is so slight as to be immaterial. The copper by Cu<sub>2</sub>O is appreciably higher than by CuO, the difference being practically as great, calculated to percentages of glucose content, as in the case of final molasses.

Two series of tests with kieselguhr using no lead were run on another sugar. No further comparison with other methods was considered necessary, in view of the extended work already done with molasses.

TABLE XIV.—WEIGHTS OF CuO FROM 5 GRAMS OF SUGAR

5 g. of Raw Sugar to 50 cc. of Solution, using Kieselguhr and no Lead	
Two Series of Tests on the Same Sugar	
0.2619	0.2619
0.2615	0.2633
0.2641	0.2661
0.2645	0.2637
0.2656	0.2647
Average	0.2635
Per cent glucose	1.96
Minimum per cent glucose in 10 tests	1.94
Maximum per cent glucose in 10 tests	1.98

SUMMARY—Clarification with kieselguhr only, using no lead, is quite as practicable with raw sugars as with final molasses, the greater density of the solution offering no difficulty in the filtration. The desirability of having the same method for both products is sufficient to recommend it.

Weighing the cuprous oxide direct without igniting is no more advisable in the case of raw sugars than with molasses.

#### CONCLUSIONS

1—Results differ with varying amounts of neutral lead acetate solution.

2—Carbonate, sulfates and oxalates are not interchangeable as deleading agents, oxalates giving results from 4 to 5 per cent higher on the weight of copper than where either of the others is used.

3—Kieselguhr only, without the use of lead or other

reagent, gives a clear filtrate, both with final molasses and raw sugar, and the solution offers no mechanical difficulty in the precipitation and collection of the copper precipitate. Without lead the results are slightly lower than where lead and oxalate are used.

4—The use of a thermometer to determine the beginning of the two-minute boiling period reduced the variations between tests on the same solution.

5—Weighing as cuprous oxide gives results about 5 per cent higher, on the weight of copper, than those obtained by igniting to cupric oxide, whether working with final molasses or raw sugars. Volumetric iodide determinations of the copper check the cupric oxide.

6—Under strict specifications as to the quantity and class of reagents, any method for the preparation of the solution for analysis will give results which check within themselves.

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### THE DETERMINATION OF THE GELATINIZING TEMPERATURE OF THE STARCHES FROM THE GRAIN SORGHUMS BY MEANS OF A THERMO-SLIDE

By C. K. FRANCIS AND O. C. SMITH

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The usual method for determining the gelatinizing temperature of starches requires that small quantities of the material be placed in test tubes immersed in a water bath, the temperature of which is gradually raised; then portions of the starch are removed at intervals for microscopical examination. This has been found a tedious method and the results not so accurate as desired.

The apparatus designed for our work on the starches obtained from the various grain sorghums permitted direct readings so that a large number of tests were made in a comparatively short time; triplicate determinations checked well within one degree. The thermo-slide, Fig. I, was made in this laboratory and may easily be constructed by any one having a little ability to handle tools. The material consists of:

(1) Three pieces of steel 5 in. long,  $1\frac{3}{8}$  in. wide and  $\frac{1}{8}$  in. thick, with a central opening  $\frac{7}{8} \times 2\frac{3}{4}$  in. cut in each piece, approximately 1 in. from each end and  $\frac{1}{4}$  in. from each side; two  $\frac{1}{4}$  in. nipples are fitted into the steel piece, No. 1, the holes for these being drilled  $\frac{3}{4}$  in. from each end; two openings,  $\frac{1}{4}$  in. wide, are cut in steel piece No. 2, as indicated in the top view in Fig. II. (2) Two glass slides  $1 \times 3$  in. (3) Six rubber gaskets,  $\frac{1}{8} \times 5$ , cut from  $\frac{1}{16}$  in. rubber sheets: two of these gaskets are cut to match steel plate No. 2.

The pieces of steel and rubber have two  $\frac{1}{4}$  in. holes drilled in each end through which bolts pass to clamp the entire system together. The  $\frac{1}{4}$  in. piping is connected by means of nipples fitted into the top plate. The thermometer is small enough to fit inside the T opposite the exit pipe and the opening made water-tight by slipping a piece of tubing over the thermometer and the nipple. The general arrangement of the micro-polariscope, the thermo-slide and

connections for the warm water are illustrated in Fig. I, and further details of the thermo-slide are shown in the drawing, Fig. II.

PROCEDURE—The apparatus is arranged as shown in Fig. I, and the syphon started, then the flow adjusted by means of the pinch-cock so that the water will run at the rate of not over 100 cc. a minute; a second pinch-cock may be used as a total cut-off. The temperature in the flask is brought to  $60^{\circ}$  C., then the heat controlled so that the thermometer in the flask will indicate a rise of  $1^{\circ}$  every minute. The water bath (flask) and the microscope are placed not over 18 in. apart so that there will be but little difference in the temperatures recorded in the flask and in the slide. This difference should not be over  $3^{\circ}$ .

A small quantity of dry starch is placed on the thermo-slide, moistened with an excess of water, and a cover

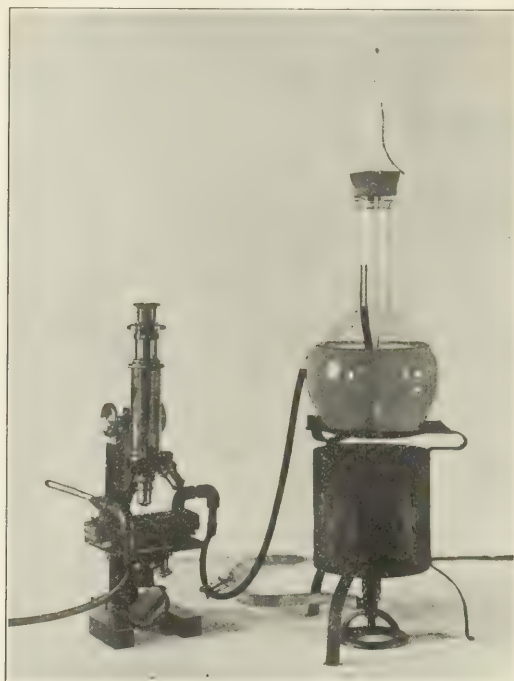


FIG. I

glass placed over it. The low power (16 mm.) objective is adjusted and focused, then the analyzer put in place and turned to the dark field. The water is now turned on and the temperature noted when all the starch granules have lost their polarizing properties. This temperature should not be considered the correct one, but is to be used as a guide.

The slide is now cleaned and a second portion prepared in the same way as has been described. The water in the flask is heated to the same degree which was recorded for the preliminary test; this gives a temperature in the thermo-slide about  $2-3^{\circ}$  below that first found, and, consequently, below the gelatinization point. The temperature of the water is



slowly raised and a second reading of the temperature indicated by the thermometer in the thermo-slide, when the observer can no longer see any signs of anisotropy, this may be considered to be the temperature of gelatinization. By repeating the determination and with a little experience, it will be found that the gelatinizing point is quite sharp, and may be usually read within a few tenths of a degree.

It is important that the starch be well covered with water during the test, because, if the water is permitted to evaporate, gelatinization may not occur, or, it may be delayed for several degrees beyond the true temperature. This action of water has been observed on potato starch (which gelatinizes from 67.4° to 67.8° C. in the presence of water) in an experiment during which the

mixing point may become indefinite, and not so uniform as when the starch is heated for a few minutes within 3° to 5° of the true point of gelatinization.

The starch was prepared from the grains by the following process: The grains were steeped in water for several days, until slight putrefaction was noticed, then crushed in a mortar. The material was next washed with water on a brass sieve, 100 mesh, until the washings became clear. After standing about 30 min. the supernatant liquid was decanted and the residue washed twice by decantation. The impure starch was suspended in water and stirred continuously, while enough 5 per cent sodium hydroxide solution was added to produce a yellow color. This was set aside for 6 hours, the liquid decanted and the starch washed 4 times with water, once with 95 per cent alcohol, and finally with ether. Prepared in this way the starch dried well when placed over sulfuric acid in a desiccator.

We have selected as the true gelatinizing temperature the complete disappearance of optical activity. E. T. Reichert<sup>1</sup> has recorded the temperature of the tube and the temperature of the water bath, when anisotropy disappeared in practically all of the granules, then selected the mean as the temperature of gelatinization. Necessarily the number of starch granules on a slide would vary; consequently, we deemed it better to wait for a total disappearance. The results are given in Table I.

TABLE I—GELATINIZING TEMPERATURE OF STARCHES FROM THE GRAIN SORGHUMS

KIND OF STARCH	THERMO-SLIDE READINGS—° C.			
	Determinations			Av.
White Kaoliang	78.0	78.0	78.1	78.0
Brown Kaoliang	76.2	76.4	76.4	76.3
Peterita	75.4	75.6	75.6	75.5
Orange Cane	72.2	72.4	72.6	72.4
Red Kafr.	74.8	75.0	75.0	75.0
White Kafr.	72.0	72.1	72.4	72.2
Pink Kafr.	64.6	65.0	64.6	64.7
White Milo	74.0	73.8	74.4	74.1
Yellow Milo	76.8	76.8	77.0	76.9
Darso	72.8	72.8	73.2	72.9
Sudan Grass	72.4	72.6	72.4	72.5

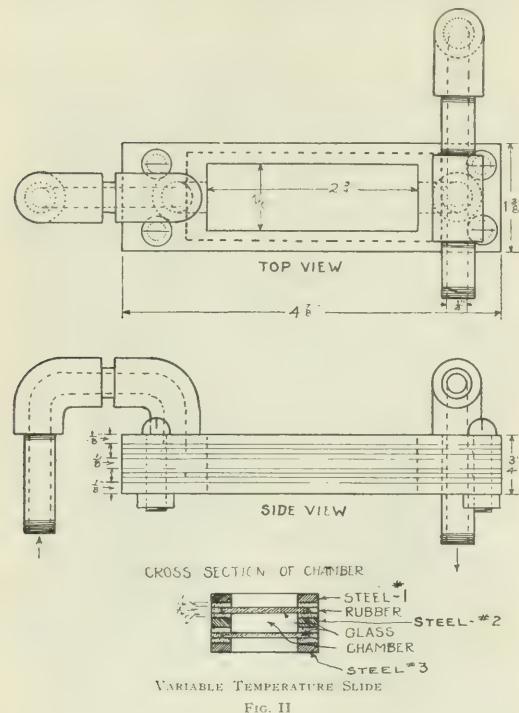
The proposed method does not require so much time as the water bath method and the gelatinizing point can be determined with more accuracy. When the determination is made by the water bath method the readings must be made on separate portions, and many minutes are required for a single determination. By means of the preliminary test, the approximate gelatinizing point may be determined and then the temperature fixed by one or two more tests on the thermo-slide. A series of tests were made by both methods, the results of which are shown in Table II.

TABLE II—GELATINIZING TEMPERATURES OF SOME COMMON STARCHES AS DETERMINED BY THE THERMO-SLIDE AND WATER BATH METHODS

KIND OF STARCH	THERMO-SLIDE METHOD		WATER BATH METHOD	
	Determinations	Av.	Duplicates	Av.
Arrow Root	74.4 74.8 74.6	74.6	74 to 75	74.5
Corn	70.6 71.2 71.0	70.9	71 to 72	71.5
Navy Bean	76.0 75.4 75.4	75.6	75 to 76	75.5
Sweet Potato	82.6 82.6 82.4	82.5	82 to 83	82.5
Irish Potato	67.6 67.8 67.8	67.7	67 to 68	67.5
Wheat	65.8 65.0 65.1	62.2	65 to 66	65.5

The advantages of the thermo-slide method over the water bath method are numerous. When working with the latter, one is compelled to withdraw portions of the starch from the tube and make a slide at each

<sup>1</sup> "Differentiation and Specificity of Starches," Pub. Carnegie Inst. 1913, p. 298.



samples were covered with glycerine and heated to 100° without any apparent action on the granules.

The test must not be prolonged because high results may be obtained, due to the fact that some granules may partly gelatinize and the resulting paste protect the remainder from the action of the water. When using the water bath-test tube method, it was noticed that arrow root starch heated from 65° to 79° did not entirely lose its anisotropic condition at the higher temperature, but when the sample was plunged into water heated to 75°, the starch lost its polarizing properties immediately. Navy bean starch, when tested by the water bath method, did not completely gelatinize at 83° but when suddenly exposed to a temperature of 76° gelatinized at once. In other words, it appears that if starch is subjected to a gradual rise of temperature, in the presence of water, that the gelat-

degree, or fraction of a degree, whereas, the thermo-slide permits constant observation of the starch. The water bath method requires more time for each test and the gelatinizing point cannot be determined with the same accuracy as by the proposed method. Moreover, the total time necessary is very much shorter, as numerous determinations have been made by the thermo-slide method, which required less than five minutes to complete each test.

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## NOTE ON THE DETERMINATION OF PHOSPHORUS IN PLANT MATERIALS

By A. W. CHRISTIE

Received February 14, 1916

In the course of certain investigations in this laboratory, it became desirable to find a quick and accurate method of oxidizing plant materials in order to determine the total phosphorus. A review of the literature suggested the following methods as being adaptable to this purpose.

Fusion with sodium peroxide<sup>1</sup> can be used in the determination of phosphorus as well as of sulfur but the care and time required by this method makes it undesirable.

Neumann's method is known to give accurate results. A modification,<sup>2</sup> consisting of digestion with sulfuric acid, 1 g. of potassium sulfate and a drop of mercury, gave fairly rapid oxidation but the subsequent precipitation with molybdate required standing over night to be complete. Digestion with hot fuming nitric acid also suggested itself as a possible method.

Ignition with magnesium nitrate<sup>3</sup> was found to be impossible in the case of many plant materials due to excessive deflagration.

The method of ignition with magnesium oxide<sup>4</sup> has been in use in this laboratory for the oxidation of organic matter in the analysis of phosphorus-containing fertilizers. Hibbard<sup>5</sup> describes this method but suggests "that some phosphorus may be lost from volatile organic substances containing it, when ignited with magnesia." This method is believed to be the quickest and most convenient of those suggested and hence the following experiment was performed to de-

	MIDDINGS	CASEIN	LECITHIN	Av. Lecithin
Ignition with magnesium oxide	$\left\{ \begin{array}{l} 0.56 \\ 0.56 \\ 0.57 \end{array} \right.$	$\left\{ \begin{array}{l} 0.87 \\ 0.86 \\ 0.87 \end{array} \right.$	$\left\{ \begin{array}{l} 3.52 \\ 3.66 \\ 3.56 \end{array} \right.$	3.58
Fusion with sodium peroxide...	$\left\{ \begin{array}{l} 0.57 \\ 0.57 \\ 0.57 \end{array} \right.$	$\left\{ \begin{array}{l} 0.87 \\ 0.87 \\ 0.86 \end{array} \right.$	$\left\{ \begin{array}{l} 3.59 \\ 3.70 \\ 3.62 \end{array} \right.$	3.64
Modified Neumann method....	$\left\{ \begin{array}{l} 0.57 \\ 0.56 \\ 0.56 \end{array} \right.$	$\left\{ \begin{array}{l} 0.85 \\ 0.85 \\ 0.88 \end{array} \right.$	$\left\{ \begin{array}{l} 3.65 \\ 3.66 \\ 3.51 \end{array} \right.$	3.61
Fuming nitric acid.....	$\left\{ \begin{array}{l} 0.37 \\ 0.39 \end{array} \right.$	$\left\{ \begin{array}{l} 0.64 \\ 0.66 \end{array} \right.$	$\left\{ \begin{array}{l} 1.56 \\ 1.61 \end{array} \right.$	1.58

termine the accuracy of the magnesium oxide method as compared with the modified Neumann and peroxide fusion methods.

Three samples, representing substances relatively high in their organic phosphorus content (Merck's

casein, Merck's lecithin and finely ground wheat middlings), were analyzed for total phosphorus by the methods mentioned above. After the preliminary digestion, the phosphorus was precipitated from the solution in the usual manner as ammonium phosphomolybdate and finally weighed as magnesium pyrophosphate. The accompanying table gives the percentages of phosphorus obtained.

The above figures show that ignition with magnesium oxide gives substantially the same results for total phosphorus in the materials analyzed as fusion with sodium peroxide or digestion with sulfuric acid, 1 g. of potassium sulfate and a drop of mercury. The sodium peroxide method has the advantage of furnishing a solution which can also be used for the determination of total sulfur. The modified Neumann method may also be used for the determination of total nitrogen. The use of fuming nitric acid alone is found to be unsatisfactory.

CONCLUSION—Ignition with magnesium oxide is a quick and accurate method of oxidizing plant materials for the determination of total phosphorus.

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## SOME EFFECTS OF LITTER ON THE FERMENTATION OF MANURE<sup>1</sup>

By W. E. TOTTINGHAM

Received February 14, 1916

Within recent years the increased use of shavings as litter in stables has raised questions regarding the possible effects of such practice upon the value of the manure. One of the most important of these questions concerns the extent of the loss of nitrogen from the manure. Others concern the rate of oxidation of the organic matter and related changes. This paper presents the results of an investigation concerning some of these questions. It is a report of the results of certain chemical changes in a fermenting mixture of manure and shavings as compared with straw-littered manure and unlittered manure.

### EXPERIMENTAL

METHODS—A basal manure was prepared by mixing one part by weight of fresh horse manure with two parts of fresh cow manure, each manure having been freed from litter. Four lots of this manure of 25 lbs. weight each were placed in galvanized iron pails with loosely fitting covers. The weighings at this point and subsequently were made on a Fairbanks platform scale sensitive to  $\frac{1}{4}$  lb., or to within a possible error of 1.0 per cent for the weights involved. Litters were prepared by sifting finely cut oat straw, oak shavings, and shavings of Georgia pine to uniform size, reserving the material which passed through a sieve of  $\frac{5}{16}$ -in. square mesh, but was retained by a similar sieve of  $\frac{1}{8}$ -in. mesh. The manure was then treated as follows:

Lot 1 was left untreated to serve as a control. Lot 2 was thoroughly mixed with 2 lbs. of pine shavings. Lot 3 was mixed with 2 lbs. of oak shavings

<sup>1</sup> Published with the permission of the Director of the Wisconsin Experiment Station.

<sup>1</sup> Bur. of Chem., Bull. 107, p. 23.

<sup>2</sup> Z. landw. Versuchs., 13, 795-802.

<sup>3</sup> Bur. of Chem., Bull. 107, p. 2.

<sup>4</sup> Z. physiol. Chem., 76, 426-32.

<sup>5</sup> This Journal, 5 (1913), 998.



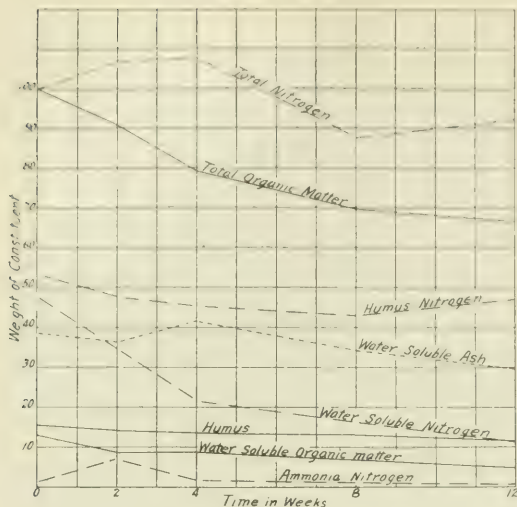


FIG. 1—MANURE ALONE

and Lot 4 was mixed with 2 lbs. of oat straw. At the beginning of the experiment on March 25th, and at two, four, eight, and twelve weeks thereafter the several lots of manure were thoroughly mixed and sampled for chemical analysis and bacterial counts.<sup>1</sup> By weighing the pails before and after sampling it was possible to determine the losses of organic matter and of nitrogen due to fermentation.

The chemical analyses were conducted as follows:

**DRY MATTER**—One hundred grams of sample were dried to constant weight at a temperature of about 98° C.

**TOTAL ASH**—The residue from the determination of dry matter was charred, extracted with hot water and the insoluble residue thoroughly ignited. Extract and residue were combined, evaporated and heated in the usual manner.

**TOTAL ORGANIC AND VOLATILE MATTER** was computed by deducting the per cent of total ash from the per cent of dry matter.

**TOTAL NITROGEN** was determined by the Gunning modification of the Kjeldahl method, employing 10 g. of the moist manure.

**WATER-SOLUBLE NITROGEN** was determined by the Gunning modification of the Kjeldahl method, employing 200 cc. of the extract prepared for the determination of total water-soluble matter as subsequently described.

**AMMONIA NITROGEN**—Five grams of magnesium oxide were added to 200 cc. of the extract employed for determining the total water-soluble matter, and distillation was conducted in the usual manner.

**TOTAL WATER-SOLUBLE MATTER**—One hundred grams of moist manure were shaken with one liter of distilled water in a motor-driven machine for five hours at room temperature. The extract was then rapidly filtered by suction through a thick layer of paper pulp in a Buchner funnel. After washing the residue with ten portions of distilled water of 75 cc. each the extract and washings were added and made to a volume of two liters. One hundred cc. of the final solution were evaporated and dried to constant weight at about 98° C.

**WATER-SOLUBLE ASH**—The dried residue from the determination of total water-soluble matter was carefully ignited in a platinum dish heated to dull redness.

<sup>1</sup> For the bacterial counts, which were made upon lactose agar plate cultures, the writer is indebted to Mr. E. E. Eldredge, formerly a member of the staff at this Experiment Station.

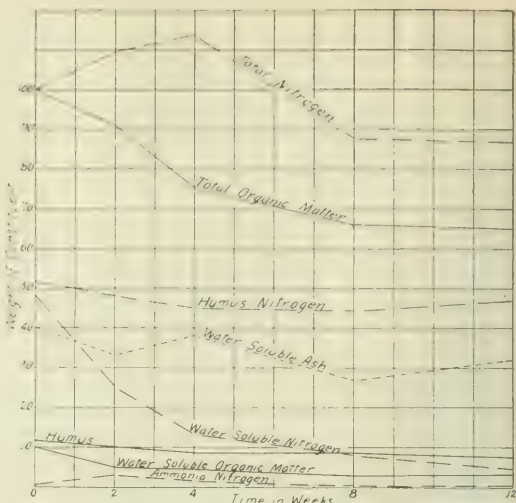


FIG. 2—MANURE + PINE SHAVINGS

**WATER-SOLUBLE ORGANIC AND VOLATILE MATTER** was computed by deducting the per cent of water-soluble ash from the per cent of total water-soluble matter.

**HUMUS**—Fifty grams of manure were drained by suction on a layer of asbestos in a Buchner funnel, washed with 1.0 per cent HCl until no more calcium was extracted and finally washed free from HCl by water. The moist residue was digested for 36 hours with 4.0 per cent solution of  $\text{NH}_4\text{OH}$ , employing 50 cc. of solution per gram of original dry matter of the manure. The ammoniacal extract was filtered and its humus content determined by evaporating and igniting in the usual manner.

**HUMUS NITROGEN**—An extract of the manure was prepared as in the determination of humus, but with the substitution of 4.0 per cent solution of NaOH for the  $\text{NH}_4\text{OH}$  solution. Nitrogen was determined by the Gunning modification of the Kjeldahl method, employing 100 cc. of the filtered extract.

**RESULTS**—The results of the analyses are presented in Table I, each value being the average derived from duplicate determinations. Attention may be called to the enormous number of bacteria in the straw-littered manure at the third analysis; at this stage it was possible only to estimate the number of organisms; only in this lot of manure was there evidence of the predominance of special types of bacteria. At the third examination an acid-producing organism was especially abundant while at the later stages, *streptothrix* formed one-fifth to one-third of the total colonies developed in cultures from the straw-littered manure.

In order to facilitate comparison of the extent of the various changes followed in the different lots of manure the percentages of the total organic matter, total ash, and total nitrogen which existed in various forms have been calculated from the data of Table I and are given in Table II.

It seems probable that the percentages of organic matter in water-soluble and humus forms here bear definite relations to the relative susceptibility of the manures to decomposition in the soil. Similarly, the soluble ash and the various forms of nitrogen may bear direct relations to the relative fertilizing values of the manures.

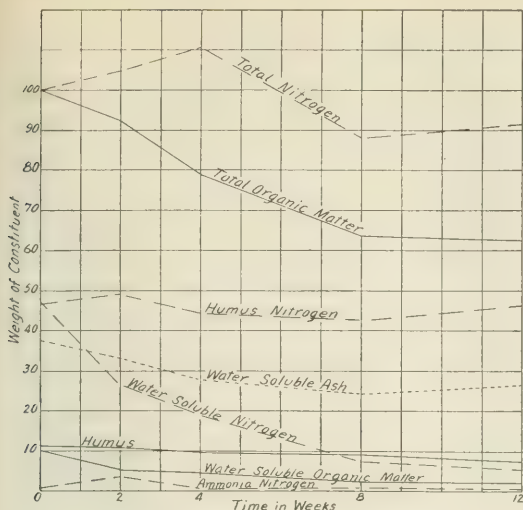


FIG. 3—MANURE + OAK SHAVINGS

The progressive losses of total organic matter in these manures during the four periods covered by the investigation are also presented in Table II. Each value is computed on the basis of the total organic matter present at the beginning of the respective period.

In a similar manner the gains or losses of nitrogen for each period of fermentation have been calculated as percentages of the total amounts of nitrogen present

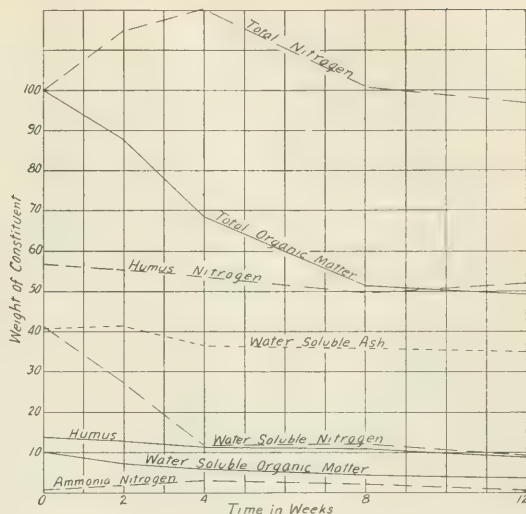


FIG. 4—MANURE + OAT STRAW

at the beginning of the respective periods. These data occupy the last column in Table II.

Assigning a value of 100 each to the total organic matter, total ash and total nitrogen of each manure at the beginning of this investigation the relative values of all the other data in Table II have been computed. The resulting values, which express the fluctuations in absolute amounts of the various constituents considered, have been plotted to form the

TABLE I COMPOSITION OF FERMENTING MANURES

COMPOSITION OF DRY MATTER—RESULTS IN PERCENTAGES OF DRY MATTER

LOT No.	ADDITION TO MANURE	TIME Weeks after starting	DRY MATTER Per cent	Total Organic and Volatile Matter	Total Ash	Total Solids soluble in H <sub>2</sub> O	Organic Matter soluble in H <sub>2</sub> O	Ash soluble in H <sub>2</sub> O	Total N	Soluble in H <sub>2</sub> O N	N as NH <sub>3</sub>	Humus N	Humus N	BACTERIA Millions per Gram of Dry Matter
1	None	0	20.37	88.24	11.76	15.98	11.44	4.54	1.69	0.81	0.020	13.68	0.90	660.0
		2	18.92	87.20	12.80	12.89	8.23	4.66	1.97	0.64	0.130	13.59	0.88	210.0
		4	17.12	85.59	14.41	13.79	9.77	6.02	2.24	0.46	0.036	14.74	0.94	25.0
		8	16.20	83.99	16.01	13.69	8.21	5.48	2.04	0.39	0.028	15.86	1.00	67.0
		12	15.72	83.36	16.64	10.94	6.00	4.94	2.22	0.27	0.020	14.73	1.13	4.1
2	Pine shavings	0	25.97	91.82	8.18	12.47	9.19	3.28	1.26	0.61	0.011	10.78	0.65	212.5
		2	24.12	91.11	8.99	8.01	5.02	2.99	1.50	0.35	0.045	10.26	0.66	250.0
		4	21.52	89.34	10.66	9.48	5.41	4.07	1.85	0.22	0.030	10.49	0.74	61.5
		8	21.00	88.07	11.93	7.11	3.90	3.21	1.57	0.15	0.012	11.68	0.80	57.0
		12	21.62	87.91	12.09	8.55	4.66	3.89	1.53	0.09	0.011	10.38	0.83	4.7
3	Oak shavings	0	26.00	91.31	8.69	12.46	9.20	3.26	1.26	0.59	0.011	10.27	0.59	272.5
		2	24.45	90.67	9.33	8.33	5.23	3.10	1.42	0.36	0.047	10.74	0.68	460.0
		4	21.58	89.24	10.76	8.21	5.22	2.99	1.72	0.29	0.008	11.11	0.69	112.5
		8	18.87	86.99	13.01	6.53	3.36	3.17	1.66	0.14	0.019	12.82	0.81	37.0
		12	18.85	86.80	13.20	6.39	2.87	3.52	1.76	0.10	0.011	10.48	0.90	3.7
4	Oat straw	0	25.25	89.03	10.97	13.56	9.07	4.49	1.36	0.56	0.010	12.23	0.77	530.0
		2	23.22	87.70	12.30	12.50	7.40	5.10	1.75	0.42	0.028	12.95	0.85	38.5
		4	19.52	84.77	15.23	12.91	7.37	5.54	2.28	0.23	0.037	14.00	1.01	10,000(a)
		8	16.65	80.76	19.24	12.66	6.77	5.89	2.42	0.29	0.052	17.15	1.19	30.0
		12	16.50	80.10	19.90	11.99	5.93	6.06	2.39	0.23	0.016	14.37	1.28	12.7

(a) See text.

TABLE II—ANALYSES OF DATA IN TABLE I

LOT No.	ADDITION TO MANURE	TIME Weeks after Starting	PERCENTAGES OF TOTALS PRESENT IN VARIOUS FORMS							PERCENTAGE CHANGES DURING FERMENTATION	
			ORGANIC MATTER		ASH		NITROGEN			Organic Matter	Nitrogen
			Soluble in H <sub>2</sub> O	As Humus	Soluble in H <sub>2</sub> O	As Humus	Soluble in H <sub>2</sub> O	As N	As Humus Nitrogen		
1	None	0	12.97	15.50	38.61	47.93	1.18	53.25			
		2	9.44	15.58	36.41	32.49	6.60	44.67		-9.1	+ 6.9
		4	11.41	17.22	41.78	20.31	1.61	41.96		-12.9	+ 0.9
		8	9.77	18.88	34.23	18.53	1.37	49.02		-12.2	-18.5
		12	7.20	17.67	29.69	12.12	0.90	50.90		-4.4	+ 5.1
2	Pine shavings	0	10.01	11.74	40.10	48.41	0.87	51.90			
		2	5.51	11.26	33.26	23.33	3.00	44.00		-8.9	+ 9.4
		4	6.06	11.74	38.18	11.90	1.62	39.73		-17.3	+ 4.0
		8	4.43	13.26	26.91	9.36	0.76	50.76		-12.5	-23.0
		12	5.30	11.81	32.18	5.67	0.72	54.25		-1.5	-3.9
3	Oak shavings	0	10.08	11.25	37.51	47.06	0.87	46.78			
		2	5.76	11.84	33.23	28.28	3.31	46.97		-7.6	+ 4.8
		4	5.85	12.45	27.79	17.14	0.47	40.00		-14.6	+ 5.6
		8	3.86	14.74	24.35	8.25	1.14	48.61		-19.4	-20.5
		12	3.31	12.07	26.67	5.91	0.63	50.97		-1.9	+ 3.8
4	Oat straw	0	10.18	13.74	40.93	41.40	0.74	56.76			
		2	8.44	14.77	41.46	23.89	1.60	48.29		-12.4	+14.8
		4	8.69	16.52	36.38	9.87	2.50	49.26		-22.1	+ 4.9
		8	8.38	21.24	30.61	12.02	2.15	49.26		-24.5	-16.0
		12	7.40	17.94	30.45	9.50	0.67	53.72		-4.0	-4.2



graphs of Fig. 1 to 4 inclusive. These graphs indicate, therefore, the relative changes in the actual amount of each constituent in the different manures as fermentation progressed.

#### SUMMARY

The results expressed in the accompanying tables and figures may be summarized as follows:

1—The loss of total organic matter during twelve weeks of fermentation ranged from 33 to 51 per cent. It was most rapid and greatest in the straw-littered manure, where bacteria were most numerous.

2—The water-soluble organic matter ranged from 10 to 13 per cent of the total organic matter in the fresh manures. It decreased continuously during twelve weeks of fermentation with the loss of from 60 to 80 per cent of the original amount. In all cases the loss of this constituent was most rapid during the first two weeks.

3—Humus ranged from 11.3 to 15.5 per cent of the total organic matter in the fresh manures. This constituent decreased continuously, but more gradually than the water-soluble organic matter. During twelve weeks it decreased from 26 to 35 per cent. The losses from the littered manures were nearly equal and about one-third greater than from the control manure.

4—The water-soluble ash ranged from 37.5 to 40.9 per cent of the total ash in the fresh manures. This constituent decreased gradually in all of the manures during twelve weeks of fermentation. The decrease ranged from 14 to 30 per cent of the amount originally soluble, being less in the straw-littered manure than in the other lots.

5—The total nitrogen increased in all of the manures until the fourth week of fermentation, the grains ranging from 8 per cent of the original amount in the control manure to 20 per cent in the straw-littered manure. More or less rapid loss of nitrogen occurred from the fourth to the eighth week of fermentation. After twelve weeks a net loss of nitrogen obtained in all of the manures. This net loss ranged from 3 to 13 per cent of the original amount of nitrogen, being less in the straw-littered manure than in the other manures.

6—The water-soluble nitrogen decreased rapidly in all of the manures during the first four weeks. It suffered greater loss than any other constituent investigated, its curve being quite similar to that of the total organic matter. This constituent formed from 41.4 to 48.4 per cent of the total nitrogen at the beginning of the investigation. Losses of the water-soluble nitrogen ranged from 77 to 90 per cent of the original amounts and were somewhat greater in the shavings-littered manures than in the other lots.

7—Humus nitrogen formed from 46.8 to 56.8 per cent of the total nitrogen in the fresh manures. Losses of this constituent ranged from 2 to 10 per cent of the original amounts, being greatest in the control manure. The fluctuation was similar in all of the manures, the humus nitrogen decreasing 10 to 20 per cent during the

first four to eight weeks of fermentation and then gradually increasing.

8—Ammoniacal nitrogen formed only 0.7 to 1.2 per cent of the total nitrogen at the beginning of the experiment. It rose to a maximum value in the control and shavings-littered manures during the first two weeks of fermentation, thereafter rapidly decreasing to about the original value after four weeks. In the straw-littered manure, on the other hand, the maximum production of ammonia was attained and passed gradually at about the fourth week. Ammoniacal nitrogen reached its greatest value in the control manure. In all cases, however, its values, ranging from 0.5 to 6.6 per cent of the total nitrogen, were too low to allow the placing of great importance on its fluctuations.

#### CONCLUSION

Undoubtedly the gain of nitrogen during the early stages of fermentation is the most important change indicated by the data of this paper. Whether so extensive gains are common is uncertain, but that gains occur has been definitely proved by further work which appears elsewhere.<sup>1</sup> In this work the writer showed that gains of nitrogen occurred in manure treated with wheat straw litter and demonstrated the presence of nitrogen-fixing organisms in the manures. Data from field plots were also presented which showed greater gains from a fermented mixture of manure and straw than from a similar application of fresh manure. For purposes of comparison the latter data are presented in Table III, together with data from shavings-littered manures. The crops referred to were grown on plots of  $\frac{1}{20}$  acre in size arranged in three sections for a three-course rotation of corn, barley and clover. Manuring preceded the entrance of the corn crop into the rotation. The writer is indebted to Prof. E. B. Hart of this department for the privilege of using this data. The control yield is the average from two unfertilized plots. Data are averaged from six crops of corn, seven crops of barley and four crops of clover.

TABLE III—COMPARATIVE YIELDS OF CROPS FROM FRESH AND FERMENTED MANURES WITH LITTERS

Crop	UNFERTILIZED CONTROL	FRESH MANURE with		STALL MANURE with	
		Straw	Shavings	Straw	Shavings
Corn grain	100	106	106	111	100
stover	100	106	109	114	104
Barley-grain	100	100	100	100	100
straw	100	99	100	98	97
Clover hay	100	101	100	96	92

A survey of the data in Table III shows that the effects of the manure are exhausted upon the first crop of the rotation. In the year of application the fresh manure gave the same results whether littered with straw or with shavings. It is only with the stall manure that different effects appear from the use of the different litters. The stall manure was prepared from amounts of the fresh manure equivalent to the direct applications of the latter, but had been given opportunity to ferment to a limited extent while stored in covered boxes during the winter. The data show a decided gain in efficiency of the

<sup>1</sup> W. E. Tottingham, "Increase of Nitrogen in Fermenting Manures," *J. Biol. Chem.*, **24** (1916), 221-225.

straw-littered manure by this process, while the shavings-littered manure shows an actual decrease of efficiency, as compared with the fresh manures. For the values in rounded figures as given here the straw-littered, fermented manure produced about 10 per cent greater yield of both corn grain and stover than did the corresponding shavings-littered manure. This difference is in harmony with the greater gain and

smaller net loss of total nitrogen in the straw-littered manure than in the shavings-littered manures, as shown by the analytical data and graphs of this paper. The results here presented seem to have opened for further investigation questions regarding the comparative value of different litters and the benefits to be derived from controlled fermentation of manure.

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## LABORATORY AND PLANT

### FLOW OF HEAT FROM SOLIDS TO AIR

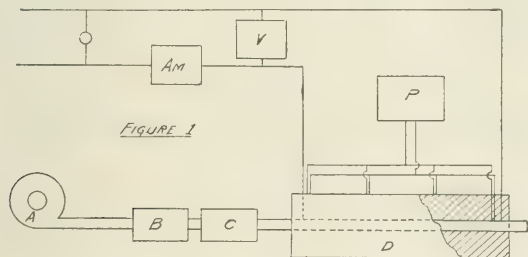
By E. E. SNYDER, C. S. ROBINSON AND W. K. LEWIS

Received May 2, 1916

J. W. Richards<sup>1</sup> makes the statement that the coefficient of heat transfer from solids to air is proportional to the square root of the gas velocity, while Irving Langmuir<sup>2</sup> states that it is proportional to the cube root of the velocity. Since these statements conflict, and since the experimental data on which they are based are not given in either case, the following investigation was undertaken:

A known weight of air was blown at constant velocity through an electrically heated tube. The temperature of the tube was measured, and the heat picked up by the gas was calculated by subtracting from the total electrical input the heat necessary to maintain the same temperature in the tube when no gas was passing through it.

The apparatus is shown diagrammatically in Fig. 1. A blower, *A*, delivers air through a  $\text{CaCl}_2$  drying



tower, *B*, to an orifice, *C*, where the gas is measured. From *C* the air passes to the furnace *D*.

The furnace consists of a brass pipe,  $\frac{1}{2}$  in. inside diameter, 27 in. long, fitted with  $\frac{1}{2}$  in.  $\times$   $1\frac{1}{2}$  in. reducing elbows into which short pipes for air connections are screwed. Four Iron-Ideal thermal-couples are attached symmetrically along the pipe, which is covered with insulating asbestos paper, and wound with No. 19 resistance wire, the winding being closer together near the ends, to even the temperature through the pipe. It is covered with magnesia insulation to a diameter of 5 in. and the whole device enclosed in a galvanized iron can, with suitable openings for lead and thermal-couple wires. The whole furnace was immersed in a water bath of measured temperature.

<sup>1</sup> J. W. Richards, "Metallurgical Calculations," McGraw Publishing Co., New York, 1906, p. 179.

<sup>2</sup> Irving Langmuir, *Phys. Rev.*, **34** (1912), 401.

Electrical measurements were made with carefully standardized voltmeter and ammeter, and the temperatures along the pipes were measured with the thermal-couples and a Leeds & Northrup Potentiometer Indicator, carefully standardized against metals of known purity. Each run, either blank or constant velocity, was continued until thermal equilibrium was reached. The data obtained are given in Table I, where the column marked *Head* is the differential pressure in inches of water or mercury, as indicated at the orifice, the diameter of which is given in the column marked *Orifice*.

The volts and amperes are those read, and are corrected in Table II.  $T_2$ ,  $T_3$ ,  $T_4$ , and  $T_5$  are the temperatures measured by the thermal-couples, and  $T_1$  and  $T_6$  are the temperatures of the water bath at opposite ends of the furnace.

The average temperature of the furnace for a given run was found by plotting the temperature gradient against the length of the furnace and determining the average temperature difference by means of a planimeter. For each series of runs at constant velocity the power input was plotted against the average temperature difference between pipe and air. By subtracting the power input for the blank runs the net energy taken up by the gas was obtained. The values of *K* were then calculated and tabulated in Table III, which, however, includes only runs at a velocity of 0.01 lb. per second. The values of *K* at other velocities were calculated in an exactly similar way. The values of *K* for each velocity were plotted against the temperature of the furnace, but it was found that all these curves were practically horizontal straight lines, *i. e.*, the value of *K* was independent of the temperature of the furnace. The values of *K* were then plotted against velocity; this plot is shown in Fig. 2. Points were put on this plot for furnace temperatures of 150, 250, and 350° C. and these points as indicated were practically coincident except for a velocity of 0.005. The discrepancy at this point is probably experimental. We may therefore conclude that the value of *K* up to the temperature employed is independent of the temperature and a function of the velocity alone. The equation of this curve is

$$K = \frac{39.6V}{V + 3.67}$$
 wherein *K* is the coefficient of heat transfer from solid to air in B. t. u. per sq. ft. of heating surface per °F. difference in temperature per hour, and *V* is the pounds of air per second flowing



TABLE I

Run	Head Inches	Orifice Diam. Inches	ACTUAL READING		TEMPERATURES AS READ(b)					
			Volts	Amperes	T <sub>1</sub>	T <sub>2</sub>	T <sub>3</sub>	T <sub>4</sub>	T <sub>5</sub>	T <sub>6</sub>
1	0	0	68.8	5.32	14	327	675	673	338	11
2	0	0.083	68	5.0	7	348	656	586	275	7
3	0	0	72	5.5	10	345	711	711	339	10
4	0.18	3/32	73	5.4	6	378	680	591	282	6
5	0.08	3/32	72	5.4	6	376	693	616	292	6
6	0	0	73	5.5	11	349	719	718	367	12
7	0.035	3/32	73	5.4	7	378	708	650	309	7
8	0.035	3/32	63	4.75	8	311	586	535	250	7
9	0	0	63	4.75	14	293	596	592	297	14
10	0.085	3/32	63	4.8	7	315	576	507	239	7
11	0.18	3/32	62	4.7	6	297	530	455	216	6
12	0	0	57	4.38	10	257	528	522	262	10
13	0.180	3/32	57	4.38	7	262	465	401	192	7
14	0	0	56	4.38	7	218	322	257	119	7
15	0	0	49	3.75	15	208	420	416	207	15
16	1.18	1/4	48	3.75	6	161	247	190	102	7
17	0	0	49	3.75	12	205	412	410	205	12
18	0.3	3/8	47	3.75	7	160	238	187	100	7
19	0	0	60	4.75	13	284	563	564	286	13
20	0.6	3/8	61	4.75	12	234	327	251	137	12
21	0.6	3/8	72	5.5	8	301	431	345	179	8
22	0.6	3/8	83	6.38	8	376	546	438	231	8
23	0.6	3/8	91.5	6.9	11	444	644	517	276	11
24	0.3	3/8	88	6.95	11	480	718	599	316	11
25	0.75	3/8	60	5.0	10	139	146	112	92	10
26	0.75	3/8	53	4.42	19	122	127	98	82	19
27	0.75	3/8	68	5.5	22	177	188	142	120	22
28	0.75	3/8	96	7.5	15	306	347	255	201	15
29	0.83	1/2	59	5.0	13	117	120	91	90	13
30	0.83	1/2	70	5.75	12	148	151	116	114	12
31	0.83	1/2	99	7.9	15	260	270	214	196	15
32	0.83	1/2	86.5	6.95	12	212	216	160	159	12
33	0.15	1/2	85	6.75	13	279	317	242	188	13
34	0.15	1/2	57.5	4.75	13	144	159	118	102	13
35	0.15	1/2	103	7.95	13	368	424	309	253	13
36	0	0	21	1.88	14	55	104	55	14	14
37	0	0	35.5	2.83	15	124	236	236	122	15

(a) Runs 1 to 24 in inches of Liquid; Runs 25 to 37 in inches of Mercury.  
 (b) T<sub>1</sub> to T<sub>6</sub> as read by thermal couples; T<sub>1</sub> and T<sub>6</sub> temperatures of water bath at opposite ends of the furnace.

through each square foot of section, the section being taken at right angles to both heating surface and direction of flow of the air. The expression is apparently independent of temperature up to 750° F.

In the derivation of this formula we have expressed velocities as lbs. of air per sq. ft. of section of path per second. Our reason is that otherwise velocity past various points in the path of flow is a variable

TABLE II

Group	Run	Area Sq. in.	Av. In.	Ht. Av. Temp. ° C.	CORRECTED—		
					Volts	Amperes	WATTS
A <sub>1</sub>	33	18.20	2.43	243	83.3	6.65	554
	34	8.72	1.16	116	55.5	4.60	255
	35	24.32	3.24	324	101.3	7.85	795
A <sub>2</sub>	2	37.48	4.99	499	66.0	4.87	321
	10	32.80	4.37	437	61.5	4.65	286
	5	39.75	5.30	530	70.0	5.28	370
B <sub>1</sub>	29	6.64	8.85	885	57.3	4.80	275
	30	8.71	1.16	116	68.0	5.65	385
	31	16.07	2.14	214	97.3	7.75	755
B <sub>2</sub>	32	12.67	1.69	169	84.7	6.85	580
	21	17.65	2.35	235	59.0	4.60	271
	22	24.00	3.20	320	70.0	5.40	378
C <sub>1</sub>	22	29.92	3.99	399	81.2	6.28	510
	23	36.05	4.81	481	89.3	6.80	608
	25	8.33	1.11	111	58.0	4.87	282
C <sub>2</sub>	26	6.55	8.73	873	51.0	4.30	218
	27	10.05	1.34	134	66.0	5.40	356
	28	19.38	2.58	258	94.3	7.42	700
D <sub>1</sub>	18	12.96	1.73	173	45.0	3.55	160
	24	41.19	5.49	549	93.3	6.85	639
	14	17.65	2.35	235	53.5	4.23	227
D <sub>2</sub>	16	13.50	1.80	180	46.0	3.55	163
	4	38.79	5.17	517	71.0	5.28	375
	11	29.84	3.98	398	60.0	4.55	273
Blanks	13	26.07	3.48	348	55.0	4.23	233
	1	40.36	5.38	538	67.0	5.10	342
	3	43.03	5.74	574	70.0	5.40	378
	6	43.59	5.81	581	71.0	5.40	383
	9	35.45	4.73	473	61.0	4.60	281
	12	31.58	4.21	421	65.0	4.23	233
	15	24.78	3.31	331	47.5	3.54	166
	17	24.46	3.26	326	47.0	3.55	167
	19	33.95	4.53	453	58.0	4.60	267
	36	5.41	0.72	72	18.9	1.65	31
	37	14.37	1.91	191	33.5	2.63	88

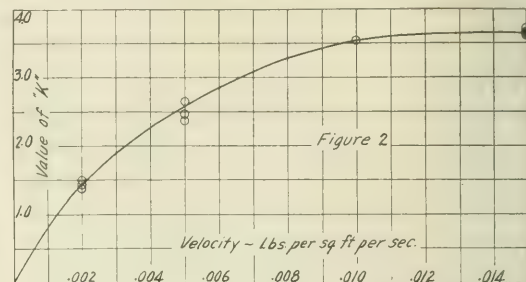
quantity owing to the expansion of the gas in heating. On the assumption that the resistance to flow of heat from a solid to air is due to a surface film of gas around the solid and that the increase in heat conductivity with increasing velocity is caused by the ripping off

TABLE III

Av. Temp of Furnace	Input Net Watts	Temp. Exit Gas	Average Temp Difference	Value of "K"
111	253	80.7	53.3	3.84
161	380	108.7	87.5	3.52
211	523	140.0	119.0	3.56
261	662	171.0	151.0	3.54
311	804	202.0	183.0	3.56
361	925	239.0	218.0	3.44

of this film, the shearing effect upon this film should be determined by the mass of gas passing the heating surface in unit time rather than by its linear velocity, and the use of the above unit of velocity is rational. The constancy of the results of our calculations by this method are, however, its best justification.

We believe that the above equation represents the best figure which is at present available to employ



for the value of  $K$  from solids to air and feel that it is decidedly preferable to the figure of Richards, the one hitherto most frequently employed, because Richards' formula indicates indefinitely high values at high velocities, whereas our formula indicates, as the experimental results show, that at high velocities the value of  $K$  reaches a limiting value beyond which it cannot rise.

RESEARCH LABORATORY OF APPLIED CHEMISTRY  
 MASSACHUSETTS INSTITUTE OF TECHNOLOGY

## LABORATORY PROBLEMS IN INDUSTRIAL CHEMISTRY

By H. K. BENSON

Received March 23, 1916

The field of industrial chemistry is so large that the planning of courses in this subject involves many factors. It has been the experience of the writer that instructors in industrial chemistry formulate their courses largely from the standpoint of their previous personal experience. It is believed that an exchange of views detailing the practice followed by various instructors would prove of great value to individuals as well as be an aid in standardizing the subject matter and in working towards some degree of uniformity.

With this end in view a series of problems are here outlined showing the character of training furnished by such problems. Such a course is not to be regarded as ideal but rather is proposed as an aid to a discussion that might be of value to those who are feeling their way along paths that are not as yet well defined.

The problems were assigned to chemistry students of Junior standing. They had completed courses in general inorganic chemistry, qualitative analysis, quantitative analysis, and were taking organic chemistry coincident with industrial chemistry. The general plan followed was the statement of the problem by

the instructor after which the student was expected to devise his own methods for solution. The instructor answered specific questions but refused to suggest an outline or general plan of procedure, requiring the student to work out his own methods from the literature. A full discussion and exchange of methods among the students in the laboratory was, however, encouraged. Experience has shown that students attack such problems in a wide variety of ways and frequently with varying results. These are criticized and amended in class discussions at the end of each semester.

**PROBLEM I**—Given a sample of crude California petroleum, obtain the yield of kerosene oil which complies with the requirements of the state law.

*Requirements:* An examination of the state law, reference to the literature of petroleum refining and familiarity of the student with the varying effects of the rate of distillation, the design of distilling apparatus, the effects of acid and alkali treatment, the removal of water from oily distillates, and the various forms of oil testing apparatus.

**PROBLEM II**—Given a sample of coal-gas tar at a local cost of 6 cents per gallon, determine the yield of creosote complying with the specifications of the city of Seattle and the cost per gallon, f. o. b. plant, of the creosote.

*Requirements:* The specifications of the city for creosote, the distillation of the coal tar, computation of fractions and the derivation of the process of distillation, the analysis of the creosote by the official method, a study of the uses and values of the by-products such as light oil and pitch, the selection of a unit charge for commercial operation, a field study of a Barrett plant, and itemization of costs of production.

**PROBLEM III**—Prepare a bituminous enamel containing 20–35 per cent carbonaceous matter insoluble and 55–65 per cent ash, with physical properties specified by the United States War Department.

*Requirements:* A study of the commercial pitches, methods of analysis of bituminous materials and selection of a paint filler.

**PROBLEM IV**—Determine which one of two commercial boiler compounds shall be selected to prevent scale formation in the University Power Station.

*Requirements:* Analysis of scale, of feed water and of the boiler compounds; a study of the causes and prevention of scale formation and the application of the data to the given case. A description of the problem has already been published in *THIS JOURNAL*, 8 (1916), 435.

**PROBLEM V**—Determine the effect of blending Portland cement with Washington tufa.

*Requirements:* Reference to the literature of blended cement products; testing of cement by standard methods; and a study of cement specifications.

**PROBLEM VI**—Determine the proportion of cement, sand and gravel in concrete.

*Requirements:* Method of mechanical analysis; grading of aggregate; specific gravity determinations; chemical analysis of cement; and computations.

**PROBLEM VII**—Determine the effect of adding lime and sand to a plastic red burning clay.

*Requirements:* Methods of clay testing; study of range of vitrification; grinding and mixing operations.

**PROBLEM VIII**—Classify the oil obtained from samples of Philippine nuts.

*Requirements:* Extraction of oil from nuts; comparison with the known constants of fatty oils; and the relation of constants to uses of the oil.

**PROBLEM IX**—Determine the yield of rosin in western yellow pine.

*Requirements:* Methods of sampling; extraction by various solvents; and efficiency of commercial solvents.

**PROBLEM X**—Determine the efficiency of the recovery of ammonia in the extraction of rosin from Douglas fir.

*Requirements:* Separation of rosin and humus; Kjeldahl determinations; removal of ammonia from wood; and computations.

**PROBLEM XI**—Devise a method for the extraction of cedar oil from the destructive distillation of Port Orford cedar and determine the nature and probable uses of the residues of the distillate.

*Requirements:* Methods of steam distillation and of vacuum distillation; study of literature relating to Port Orford cedar oil; determination of constants of oil; study of wood tars and their uses.

**PROBLEM XII**—Prepare a rosin paint drier soluble in raw linseed oil.

*Requirements:* Preparation of metallic resins; methods of paint testing; and commercial requirements of driers.

During the present year similar problems dealing with the study of cactus, wood humus, potash salts, recovery of iodine, cost of manufacture of hypochlorites, etc., have been undertaken. It is apparent that the problems are capable of great diversification, which adds to the interest. The chief objects in view are to throw the student upon his own resources, make him acquainted with chemical literature and force him to make use of the tools of knowledge already in his possession.

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## AN UNUSUAL EXPLOSION IN CONNECTION WITH POTASSIUM CHLORATE

By FLOYD E. ROWLAND

Received May 3, 1916

There was nothing unusual about the explosion itself, but the manner in which it occurred is well worth mentioning and bringing to the attention of all who have occasion to use pestles which have wooden handles.

Everyone knows that disaster is sure to follow when potassium chlorate and sulfur are ground together; but to have a perfectly clean mortar and pestle suddenly explode with great violence, when one is grinding an inert substance like pumice stone, makes one pause and wonder why.

A pestle and an 8-inch mortar were thoroughly cleaned and about fifteen pounds of potassium chlorate were ground with no disastrous results. The mortar



and pestle were washed and dried. A few days later some crushed pumice stone was required in the laboratory and the same mortar and pestle were used. A loud explosion resulted. The mortar and pestle were broken into many pieces and thrown violently about the room. One piece passed through a window scarcely chattering the glass. The room was filled with sulfur dioxide and fine particles of sulfur were scattered over the floor and table. An examination of the pieces of the mortar showed no traces of sulfur but quite large quantities of sulfur were found adhering to the fragments of the pestle. The wooden handle of this pestle had been sealed into the ball part with sulfur. Evidently a small amount of the potassium chlorate worked into the crevice with the sulfur and caused it to explode when given a sudden jar.



FRAGMENTS OF BROKEN MORTAR AND PESTLE

An examination of other pestles of the same type showed them to contain as much as 10 to 20 g. of sulfur.

This explosion might have been more disastrous had not the mortar been used at this time for grinding the pumice stone, as, in a few days it would have been used again to pulverize more potassium chlorate, and with the excess chlorate the explosion would have been more violent.

It certainly is not generally known that the handles of these pestles are sealed in with sulfur, for if it were they would never be permitted in the laboratory.

The pestle was of German make and whether or not they still employ sulfur for this purpose is difficult to say. If any companies in this country are using sulfur for this purpose they should substitute in its place some inert cement. Laboratories should bar the use of this type of pestle until the sulfur has been replaced by some safe material.

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#### A RAPID METHOD FOR COMPARING THE DECOLORIZING EFFICIENCY OF CHARCOALS

BY LEONARD WICKENDEN AND JOHN W. HANSLER

Received February 18, 1916

The various methods in general use at the present time for comparing the decolorizing values of charcoals, possess features which render them, for one reason or another, unsatisfactory. In most oil laboratories, direct tests are made with the oil which is to be treated. Such tests are satisfactory as far

as they go, but filtration is slow and small differences in the decolorizing powers of charcoals are difficult to detect, even with the aid of a colorimeter. When the operation is repeated on a manufacturing scale, these small differences become magnified and may mean a considerable difference in the final product. The same argument applies, though perhaps to a lesser degree, to the testing of charcoal on argols solution and on various pharmaceutical products.

The use of an alcoholic solution of caramel, as suggested by Laube, is open to the objection that the solvent is volatile and the solution cannot, therefore, be used at high temperatures. If an aqueous, instead of an alcoholic, solution of caramel be used, trouble is experienced in obtaining clear filtrates, and, moreover, the solution will not keep.

An aqueous solution of an aniline dye gives unreliable results owing to the fact that many charcoals on the market contain appreciable amounts of soluble ash, and the alkalinity of this ash produces color changes which vitiate the results obtained.

A method has been devised in these laboratories, which is very rapid and which enables charcoals to be classified with great ease and accuracy according to their decolorizing efficiency. A solution of Aniline Red, Soudan III (oil soluble), in kerosene is used. The strength of the solution is largely a matter of choice, but we have obtained the most satisfactory results with a 0.025 per cent solution (0.25 g. per liter). One hundred cubic centimeters of this solution are measured into a 150 cc. beaker, 5 g. of the charcoal are added and the beaker placed on a boiling water bath in such a manner that the beaker is entirely enveloped in steam but does not dip into the water. The charcoal is kept in suspension by frequent stirring and at the end of ten minutes the beaker is removed from the water bath and the mixture filtered. The kerosene solution filters very rapidly and comes through clear and bright. Its color is compared with a scale prepared in the following manner:

One hundred cubic centimeters of the kerosene solution of Soudan III are treated with 1 g. of a charcoal of average quality. The solution thus obtained is given the value 10. A second solution, obtained by treatment with 2 g. charcoal, is given the value 20, a third, obtained with 3 g. charcoal is numbered 30, and so on up to 100.

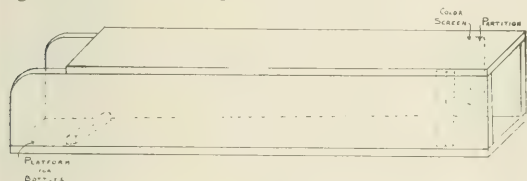
The scale thus obtained is, of course, of a purely arbitrary nature, but it has, none the less, a real meaning. Thus, if, by treating the standard solution with 5 g. of charcoal according to the method above described, a solution is obtained of the same depth of color as that which has been given the value 70, it means that 5 g. of the charcoal under examination will do the same work as 7 g. of the average charcoal, and thus possesses a 40 per cent greater efficiency.

By using a solution of the strength indicated, the difference in color between the solutions forming the scale is sufficiently marked for comparisons to be made without the aid of a colorimeter. In order, however, to make our comparisons easier and more exact, we

have devised a simple form of colorimeter whose effect is to increase the contrast between one color on the scale and that next above or below it.

The colorimeter consists of a wooden box, 18 in. long, as shown in the sketch, painted black on the inside. Set back 1 in. from the front is a partition in the center of which is a hole,  $1\frac{1}{2}$  in. in diameter. Immediately behind this is placed a color screen, whose effect is to increase the contrast between the colors of the solutions being compared. This may consist of a glass cell filled with a very dilute aqueous solution of aniline blue (we use Indigo-disulfonic acid, No. 692) or of a piece of blue glass. If the latter is used, care must be taken to choose the right tint, as some deep purple-blue glasses are useless for the purpose.

At the further end of the colorimeter is a platform on which are placed the solutions under examination. As containers, we use square glass jars with screw tops<sup>1</sup> of 2 oz. capacity, and the platform is made sufficiently wide to accommodate three of these jars. The solution under examination is placed in the middle and a standard solution is placed on either side—the one of a slightly darker shade, the other of a slightly lighter. With a little practice, it is easy to give a value



to the tested solution with considerable accuracy. Thus, if a solution is found to be between 50 and 60, it is easy to determine whether the value should be 52, 54, 56 or 58.

As far as oils are concerned, the test with the kerosene solution of Soudan III appears to be absolute. We have compared a very large number of charcoals from various sources, both of vegetable and animal origin, and in every case we have found that charcoals which give equally high results with the kerosene solution show equally high efficiencies as decolorizers for cottonseed, coconut and palm kernel oils. As regards sugar solutions, since the sugar chemist has other things to consider besides the removal of color, he will probably not be able to substitute the kerosene test for his present tests with molasses. The method should, however, be of great service to him in enabling him to eliminate charcoals which are not worth a more elaborate examination.

We find that animal charcoals, when used for decolorizing some aqueous solutions, show a higher efficiency than would be expected from the results obtained with the kerosene solution of Soudan III (see Table I—Argols Solution). Also, there are many charcoals on the market which give eminently satisfactory results with oils and other liquids, but are worthless for glycerine. In testing charcoals, therefore, which are to be used for either of these purposes, these facts must be taken into consideration.

We have kept a solution of Aniline Red, Soudan III, standing in our laboratory for several weeks and no perceptible fading has occurred. It is well, however, to reserve a portion of the charcoal used for mak-

TABLE I DYE TEST VALUES OF CHARCOAL COMPARED WITH COLOR REMOVAL TESTS BY LOVIBOND COLORIMETER

LIQUIDS TESTED	No.	CHARCOAL Origin	USED %	TEST VALUE	
				Soudan III Solution	Per cent color Removed from Oil (Lovibond)
Cottonseed Oil...	1	Animal	2.0	8	3.0
	2	Animal	2.0	10	5.7
	3	Vegetable	2.0	28	12.3
	4	Vegetable	2.0	38	19.4
	5	Vegetable	2.0	48	27.2
	6	Vegetable	2.0	50	27.3
	7	Vegetable	2.0	75	33.9
	8	Vegetable	2.0	75	34.0
	9	Animal	2.0	80	34.4
	10	Vegetable	2.0	85	35.0
Coconut Oil...	1	Animal	0.5	10	47.0
	2	Vegetable	0.5	48	65.6
	3	Vegetable	0.5	50	65.6
	4	Vegetable	0.5	55	66.8
	5	Vegetable	0.5	72	71.2
	6	Animal	0.5	80	76.1
	7	Vegetable	0.5	85	78.5
Palm Kernel Oil.	1	Animal	0.5	10	26.2
	2	Vegetable	0.5	30	36.3
	3	Vegetable	0.5	50	41.3
	4	Vegetable	0.5	72	46.3
	5	Animal	0.5	80	46.3
Argols Solution.. (saturated)	1	Animal	0.8(a)	8	45.0
	2	Vegetable	0.8	15	25.0
	3	Vegetable	0.8	30	46.0
	4	Vegetable	0.8	50	87.0
	5	Vegetable	0.8	75	90.0
	6	Animal	0.8	80	93.0

(a) 0.8 g. charcoal per 100 cc.

ing the scale of colors and to make a test every few weeks in order to ascertain if any color change has taken place.

NOTE—Since the above article was written we have ascertained that it is no longer possible to obtain Aniline Red, Soudan III. We have substituted for it Oil Red R N, manufactured by the Schoellkopf, Hartford & Hanna Co., Buffalo, N. Y. We use a solution of 1 gram of the Oil Red R N per liter and find it to give satisfactory results.

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## A NEW COLORIMETER

By C. FRANK SAMMET

Received March 14, 1916

The fact that it is rarely possible exactly to match the color of one liquid with another colored liquid or with colored glass often leads to considerable error in determinations where colorimetric methods are used. These difficulties of color matching may be due to a number of causes, the most important of which are the differences in luminosity, refractive index, turbidity and color composition of the materials to be matched.

The colorimetric determination of ammonia by the Nessler procedure or of phosphoric acid in soil solution by comparison with a standard solution of phosphomolybdate, or of either by comparison with standard colored glasses, are examples which well illustrate the differences existing in the usual methods of colorimetric matching.

Similar differences which are often very striking are also observed in the determination of the color of oils. With pure oil of turpentine, which is sold on the primary markets exclusively on the basis of its color, the color match is a matter of much commercial importance. The arbitrarily fixed grades have given

<sup>1</sup> Eimer and Amend, Catalogue 4142.

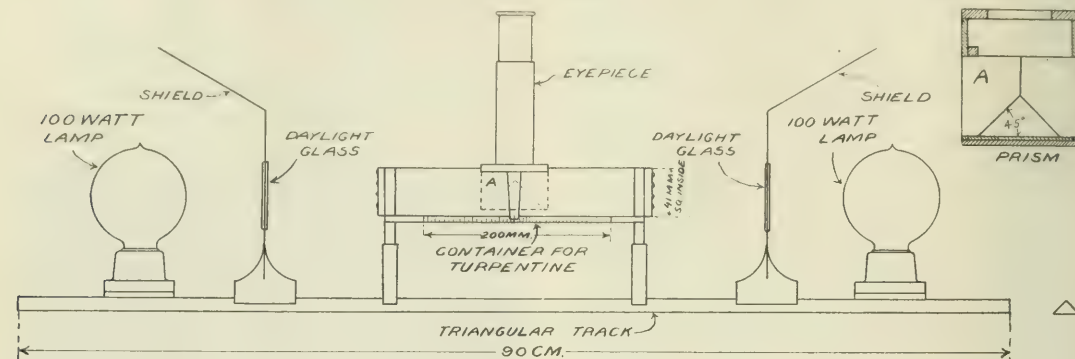


rise to many disputes because of the lack of proper methods by which to match or reproduce them.

For ordinary purposes it has been found satisfactory to use two polished bottom colorimeter tubes graduated in millimeters. These are viewed over a white background (a block of magnesium carbonate preferred) placed in a good light. The turpentine to be standardized is poured into one tube to a depth of 25 mm. and the tube covered with a No. 2 yellow glass of the Lovibond scale. A No. 1 yellow glass is

mounted and may be placed in any position between the ends of the cell and the light to secure any desired intensity. The cell is filled with a dark colored turpentine and the lights adjusted so that the fields appear evenly illuminated in the eye piece when the same is exactly half way between the two ends.

The equal illumination of the fields can be effected most easily and accurately with a dark-colored turpentine. A slight movement of the eye-piece to either side of the zero, on the scale, is readily seen with a



placed over the top of the second tube which is filled with a portion of the same turpentine to a depth where the colors of the two tubes match when viewed through the Lovibond glasses. The difference in depth between the turpentine in the tubes is the depth, in millimeters of turpentine, required to match a No. 1 yellow glass.

Several other types of colorimeters were tested but none of these proved as convenient or satisfactory as this method of matching in tubes. The method, however, has its defects in that the fields are not adjacent, the attempt at close matching of color by adjusting the height of the turpentine in the tubes is cumbersome and inconvenient, and the attention of the observer is diverted, especially at the moment when the greatest attention is required in the matching.

The colorimeter herein proposed is much easier to manipulate, eliminates the above mentioned objections and permits accurate values to be obtained.

A long, narrow, metal cell with glass ends is fitted with an eye-piece which may be easily moved along the cell and its distance from the middle read off on a millimeter scale.

At the end of the eye-piece, and immersed in the turpentine, are suspended two prisms cut at 45° angles. These prisms are encased on the bottom and sides with glass, leaving the ends and top uncovered. This is for the purpose of preventing the liquid from coming in contact with the reflecting faces of the prisms and thereby preventing the reflection into the eye-piece. Shellac is the cementing material used.

The light coming through the respective ends of the cell is reflected by the faces of the prisms into adjacent fields in the eye-piece. The illumination at each end of the cell is produced by a 100-watt, round, frosted bulb (Mazda), the light from which is intercepted by a disc of daylight glass,<sup>1</sup> which is properly

change of the position of the lights. This position of the lights when once determined may be fixed for all subsequent matching, provided the illuminating power of the lights does not change unequally. It is advisable for this reason to check the illumination at least daily.

A No. 1 yellow glass of the Lovibond scale is then placed at one end of the cell and a No. 2 yellow glass

TABLE I—COMPARATIVE READINGS (TWO OBSERVERS)

Sample No.	WITH MACHINE—OBSERVER		Mm.	—IN THE TUBES—OBSERVER	
	A	B		A	B
1	162	167	155	Light	Light
	169	167	157	Light, close	Light, close
	173	168	168	Match	Match
	166	162	175	Dark	Dark
	162	164	158	Light	Light
	162	162	162	Light, match	Light, match
Average	166.4	165.6	167	Match	Match
2	84	83	95	Dark	Dark
	84	79	81	Light	Light
	84	80	85	Light, close	Light, close
	85	81	86	Dark, match	Dark, match
	80	84	79	Light	Light
	80	84	79	Light	Light
Average	83.4	81.4			
3	62	63	59	Light	Light
	61	63	75	Dark	Dark
	60	59	58	Light	Light
	64	63	62	Doubtful	Doubtful
	66	59	68	Dark	Dark
	66	59	65	Dark, match	Light, match
Average	62.6	61.4			
4	27	31	30	Light	Light
	29	29	33	Light	Light, match
	30	32	31	Light	Light
	30	32	27	Light	Light
	31	28	30	Light, match	Light
	31	28	32	Dark, match	Light
Average	29.4	30.4			
5	20	20	24	Dark, close	Dark, close
	20	20	28	Very dark	Very dark
	22	21	20	Light	Light
	21	22	22	Light, match	Light
	22	21	24	Dark	Dark
	22	21	21	Light	Light
Average	21.0	20.8	23	Dark, match	Light, match

is placed at the other end. The eye-piece is moved backward and forward until a position is reached where the fields appear matched. Double the distance that the eye-piece has been moved from the

<sup>1</sup> Science, New Series, Vol. 42, No. 1085, page 534.

center is the actual depth of turpentine equivalent to a No. 1 yellow glass.

The details and operations can probably be better followed from the diagram.

In Table I the comparative readings in the cell and in the tubes on five different turpentines by two observers are given. It will be seen that the two procedures in the hands of experienced operators give essentially the same results. This demonstrates further that had irregularities existed in the daylight glass they had no material effect. The cell with the eyepiece has a decided advantage, however, in that matchings can be made more quickly and with less effort.

Table II shows the concordance between individual readings and also the average of five readings on each of fifteen different turpentines, by two observers.

SAMPLE	OBSERVER	INDIVIDUAL READING					AV.
1	A	154	152	154	154	148	152.4
	B	155	158	159	153	152	155.4
2	A	116	116	112	114	117	115.0
	B	116	122	118	118	120	118.8
3	A	143	145	146	144	152	146.0
	B	144	150	146	144	143	145.4
4	A	64	64	65	65	65	64.6
	B	62	66	64	66	62	64.0
5	A	56	51	55	54	51	53.4
	B	56	54	52	52	51	53.0

SAMPLE	OBSERVER	INDIVIDUAL READING					AV.
6	A	66	69	69	70	70	68.8
	B	69	71	70	69	68	69.4
7	A	51	52	48	47	49	49.4
	B	50	51	51	48	49	49.8
8	A	52	51	49	49	48	49.8
	B	49	50	51	51	49	50.0
9	A	52	48	49	46	46	48.2
	B	48	48	51	46	46	41.8
10	A	26	28	29	24	26	26.6
	B	26	28	25	25	28	26.4

SAMPLE	OBSERVER	INDIVIDUAL READING					AV.
11	A	27	23	25	26	28	26.2
	B	24	26	25	28	27	26.0
12	A	32	30	32	28	29	30.2
	B	29	30	32	28	28	29.4
13	A	17	14	14	16	16	15.4
	B	14	16	14	16	16	15.2
14	A	16	14	14	16	15	15.0
	B	14	15	15	14	15	14.6
15	A	16	18	15	14	14	15.4
	B	15	16	15	16	15	15.4

The results indicate that variations between the individual readings may be considerable, but that the averages of five readings are well within the limits necessary for this character of work.

When a column of 150 mm. of turpentine is equivalent to a No. 1 yellow glass a difference of 10 mm. in the length of the column is equivalent to less than 0.07 yellow. This variation in the color scale seldom occurs between the averages of five readings. In no case has the color between the averages of five readings exceeded 0.08 yellow, which is well within the limits required in the grading of turpentine.

The instrument is easily adjusted, and the readings are made rapidly and with little strain and annoyance. Though it has been used here only in reading the color of turpentine it is obviously equally adaptable to colorimetric work when the standard glasses can be employed and when the solution does not attack the metallic cell, in which case the cell should be made of a resistant material.

LEATHER AND PAPER LABORATORY  
BUREAU OF CHEMISTRY, WASHINGTON

## A KJELDAHL FUME REMOVER

By F. G. MERKLE

Received March 30, 1916

Anyone who has ever had occasion to make Kjeldahl nitrogen determinations knows the irritating nature of the fumes given off in the early stages of digestion. Some of the common appliances for the removal of these fumes are the following:

1—Closed hood with ventilator.

2—The Johnson digestion pipe, which may lead directly into a flue or into a tile receiving a spray of water as proposed by Wagner.<sup>1</sup>

3—The invaginated pipette (Folin).<sup>2</sup>

4—The bulb condenser (Sy).<sup>3</sup>

The strong suction in the Folin and also the Sy apparatus has a number of disadvantages: (1) It reduces the pressure on the liquid, thus increasing the time required for digestion; (2) it produces a partial vacuum which increases the tendency to foam, especially with organic materials; (3) it causes spattering and blackening in the neck of the flask which is greater as the pressure on the surface becomes less. Bits of digesting material and drops of acid may be carried far up into the neck of the flask necessitating attention during the operation.

### A NEW APPARATUS

The apparatus illustrated by Fig. I has been in use for a year in the course in General Chemistry of the

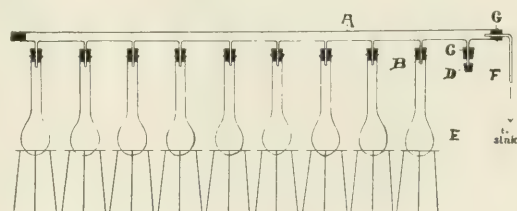


FIG. I

institution with which the writer is connected and has given good results. It consists of a lead pipe (A),  $1\frac{1}{2}$  in. inside diameter, to which are soldered as many 3-in. lead tubes,  $\frac{1}{8}$  in. in diameter, as there are Kjeldahl flasks. Each small tube is fitted with a rubber stopper (C) to accommodate the mouth of the flask. Caps (D) made by boring holes one-half way through rubber stoppers are handy to plug up unused tubes. One end of the main pipe (A) is plugged with a stopper, the other fitted with a bent glass tube which serves as an outlet for the fumes. The whole is supported by clamps as seen in Fig. II. The pipe is easily bent so it should be supported at intervals of not more than  $1\frac{1}{2}$  to 2 ft. It is sometimes found advantageous to lower the end of the pipe nearest the sink so that there will be a fall of 2 or 3 in. in 5 ft. of pipe. This aids, somewhat, the outward movement of the fumes of condensed acid.

The expanding fumes force their way slowly out of the tube (F) and may be disposed of by letting it project a foot down the sink pipe which is washed with a small stream of water.

<sup>1</sup> Chem.-Ztg., **36** (1912), 1438.

<sup>2</sup> J. Biol. Chem., **2** (1912), 503.

<sup>3</sup> THIS JOURNAL, **4** (1912), 680.



MODIFICATIONS: 1.—In place of a rubber stopper (G) and glass tube as shown in Fig. 1, it would be more desirable to continue the lead pipe down into the sink by means of a right angle bend.

2.—A more convenient design consists of a lead tube  $\frac{3}{4}$  in. inside diameter with the small side tubes bent as shown in Fig. 11 to prevent any back flow of condensed acid into the digesting flask. This modification, however, has not been as extensively tested as the one described.

3.—A modification of the apparatus shown in Fig. 111 is easily made for the small laboratory. Only



FIG. 11

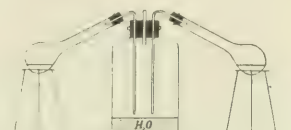


FIG. 111

two Kjeldahl flasks are shown in the diagram, but five or six may be conveniently set up around the absorbing flask which is provided with a single outlet leading to the sink pipe.

ADVANTAGES: 1.—The expanding gases create an increased pressure, which, though slight, has the effect of raising the boiling point and thereby hastening digestion; also, of decreasing the tendency to foam and spatter. The decrease in foaming is quite marked and is a valuable feature.

2.—Digestion may be carried on in the open laboratory.

3 and 4.—The apparatus is portable and inexpensive.

DISADVANTAGES—The fumes acting continually on the rubber stopper naturally cause a decomposition which may be prevented, in a measure, by dipping the stopper in melted paraffin. It is well to use the long-necked flasks so that the fumes will be cooled as much as possible before reaching the stopper.

#### SUMMARY

A simple apparatus has been described which effects a complete removal of the fumes produced in Kjeldahl digestion without the aid of aspiration.

Thanks are due to Dr. C. A. Peters of the Massachusetts Agricultural College for valuable criticisms and suggestions.

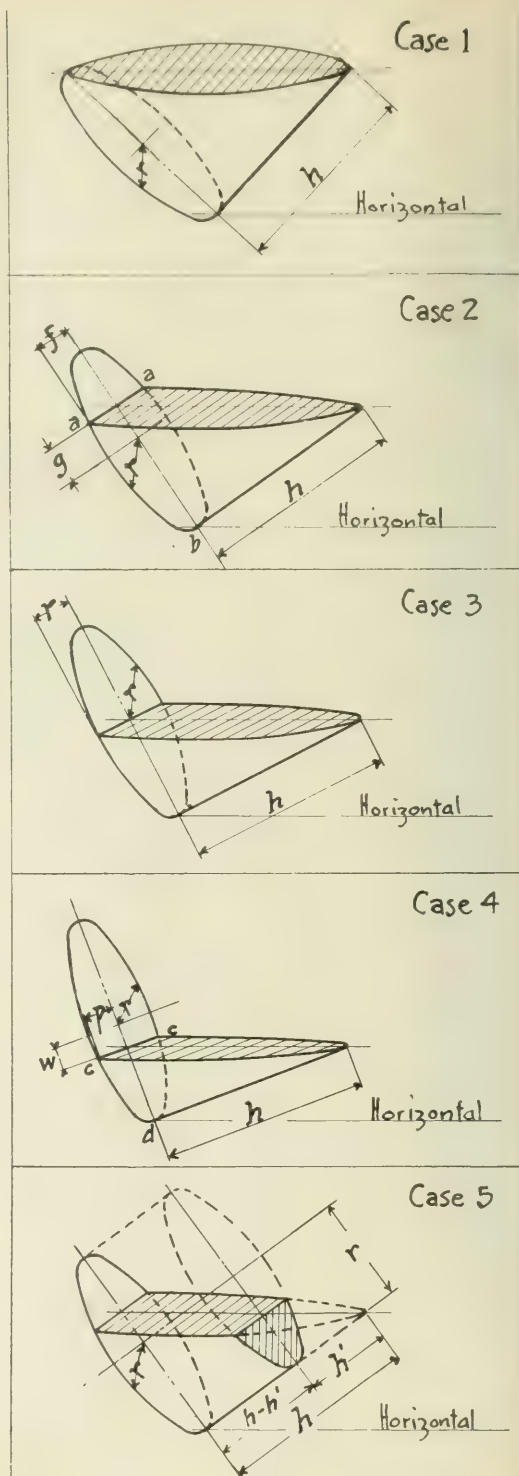
DEPARTMENT OF GENERAL AND AGRICULTURAL CHEMISTRY  
MASSACHUSETTS AGRICULTURAL COLLEGE, AMHERST

#### FORMULA FOR OBTAINING THE VOLUME AND LATERAL OR CONVEX SURFACE OF AN UNGULA OF RIGHT, REGULAR CYLINDER

By HARRY B. WRIGLEY

Received December 4, 1915

In THIS JOURNAL, 6 (1914), 517, appears a "Formula for Contents of Cylindrical Tanks with Spherical Ends." The author of this formula states that it is a comparatively simple matter to calculate the volume per inch of the main portion of the tank. This statement, no doubt, is made upon the assumption that the tank is horizontal. Where a tank is inclined the fol-



Following formulae for obtaining contents, etc., of an Ungula of Right, Regular Cylinder will be found useful.

$V$  = Volume,  $S$  = Lateral or Convex Surface

$r$  = Radius of Cylinder;  $h$  = Length of Cylinder

$A$  = Area of Segment,  $a, b, a$ ;  $B$  = Length of arc,  $a, h, a$

$A^1$  = Area of Segment,  $c, d, c$ ;  $B^1$  = Length of Arc,  $c, d, c$

CASE 1, where Base = Circle CASE 2, where Base = Segment,  $a, h, a$

$$V = \frac{1}{2} \pi r^2 h$$

$$V = \left( \frac{1}{3} B^1 + gA \right) \frac{h}{r+g}$$

$$S = \pi r h$$

$$S = (2rf + gB) \frac{h}{r+g}$$

CASE 3, where Base = Half Circle

CASE 4, where Base = Segment,  $c, d, c$

$$V = \frac{2}{3} r^2 h$$

$$V = \left( \frac{2}{3} B^1 + wA^1 \right) \frac{h}{r-w}$$

$$S = 2r h$$

$$S = (2rf - wB^1) \frac{h}{r-w}$$

CASE 5, Frustum,  $h-h^1$ , of Ungula of Right, Regular Cylinder

Let  $V$  = Volume of imaginary cylinder of length  $h$ ,  $h^1$

$V'$  = Volume of imaginary cylinder of length  $h^1$

$V''$  = Volume of Frustum, of length  $h-h^1$

Then  $V'' = V - V'$

THE INSTITUTE OF INDUSTRIAL RESEARCH, WASHINGTON

## A RAPID FILTER FOR TURBID LIQUIDS

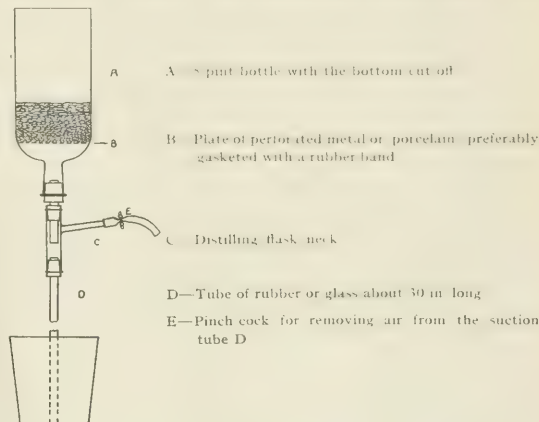
By RALPH C. SHUEY

Received January 17, 1916

The simple apparatus here described contains no new elements but since it has proven far superior to other filters for turbid liquids of high viscosity, it may be of interest. The paper pulp used by distillers is probably the most satisfactory filter mass for such purposes, but in a Buchner the mat cannot be built deep enough to run any length of time without clogging, and when clogging commences the suction packs the mat so that it blocks almost immediately.

The filter pulp is thoroughly macerated with hot water and poured into the funnel (Fig. I) a little at a time, packing down after the formation of each half inch of mat. For very muddy liquids the upper surface is but slightly packed. The water drained from the pulp sweeps practically all the air from the tube  $D$

and starts the suction column. The liquor to be filtered is poured in on the mat before the column is broken and any accumulated air removed from time to time through  $E$ . As the filter still contains nearly its own volume of water the liquor is allowed to flow into the water receptacle until the filtrate begins to appear in the narrow tube, as shown by a change in color or refraction, then a new receptacle substituted. No



further attention is required except to keep the funnel filled and if there are any leaks, to remove the air through  $E$  occasionally.

With a Bunsen pump the suction is irregular and also tends to build up until the filter blocks or breaks through. The efficient working of this arrangement is attributed to the slight but uniform suction obtained. Neither does the filter suck through when empty.

ARMOUR GLUE WORKS, CHICAGO

## THE DEDICATION OF THE NEW CHEMISTRY BUILDING UNIVERSITY OF ILLINOIS

The new Chemistry Building of the University of Illinois was formally dedicated on the 19th of April. The exercises were held in the Auditorium and the program was as follows:

HONORABLE EDWARD F. DUNNE, GOVERNOR OF ILLINOIS, Presiding  
SCRIPTURE READING AND PRAYER, REV. GEORGE P. HOSTER, D.D., Rector  
of Emmanuel Episcopal Church, Champaign

MUSIC  
ADDRESS, "The University of Illinois," PRESIDENT EDMUND JAMES JAMES  
ADDRESS, "THE TRAINING OF CHEMISTS," ALEXANDER SMITH, Professor of  
Chemistry, Columbia University  
ADDRESS, "RESEARCH AS A NATIONAL DUTY," WILLIS RODNEY WHITNEY,  
Member of the U. S. Naval Board, Director of the Research  
Laboratory of the General Electric Company  
MUSIC

The addresses by President James, Professor Smith, and Dr. Whitney are printed in full below, and are followed by an illustrated description of the building, prepared especially for us by Dr. B. S. Hopkins of the Chemistry Department of the University.—[EDITOR.]

### INTRODUCTORY ADDRESS

By PRESIDENT EDMUND JAMES JAMES

The dedication of a great and expensive building, erected for university purposes, always raises the question whether a university is not spending an un-

due amount of its funds upon the mere piling up of brick and stone. The well-worn statement that a satisfactory college is a log with a man at one end and a boy at the other was the beginning, perhaps, of the serious criticisms made upon many of our American institutions that they were in the habit of spending too much money on brick and mortar, and too little on flesh and blood. You will remember that Johns Hopkins University started its beneficent and epoch-making work in the field of American education in a very inferior and in some respects, for its purposes, poorly adapted set of buildings, and that it has been pointed out many times as an illustration of how to do things worth while in the field of university education, as compared with some other institutions in the country which spend large sums of money upon the erection of great buildings and have comparatively little left for equipment, running expenses, and the payment of the salaries of the university professors.

There is undoubtedly a great deal of truth in the general view that we Americans run to large accumulations of brick and stone, instead of accumulations



of brains, and I will confess that for many years I was not only a thorough believer in that view, but one of the sharpest critics of the tendency in many institutions to provide adequate and suitable buildings for university work.

I have changed my mind somewhat on this particular point since I have been responsible for recommendations as to university policy in this and other important matters. I have come to appreciate a side of the subject which did not appeal to me with very much force twenty-five years ago. In building up a great institution one has to have regard to the character of the people in whose service it is expected to function, and upon whom it must rely for its support.

For some twenty years, in three of the largest American universities, Pennsylvania, Chicago and Northwestern, I was intimately associated with the administrative work of departments, for whose support I was also expected to help win the contributions from private citizens. In other words, it was the worthy and beneficent benefactor whose interest I was expected to enlist, and whose money I was expected to persuade him to give for the support of the particular departments for which I was responsible. I found then that many men were willing to give money for buildings, who would not give money for their endowment; that many people would give money for collections, who would not give money to pay the salary of curators; and that many men who you might think would know better, were deeply influenced by the mere size of an institution, by the mere accumulation of brick and mortar in one great aggregate. I found that after all, the average man, that is the average successful business man, was impressed by mere bulk in a way which one would think he ought not to be if he had the brains which he must have had in order to accumulate the money which made it desirable for the university to cultivate his acquaintance.

And since then I have noted that the great endowments have in some instances come from men who were impressed by the importance which their fellow-men attributed to the enterprise as evidenced by the buildings and plant which had been erected for its conduct. When I became responsible for a certain portion of the policy involved in recommendations to the Legislature of Illinois, I saw another side of the same proposition.

We cannot expect the average man to appreciate the importance of certain phases of scientific work. In fact, it is very difficult for one academic man to appreciate fully the importance of the work which his fellow academician is carrying on in a, to him, remote field. I heard only yesterday a very distinguished member of this body remark that while Assyriology and Egyptology were undoubtedly very important subjects, yet certainly no one could claim for an instant that they ranked in importance with chemistry: moreover they had waited so long for development they might wait a while longer. And he was inclined, therefore, to feel that a university ought to be spending all its funds on chemistry, and post-

poning the time when it would be making collections of Egyptology and Assyriology. I called his attention to the fact that the building of the dam at Assuan had destroyed irremediably some of the very finest archaeological remains of the ancient world, and that because the universities did not bestir themselves and collect these materials in time, they had lost the opportunity forever. I also called his attention to the fact that the great war was probably playing havoc with the great collections of Babylonian and Assyrian brickbats in the valley of the Tigris and Euphrates, whereas the knowledge of chemistry which we have not yet attained would be perfectly safe locked up in the bowels of nature for many generations to come if it were necessary, that is, if we couldn't get around to discovering it and unlocking it before.

Still more difficult is it for the average man who has not come in contact with academic things and university ways of doing things, who has little knowledge of human history and little perception of how one thing is tied to another, to understand in any thoroughly satisfactory way the importance of all these things which we academic men are urging upon the attention of the public.

Now chemistry is, of course, a rather concrete subject. Nearly every man, no matter what his education may have been, or whether he has any education at all, if he has simply read the newspapers or read the children's periodical literature, has some conception at any rate of what chemistry means and some little idea of the importance of the subject in the history of human culture and the importance of developing it in the interests of human health and human welfare in general. And yet, I think, there is no doubt that the average man who has given his attention chiefly to Egyptology or Assyriology or to Latin and Greek, even though a cultivated and educated man, has little or no conception of the fundamental importance of the development of chemistry to the progress of human life.

Now, of course, the simplest way, the most direct way, and the proper way to induce this appreciation of the work of this great subject in the mind of the average man is to educate him directly upon the importance of chemistry; try to get some chemical ideas into his head; point out the relation of chemistry to the practical things that he himself is trying to do every day, etc., etc. But this is not always very easy to accomplish. I have found it to be so, as to the members of the faculties to which I have belonged and as to the members of my own family and acquaintances who were not connected with the universities; from a study of the remarks and views of the average man who comes to visit the University of Illinois, from the ranks of the advertising men, from farmers, from bankers, and men in general whose profession has not brought them necessarily in touch with academic methods and academic standards and academic ideals. I have come around quite strongly to the view that the most direct method of educating such people as to the importance of certain things is to let that importance be shown in some visible structure of steel and

iron, of concrete and brick, which impresses his senses and may impress his imagination.

I am quite sure that no farmer in Illinois, that no laboring man in Illinois, that no advertising man, or banker, or lawyer could view this great building which has been erected upon the campus of the University of Illinois in the interests of chemistry, even though he look at it merely from the outside, without unconsciously experiencing the feeling—you might almost say the conviction—"Why, that must be a mighty important subject on which the University of Illinois is willing to spend so much money!" And if he goes into the laboratory, though he doesn't understand what all these test tubes and all these pipes, etc., mean, but simply sees all the amount of labor and effort and human capital that has gone into the enterprise, he is converted to the fact that that must be an important subject; and before he is convinced that it is not, somebody must establish the fact to his satisfaction that this investment of money has been a foolish one. In other words, the existence of such a building creates a *prima facie* case for the importance of the subject,

After all, friends, there is a certain symbolic significance in all of this. I am not, of course, arguing for the waste of money on great buildings. I am not arguing for spending money on buildings which ought to be spent on men. I agree entirely with the fundamental view which all of us hold. I am simply emphasizing the results which the investment of money in this form may produce upon the public mind, leading, in all probability, to a greater willingness to spend money for men and for equipment and for the real things for which the building is constructed, than would otherwise be the case. After all, a building is nothing but the body which is going to house the soul, and, speaking generally in a large way, the body is always constructed in advance of the soul, or at least with the development of the soul, and we can hardly expect any of those creations which combine body and soul to be developed without a body to a very great extent. You will remember that according to the Jewish conception of the world, even God Himself had to make the human body complete, ready to function, before, by breathing the breath of life into it, He created man.

And so I have stood in these later years of my life, for a worthy housing, in our great institutions of learning, of the subjects and departments for whose cultivation these institutions exist, looking at them as centers of teaching and research. Some of you have seen, for example, the Armory of which the University of Illinois has begun the erection over in our military field. I think it is not too much to say that the existence of this building, the mere sight of the building, the examination of the building, the mere going into the building has done more to convert the people who have actually come in contact with it to the necessity of more adequate appropriations for our military work than any speech I or anybody else could make. And I am quite sure that if we had upon the campus of the University of Illinois an ade-

quate library building, adequate to house five million books, as we hope to have in the course of time, the mere existence of that building, the mere impression which it would make upon the public mind, and I mean by that, the mind of the State, the minds of the taxpayers, the minds of the people who are contributing to the support of the institution, would be the most potent influence in getting an adequate fund for the purchase of books necessary to fill those shelves and the creation of a staff necessary to organize and develop such a library.

Friends, we are glad to have you here, rejoicing with us over the erection of this great structure, because it is going to be one of the most powerful agencies in helping us to secure for chemistry, for chemical investigation, for chemical teaching, for the spread abroad of chemical knowledge an ever greater influence.

There was always something symbolic and significant in laying the foundations and in completing the dedication of a great building for the uses to which it is to be devoted. The human being has, somehow or other, an unconscious feeling of the importance of the initial steps, and then the importance of the final steps, a sort of unconscious idea that a great structure of this sort represents in itself and shadows forth in itself the efforts of humanity directed toward higher things; and so, many tribes of men have made human sacrifices, have buried human beings alive under the corner stones of such buildings, have shed their blood in the final dedication, a symbol of what the great effort involved in erecting the building has signified.

We have been at work on this building now for many years. In fact, the older portion of this building had no sooner been completed than the members of the chemical staff, themselves, set about planning for an enlargement of the structure, for an addition to it; and I believe that even now, before we have fairly dedicated this building, Professor Noyes and his associates are casting long and lingering glances at the open lot opposite the present building, with the hope that the University may get that against—I will not say, the time when we need more space for chemistry, for that is already here; these gentlemen have more than filled this building, and are pressing urgently for additional space—but against the time when funds may be available for actually beginning the erection of such a building. These chemical men have been at work for years planning for this structure, trying to work out its details; and then if you stop to think of all the results of human toil and effort that have gone into the building itself, that every one of these devices utilized in the heating, in the lighting, in the ventilation, every one of these pipe combinations bringing compressed air, or gas, or the wire conduction of electricity; the discoveries as a result of long and anxious toil which have resulted in making the brick which enter into the structure itself; the evidences in the architecture and the style of the building, that into it have gone the results of the thought and creation of human beings since the dawn of history, one gets a real idea, a real notion of what infinite toil on the part of "the much enduring race of man" has



gone to prepare the structure. And when one thinks of the countless generations through which the human race has elaborated the knowledge and experience necessary to erect and equip such a building, and then thinks of the countless generations of young people who will go in and out through this building in all the years to come, carrying out into human life in every direction the results of the knowledge which they may have gained within these walls, one realizes how the whole future is dependent upon and tied up to the past, and how we are, after all, one race, we might almost say, one individual.

The description of this building you have found already in the little circular prepared about it. We believe that it is going to be well adapted to its purposes when it is finally completed. We believe that the people of the commonwealth, who have erected this great building as a testimonial of their confidence and belief in human science and as evidence of their faith in the men who are trustees of this great gift, the men in the laboratories and the men in the teaching work, will be satisfied that they have done well, and will be willing to do more.

It seems to me that the chemical staff to whom this building will be handed over, ought to keep in mind three great things, three great duties, if you please, three great obligations: by which they will carry out their duties as trustees.

First of all, they should recognize that this is an agency of teaching, of getting hold of the young men and women of this commonwealth and other commonwealths and other countries who may come here to study, in such a way as to impress them with the importance and with the value of the study of chemistry, and inspire them with the ambition to do their part in making this study effective and helpful to their day and generation.

In other words, that the members of this staff shall feel it incumbent upon them not to lop off their students as rapidly as possible, not to pride themselves on the number of students they drive away from the study of chemistry, or cut off from the possibility of studying it; but on the contrary, to pride themselves on the number of students whom they have taught to love chemistry, whom they have fired with an ambition to know more and ever more of the secrets locked up in this great field, and enlighten their minds to such an extent that they will appreciate in an ever larger way what chemistry has done and is doing and may do for the welfare of the human race.

Every member of the staff of this chemical department, it seems to me, ought to feel that it is his business first of all to be a teacher, a good teacher, a thoroughly efficient teacher, an inspiring teacher and guide and counsellor in this field of chemistry to the young people who may elect, or who may be forced into this important branch of study.

In the second place, it is certainly a great and fundamental function of the staff of such a great laboratory as this to be enlisted with a truly religious fervor in making their contributions to an ever-wider knowledge of chemistry; fired with the ambition to add each year

some little increment or other to our knowledge in this field, to our control over nature, which comes from a knowledge, a thoroughgoing knowledge of this field. Every member of this staff should feel that it is incumbent upon him to be an investigator, a research worker, and if he ever feels that he neither has the brains nor the ambition to do something in that line, he ought to resign his position on the staff and select some other career, for certainly no man who isn't fully imbued with his fundamental responsibility in this respect has any business being a trustee of this enormous agency for the benefit of the public. If he is not doing this, he is a false trustee, he is betraying the interests of the people who have vested this power in him.

A third very important matter, which every member of this staff, and the staff as a whole, ought to keep in mind is that you should let your light shine. In other words, you should let the world know something about what you are doing through the publication of the results of your investigations and by a conscious and direct effort to educate the public as a whole upon what the chemical laboratory and chemical investigation and chemical teaching have in them for the common welfare. I should call this work extension work in the large sense, and I think every member of this staff ought to be interested in it. I don't mean that every member of the staff should go out and give courses in chemistry in high schools, or go out and lecture to the general public upon the value of chemistry, though some men on the staff certainly ought to be able to do this in an acceptable way; and the history of how some of the greatest chemists of the world have come to be through the inspiration of these general extension lecture courses, that is, courses given by eminent chemists to people who could not be expected to understand their lectures unless they were couched in non-technical and plain terms, demonstrates the importance of the work.

I feel, my friends, that we do not realize how ignorant the common man is as to what is going on in these great universities. He is very apt to look upon them with indifference, or regard them as mysterious centers of thought and work which he doesn't understand, and which have little connection with him or his interests.

The question has often been raised in meetings of professors and administrators in our state universities, as to the function of research and investigation in a state university.

I should say that function was exactly the same as in any private university, and it is far more insistent and far more necessary for the welfare of the institution than even in the case of the private universities. I have always maintained that in the long run the community will support the state universities in a large and liberal way much more because of what they are doing for the advance of science, than what they are doing in the work of teaching.

*My friends and colleagues of the chemical staff of the University of Illinois:*—We are expecting from you the adequate performance of this threefold function of

effective and inspiring teaching, valuable investigation, and diffusion of the results of this work, first among scientific men through your scientific periodicals, and then among the great mass of the community by newspaper and magazine articles, popular addresses, etc.

I wish you Godspeed in your future work in this magnificent structure, and I think I can promise you for the Board of Trustees, and, if I understand the people of this state rightly, for them and their children, the heartiest support in this great undertaking that is now committed to your charge.

### THE TRAINING OF CHEMISTS

By ALEXANDER SMITH

The address on research, which follows mine, deals with that aim of the chemist which always receives the most enthusiastic recognition. But thorough training is indispensable before original work can begin. A genius, without adequate training, seems to know by instinct what information he needs and where to find it. He devises new methods when those which he has learned fail. He reaches the goal, in spite of all handicaps. Better training would have saved him some needless loss of time, but often would not have improved the final result. Geniuses, however, are few and far between. The advancement of the science would be fitful, if it depended upon them alone. The greater part of the additions to chemical knowledge are made by men with an aptitude for the science, it is true, but with nothing approaching genius of the higher order. With them, the thoroughness of the previous training is, therefore, a very potent factor. At the other extreme, in the case of the chemist who does mainly routine analyses, who corresponds to the draftsman as distinct from the architect, the training he received must determine largely the value of his results. In all the intermediate cases, where intelligent study of an individual situation is demanded, and new adaptations to special purposes are required, training in the principles of the science and previous exercises in applying them to new cases, with the alertness and mental adaptability which such training produces, are the chief factors in success. The training of chemists is, therefore, a matter well worthy of careful study.

It is not my purpose to discuss the subject as a whole. I desire rather to emphasize four points which, after nearly thirty years' experience as a teacher, I am inclined to think are of vital importance, yet receive too little consideration, and indeed are often entirely ignored.

#### OVERLAPPING COURSES

Take, for example, the treatment of the freshman who, on entering a college or university, offers chemistry for admission. In the vast majority of cases he is placed in the same class with those who have never studied the subject before. All agree that the result is unsatisfactory, but many attribute this result to the wrong cause. They say that the chemistry of the High School is valueless, and that their pupils

would be better off without it. The actual fact is that, to such pupils, the introductory parts of the course seem trivial and boresome. They become indifferent. Later, when matter suited to more mature minds comes up, they do not observe the change. Soon they fall behind the beginners, and finally they barely pass in the course, if they pass at all. The result is not the fault of the student or of the High School, however—it is an inevitable result of ignoring the most familiar features of human psychology. Administer the admission requirement with reasonable strictness, place those credited with chemistry in a class or section *by themselves*, make them feel from the start that they are getting something that is new to them, and they will respond accordingly. Of course, elementary matters cannot be omitted. No two members of the class come from the same school, their training is very diverse, and there is hardly one fact, no matter how simple, which is known to every one. The elements must be reviewed at the same time that new matters are introduced. But a pace much more rapid than that of the beginners can be maintained. In Chicago, my experience showed that this class secured in two quarters a much better knowledge of chemistry than a class of beginners could obtain, under the same conditions, in three quarters.

If the school course is valueless, why give admission credit for it? If it represents a real advance into the science, as experience shows that it does, why ignore it? Why not accept it, and start at the higher level? Overlapping of courses is all too common in chemical training, and it often begins by duplicating all the work of the High School, and not taking it for granted and proceeding beyond it.

Overlapping affects many of the later courses in every university. The instructor in qualitative analysis, instead of ascertaining exactly what is taught in the inorganic course preceding it, and confining himself to the briefest possible references to what he has a right to assume as known, too often spends many hours repeating such parts of the elementary facts and such elementary principles as are required in his work. I have known of instructors in quantitative analysis who ignored all the content of the previous instruction—both facts and theory—and reduced the subject to a series of mechanical processes, which could have been performed equally well (or equally badly) by a beginner. The students respond quickly to this situation, just as in other circumstances they would respond to demands on their previous training, and soon work with due lack of intelligence. Thus not only may the previous training remain unused, where continuous and most effective use could have been made of it and much might have been added, but, being unused, it is soon forgotten. At the end of two or three years of work, the pupil may actually know less of the science than he did at the end of the first year. Even if each course overlaps only about half of the preceding course, the inevitable result is that the pupil gains in four years only what, with better coordinated instruction, he could have secured in two years.

Curiously enough, the opposite fault affects much



of our organic chemistry. Here the books, instead of striving to link the subject intimately with inorganic chemistry, and thus aiming at continuity, too often give the subject as far as possible the appearance of a different science. Unfortunately many instructors follow the same lead. I have known cases where a law of chemistry was hardly ever mentioned, an experiment was never shown, a substance was almost never exhibited, and the only chemical material in evidence was pulverized gypsum in streaks and curves on a black background. There are notable exceptions, of course, but too much so-called organic chemistry is nothing but a riot of symbols and "bonds." Some overlapping is necessary here, to offset the real differences in the nature of many of the reactions and of many of the experimental methods. The course might well be made essentially a part of the elementary general chemistry, and less like a separate science.

In respect to loss of time by overlapping, the university, with its numerous instructors, is at a disadvantage when compared with the college. In the latter, three or four years of chemistry are all given under the immediate direction of one man, and continuous work and rapid progress by the pupil are more likely to be secured.

#### STANDARD COURSES

In different institutions in which the training in chemistry serves the very same purposes, there is too little agreement in regard to the weight, the content, and the quality of the regular courses. In many universities and colleges, the course in inorganic chemistry based on High School chemistry is standardized, and demands two or three classroom periods and six hours of laboratory work weekly for twenty-four to twenty-eight weeks. But the graduates of one large university tell me that their course in this subject is inferior in quality and extent to the average High School course, and that previous work in the science is neither required for admission to it nor recognized in any way when existent. Courses of all kinds, intermediate between these extremes, are common. Now, the establishment of a more uniform standard is most desirable for many reasons. Migration from one school to another is rapidly increasing. Schools of medicine are requiring previous college work, but the boy who has had about half a course each in inorganic chemistry and in qualitative analysis or organic chemistry can neither be admitted, nor can he be directed to any course in which his peculiar deficiencies can be made up. The student who decides to move to a school of engineering often finds that he has been provided with a similarly extensive, but superficial, preparation which leaves him a misfit. When the student attempts graduate work in another institution, he encounters the same handicap. Naturally, a slight course in inorganic chemistry can be followed only by a course in mechanical qualitative analysis, such as prevailed forty years ago, and any attempts in each successive course to develop a grasp of the modern aspects of the science must be given up. A separate and distinct course in physical chemistry, taken later, can never

solve the problem. In such a course only a few illustrations can be given, whereas continuous application of the same principles in study and in the laboratory during the whole training is necessary to success. The student keeps the different courses in separate, water-tight compartments in his mind, and only a genius will make the thorough-going applications and connections that are required to weld the whole into a science. Modern chemistry simply teems with applications of physical chemistry. This is the case both in the laboratory and in the factory, both in the biochemistry and physiology of the school of medicine and in the courses required of the student in chemistry and chemical engineering. The institutions of learning must respond to the obvious demand. We are not training students to use four or six years hence even the chemistry of to-day, much less the chemistry of 1880 or 1890. We are training them to understand the chemistry and biochemistry of the future and to apply and expand the science as it will be several years hence. All that we know for certain about that chemistry is that it will be less capable of mechanical, unintelligent use than the chemistry of the past, and that ability to apply theoretical conceptions will be more desirable, nay, more indispensable than ever. Standardizing our elementary courses, both as to extent and as to character is an essential part of preparedness to meet the demands of the future.

In this connection, a word is in place in regard to the training of candidates for the degree of Doctor of Philosophy, a class of students which is rapidly increasing in numbers and importance. Their training in the fundamental branches of chemistry is at present very various and unequal in quality, even when sufficient in quantity. They can take advanced courses, but piling knowledge on a shaky foundation is unwise. The advanced principles can perhaps be used, albeit mechanically, when, as given, they happen exactly to fit the problem. But when they have to be adapted to a different situation, only a chemist who has an absolutely sound understanding of the fundamental elements of the science can make the adaptation with certainty. We are all familiar with published researches which were in reality futile and valueless because fundamental principles were overlooked or were not correctly brought into relation to the observations.

One remedy is to require graduate students to attend the elementary classes. This, however, is only a half-measure. Review courses in general chemistry, analytical chemistry, and organic chemistry, in which these subjects are examined in retrospect, can be given so as to occupy less time, and yet achieve the object much more effectively. Emphasis can be laid on application of modern views, the oddities which pervade most courses in chemistry can be discussed, a broader and more critical scrutiny of the principles can be undertaken. Of especial importance is the fact that the classification of the content of chemistry can itself be discussed, although with beginners the classification can only be *used*. Also, the reasons for preferring certain definitions and certain conceptions can

be considered, and less advantageous or even erroneous statements commonly encountered can be brought out as they could not be in a class for beginners. We learn much more by a study of wordings that are open to criticism than by simply memorizing uncritically faultless ways of stating the same things. Thus, the preparation of the graduate student can be standardized also, at least in respect to its most essential features.

#### AN ALTERNATIVE TO LECTURING

In a lecture one states the facts or explanations clearly and, *for the moment*, the attentive student understands perfectly. But, is it our object to train him to understand statements made by others—does ability to do that constitute a knowledge of chemistry, and play an important part in making a chemist? Is a watchmaker a person who recognizes a watch when he sees it, who knows what makes it run, and when it is running well, or is he a man who can make and repair a watch? Is not a chemist one who can himself make correct statements about chemical topics, and can himself put together the necessary facts and ideas, and himself reach a sound chemical conclusion? Listening to a lecture keeps the student in a *receptive* attitude of mind, whereas the attitude we desire to cultivate in him is the precise opposite of this. The student should begin by himself acquiring the ability to state simple ideas correctly, and later himself practice putting facts and ideas together and reaching conclusions. The conclusions are not new, but going through the operation of reaching them for himself is new to the student. No one would explain to a group of people who were not musicians how the piano is played, and perform a few lecture experiments on the piano, and then be foolish enough to expect the audience to be able at once to play the same pieces themselves. Of course not, because we all know that every kind of mechanical dexterity has to be acquired by practice and by the formation of habits, nervous and muscular. But we do not all realize that mental operations are also *largely mechanical*. For the most part they are made up of half-unconscious responses, each of which is an idea previously acquired by practice, and only the selection of the units of which the whole mental operation consists, and the arranging of them in due order, are the results of actual thought and conscious reasoning. After explaining some point to the class, such as the reasons in terms of the ion-product constant for the precipitation of calcium oxalate, one might assume that they all understood the explanation, and perhaps they all do. But ask them individually to *state* briefly the reason for the precipitation, and some will make remarks that have no bearing on the subject, some will make partly incorrect statements, many will make statements that are correct so far as they go, but are incomplete. Only one student in thirty will give a correct and complete answer. Many of the others undoubtedly understand the matter perfectly, but unless they have an opportunity themselves to put the answer together, the impression will be slight and fleeting. It is the exercise of going through the reasoning and the wording of the answer, for oneself,

that alone can make the impression a permanent one and fix the explanation in the mind.

Evidently, the pupil would better study the subject in the book, taking much or little time according as his powers of acquisition are slow or fast, until he can state each important point in his own words. Then the classroom work can be confined to testing the preparation, discussing difficulties, showing illustrative experiments, and asking questions about the cases illustrated. Before printing was invented, oral instruction was necessary. It seems to me that a good many university men have not yet realized that the printing press is now available. It is right that we should know the history of our profession, but not necessary to adhere to all the practices of antiquity. We all know walking was invented before the locomotive, but none of us walked to Urbana to this meeting. Was that thoroughly consistent?

I am not proposing to abolish lecturing. In courses taken by students who already know how to study, that is, in the more advanced courses, lectures are of great value. They give a general view of the territory as a whole, they distinguish the more important from the less important items, and they enable the student to conduct his *own private study* of the subject with intelligence. I am referring mainly to the elementary course for freshmen, where not one member of the class in twenty has ever studied in the true sense, or has any knowledge of how to study. It is a part of the benefit he gets from the course that he learns how to study and acquires the necessary habits. Listening to lectures, in such a case, if the lectures are well constructed, only deludes him into thinking that he has fully grasped the subject, and *prevents* him from studying. Additional class exercises given by assistants and subordinate instructors do not help the situation materially. Often the assistants do not keep in close touch with the mode of presentation of the lecturer. Always the students feel that, since assistants handle this work, it must be less important, and so it suffers in effectiveness. After trying both plans, it will be found that incomparably better results are obtained by giving two or more sections, of thirty to forty students each, to a competent instructor, and letting him conduct the whole work of each section. The lessons are assigned in advance, and due preparation is insisted upon.

There are other disadvantages of the lecture method for freshmen. The lecturer must adjust his speed to that of the slower, if not the very slowest members of the class, although many of its members could follow equally well if the pace were tripled. With the slower students spending more time in preparation, and this and the other variable factors thus relegated to the home study, the class becomes more uniform, and either twice as much ground can be covered in the hour, or the ground can be covered twice as thoroughly, according to the nature of the topic.

That the student has thus acquired a more thorough foundation in chemistry, and that he has learned how to study, are both of great advantage when the next course is taken. When the lecture method has been



used, the student have still to be taught the necessity for continuous study and how to do it, and progress in the next course is slow. Then also, the fleeting impressions, detained temporarily by a few days of violent but superficial study just before the examination, have almost entirely evaporated, and overlapping and repetition of all the necessary facts and principles is an absolute necessity. For this reason, also, much time is lost. Efficiency demands that something of permanent value be accomplished *each year*, and there is every reason against postponing the application of efficient methods to the second year.

Again, questioning shows at once which points have been understood by all, and which points have remained unclear, and the time is spent on the latter. Also, the recollection of past topics, when the need of applying them arises, can be tested, misunderstandings can be recognized and removed, and lapses of memory can be remedied. The method finds out infallibly what is needed, and how much in each case is needed, and permits the doing of precisely what is necessary. The process involves continual measurement of the existing results. A *lecturer* can only guess at what is needed, and how much of it, and must necessarily be more or less in error on every occasion. The method advocated has for the chemist the attraction of being quantitative and, with practice, the experimental error becomes negligible.

Still again, since the lectures are systematic and orderly, while the laboratory work is necessarily more or less topical, the pupil thinks the lectures are the kernel of the course. Yet, in point of fact, the real contact with the subject takes place in the laboratory, and it is better therefore to make the student feel that the laboratory work is the principal feature of the course, and that the classroom work is simply a discussion and adjustment of what has been learned in the laboratory and at home. Individual observation, and reasoning from observation, can thus receive that strong emphasis which they deserve, but in a lecture can never receive. Naturally, every week each student must begin with the experiments for that week, since he cannot otherwise prepare himself for the class meetings.

Finally, many chemists admit that they learned little chemistry from the first lecture course, but insist that the personality and point of view of the lecturer—not only in matters chemical, but in respects quite remote from that science—exercised a profound influence upon their own point of view and their subsequent attitude towards life. In reply, it need only be pointed out that, in the free interchange of thought which is a necessary part of the method suggested, the opportunity for the personality of the instructor to assert itself is even freer than it ever can be in a lecture, and that the digressions, if they are such, since they will usually be suggested by reactions shown by the students themselves, will be much more likely to strike some target effectively and forcefully than will the random shots of a lecturer, who knows only what is in his own mind, and nothing of what is in the mind of the listener.

#### IMPROVED LABORATORY FACILITIES

The mechanical equipment of a chemical laboratory is an important efficiency factor in the training of chemists. There is perhaps no department in the college or university where the ratio of results achieved to time spent is so small. This is particularly true of the quantitative and organic laboratories, although it is conspicuous in all branches of the science.

For example, the evaporation of a solution on a steam bath may take five or six hours. The temperature of the liquid may never greatly exceed  $90^{\circ}$ . A vigorous attempt is made to train the student to carry on several operations simultaneously, but four or five months elapse before he learns to do this effectively. A plate covered with shot and heated with steam under pressure, one at each working place, will easily give a temperature of  $130^{\circ}$ . The time required for the evaporation will become a mere fraction of that required with an ordinary steam bath, and the saving of time will begin on the first day, instead of being postponed until months of training have brought about the same result by another method. The cost of fuel will also be less. When the dissolved substance is a very soluble one, the vapor pressure of the solvent becomes rapidly smaller as evaporation proceeds, and soon the steam escaping from a bath gives to the air a partial pressure of water vapor equal to the vapor pressure of the solution, and evaporation ceases. With the steam confined in the plate, so that saturation of the air is avoided, the evaporation will proceed much further without interruption. A tube connected with a vacuum system provided on all desks will remove the vapor, and will facilitate further evaporation beyond this point to a surprising degree. Desk ventilation is, of course, required when the steam plate is used.

Ventilation at each working place, as it has been installed in the new laboratory here, also permits much saving of time. Hoods take the student away from his desk and reduce the number of operations he can carry on simultaneously. Hoods become dirty and unsightly, because no one student can be held responsible for their condition. They also furnish the students with an excuse for leaving their desks, and conversing about football, when they should be at work. In case a hood is really required, which seldom happens, a folding hood can be drawn from the supply room, and erected over the desk ventilator.

The traditional arrangement of chemicals on a side shelf is also open to many objections. Anywhere from ten to a thousand times as much of the chemical may be taken as the operation really requires, so that reckless habits are acquired and much material is wasted. When the class is following a program, and working on the same experiments, the same chemical is needed by several students at the same moment, and delays occur. For the same reason, certain bottles are quickly emptied. When one of the bottles is empty, it is not the business of any student to have it filled, and so another convenient excuse for conversation is provided. The side shelf furnishes opportunities for conversation far more plentifully than it does

chemicals. With a little initial work by the instructor, a list of the amounts of each chemical and solution required for the term's work can be prepared, and each student can be provided with a kit of chemicals which he keeps in his desk. Professors Freas and Beans, at Columbia University, tried this plan first on a class in qualitative analysis, and the instructor added between twenty and twenty-five per cent to the work of the course in order that the time thus saved might be utilized. The saving in the total quantity of chemicals consumed pays the expense of making up the kits, and the twenty to twenty-five per cent additional training is all clear profit. Every student is entitled to the set of chemicals appropriate to his course. If he wishes to use more than the allowance, which should be ample, he can obtain them from the supply room and have them charged in his bill for breakage. Thus those who prefer to be extravagant pay personally for the privilege, and the appropriations at the disposal of the department are conserved and permit the offering of better facilities to all. For example, in one term of a course in organic chemistry, one student used less than \$8 worth of chemicals, while the largest amount used was over \$28 for the performance of the same work. It was evident from this that \$12 worth of chemicals was ample, and that all students using more had been dissipating the resources of the department, and should hereafter be required to pay for the excess.

In a large laboratory, there are times of the day when the number of students trying to replace broken articles or to obtain other supplies at the stock room, becomes great, and loss of time is the inevitable result. No institution of learning can afford to multiply skilled attendants, when they are needed only during a rush hour in the afternoon. On the other hand, the use of unskilled help leads to mistakes, involving loss of money by the department and loss of time by the student. The provision of more than one supply room is an expensive remedy, and does not always prevent crowding. Instead of waiting twenty minutes or more for his turn, the student can in one minute write out his demand on the telautograph, and then return to his desk and go on with his work. A receiving clerk stamps the card in a calculagraph clock at the time the order comes in, and again when the boy returns (after delivering the article) and presents the same card signed by the student. The time required for filling the order need never exceed seven minutes: if it does, the cause of the delay is investigated. Of course, a stock of supplies equal to all ordinary demands must be available, and in the larger laboratories this stock represents an investment of at least \$60,000 to \$80,000.

In all laboratories, much glass apparatus is returned in dirty condition. Since it will not be accepted in this condition by another student, it cannot be received. It is thrown away and the student's account is charged with its value. Installing dish washing machinery will save the greater part of this expense and reduce materially the number of new articles to be ordered, received, unpacked, checked, and stored. In our own experience the substitution of a charge for washing, in place of a charge for the whole cost of

the apparatus thrown away because of being dirty, as it had been made the year before, reduced the breakage bills for an equal number of students by nearly \$1200. During the year the apparatus of instructors and the apparatus used in lectures can be washed at one central place more economically than by scattered, unsupervised labor. Then, too, in many courses, cleaning apparatus takes up much of the time of the student. A graduate student, who is paying tuition, room rent, board and other living expenses, and who is sacrificing his earning power to obtain further education, can save time which has a high money value to him by sending his apparatus to the supply room for cleaning.

Ring stands and burners are usually painted with asphalt paint. This gives an exceptionally porous covering, especially fitted to permit access of laboratory gases and to hold moisture. One investigator finds that when more than two coats of paint have been applied, rusting is not retarded, but accelerated. The sand blast will take off every trace of the paint with astonishing ease, and thus, with a single coat of new paint, of a properly chosen kind, every article placed in the outfit will look as good as new. Ill-kept apparatus fosters careless work, while nice-looking apparatus guides the student, without his being conscious of its influence, into clean-cut and satisfactory manipulation.

The sand-blast reminds us that a mechanic and a work-shop are necessary features of a large laboratory. One recent research by an eminent chemist indicated that he made an electroscope out of a tomato can tied to an empty Lydia E. Pinkham medicine box by means of tan-colored shoe laces of the latest model. A more efficient and durable instrument could have been made with the help of a mechanic, and much of the time the professor and student spent in trying to work with this aggregation would have been saved. It is more economical to purchase standard apparatus, but, when modified forms are required, when repairs are needed, and when new apparatus is devised for research, the mechanic, readily accessible in the building, is a necessity.

Another problem of the laboratory is to utilize the desk space during a larger proportion of the time. If many of the desks are to be used during only two afternoons in the week, and are to remain idle during four-fifths of the working hours, one cannot provide a desk for each student, with all the overhead cost for the building and plumbing which that implies. In some courses, three or four cupboards, each capable of holding the whole outfit, can be provided under each working space, and three or four students can be accommodated. But in many cases, as in quantitative analysis and organic chemistry, the outfit is extensive, and often only one student can use the desk. Yet the space is not really utilized. Most of the apparatus is placed on the bottom of the cupboard and on the single shelf above—with the smaller articles in the drawers—and much empty space is provided above the apparatus, in order that articles at the back may be taken out without disturbing



three in front. Cannot some way be devised of saving this space, and at the same time making it unnecessary for the student to get down on his hands and knees on the floor to explore the dark recesses of the desk?

A desk designed by Dr. Pales seems to solve this problem (Fig. 1). The door is without hinges, and is pulled straight forward. Attached to it is a set of shelves and racks of the same width as the door, and extending to the back of the cupboard. These are planned so as to provide a place for each item in the outfit. This rack moves on a small wheel in the center of the foot of the door, and is supported behind by a wheel running in a brass-lined groove. Thus, when the front panel (or door) is pulled out, the whole rack comes out into the light, each side can be examined at a glance, and any article on it can be taken out in an instant. The outfit, placed in the box in which it is drawn from the supply room, occupies 10,000 cubic inches. When set out in the rack, it

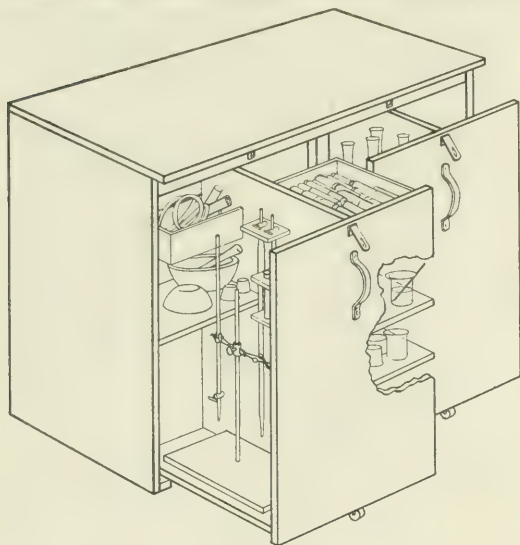


FIG. 1

occupies 24,000 cubic inches. When placed in the ordinary desk with its cupboard and drawers, it occupies 44,000 cubic inches. Since in the rack-cupboard it thus occupies only about half the space commonly required, two outfits for two different students can go where one went before. In addition, actual measurement shows that the student can take out any needed article or chemical in one-third of the time required with the common arrangement and, instead of taking three to four minutes (by measurement with a stop-watch) to ascertain that he does *not* have a chemical asked for by the instructor, he reaches the same conclusion with greater certainty in six seconds. The effort to pull out an ordinary laboratory drawer, *when empty*, requires, by measurement, a force of 4 to 12 pounds. That necessary to draw forth the rack, with its complete load of apparatus and chemicals (weight 40 lbs.), is only 2 pounds. And finally, the construction of the desk costs no more than does

that of the usual desk with two drawers and a cupboard.

There are teachers of chemistry who feel that mechanical devices for making laboratory work more efficient are beneath their notice. But, after all, the laboratory is essentially a study, in which materials take the place of books, and manipulation and thinking take the place of reading and thinking. A book is arranged mechanically for convenient and rapid use, whether it is to be read straight through or employed for reference. Why should not similar attention be given to the mechanical arrangement of the laboratory? Of course, the publisher and printer arrange the book—not the author. But the architect does not know enough about chemical work to devise anything helpful—and we are lucky when he does not knock out part of our plans by persuading the authorities that they will put the building out of harmony with the other structures on the campus. Hence, the chemist must himself tackle the problem in detail.

Then again, if the laboratory operations occupy long periods of time, the intervals between the points at which thought by the student is required, or the practice of certain manipulations is demanded, are so prolonged that the pupil forgets to think when the time comes, and bungles the manipulation because his mind has long since wandered to some other subject. Thought and physical activity are more effective when there is a more or less continuous demand for them, and so every abbreviation of the periods of waiting and of the interruptions, caused by looking for some article or going to a hood, increases the efficiency of the work as a form of study. It also, of course, permits more work to be done, and, therefore, more subjects for thought and more manipulations to be introduced, and so gives more mental training and greater technical skill.

The magnificent addition to the laboratory, the opening of which we are now celebrating, has been made at a most opportune time. A German statistician has discovered that the ratio of chemists to population in four countries is represented by the numbers: Switzerland 300, Germany 250, France 7, Great Britain 6. The corresponding number for the United States is probably nearer to the two last numbers than to the number for Switzerland. The general run of people in this country, even educated and intelligent people, have hitherto been almost entirely unaware of the important rôle which chemistry plays in the industries. When you tell them that many railroads employ fifteen or twenty chemists each, they stare in astonishment, and cannot imagine what there is for a chemist to do in such a connection. But the discussion raised by the war has suddenly drawn chemistry out of its modest retirement, placed it in the limelight, and advertised it as nothing else could have done. The number of students in chemistry, always a rapidly growing factor, has this year taken a great leap forward. The University of Illinois is fortunate in having completed a building for chemistry so carefully planned and so magnificently equipped. It is fortunate also in the splendid spirit which has characterized its work

in chemistry, and in the remarkable number of investigations of the highest order which have been, and are being carried on in its laboratory. The State of Illinois is to be most heartily congratulated both on the performance of its University, along chemical lines, in the past and, with the space and the facilities which the new laboratory offers, upon its promise of even greater things in the future.

COLUMBIA UNIVERSITY, NEW YORK CITY

### RESEARCH AS A NATIONAL DUTY

By WILLIS RODNEY WHITNEY

The object of this paper is to emphasize the importance of material research and to lay stress on its necessity to any people who are ever to become a leading nation or a world power.

I have called it material research because I wanted to exclude immaterial research. I class under this head pure thought as distinct from thought mixed with matter. It is worth while making this distinction because it is not always recognized. It is very natural for us to feel we can think new things into being. Chemistry has advanced only in proportion to the handling of chemical substances by someone. When the study of our science was largely mental speculation, and the products and reagents largely immaterial, like fire and phlogiston, we advanced but slowly. Ages of immaterial research for the philosopher's stone led only to disappointment. Successful results in modern times came from following Nature, learning by asking and experimenting, reasoning just enough from one stage of acquired knowledge to ask the next question of materials.

Professor Trowbridge, of Harvard, once said:

"Before Galvani's time men were lost in philosophical speculations in regard to subtle fluids; after his experiments their thoughts were directed to the conditions of matter immediately about them. Benjamin Franklin brought electricity down to earth from the clouds, while Galvani's experiments brought men's minds down from the heights where they were lost, having no tangible transformations to study."

We are now being shown, by systems of national development, how important is the study of the properties of matter. There is no need to raise the questions of the war, nor of the relative originality of different races, nor to compare the gifts to scientific knowledge of the various world powers. We shall go only so far as to point out that in national processes there is a certain peculiar and useful attitude towards exact and new knowledge. I want to convince you, if I can, that in the uses of science we ourselves have much to learn, and in the matter of research we are still children.

In speaking of research, I do not mean to confine my thoughts to the chemists and their knowledge and literature, but rather to that science which is back of chemistry. We may call it natural science, if we are careful. It includes, for my present purposes, all philosophy based on measurable facts. Psychology and therapeutics come under this head; so do electricity and medicine, anatomy and physics, chemistry and biology. These are inquisitive sciences, where the answers come from asking questions of Nature. If I can leave with you even a faint impression of the importance of new knowledge, the strength to be gained

from its acquirement, and the pleasure in the process itself, I shall feel repaid.

As distinct from your Illinois attitude, research is sometimes looked upon as a remote, postponable, and especially exacting undertaking, well-suited for martyrs of science and unreasoning optimists, and not at all for teachers. The historical methods of teaching have still lingering in them some of these signs. Even in our day it is sometimes said that a teacher should not be an investigator. It will take a long time to efface that idea completely, but it will be as surely forgotten as the fact that most of our older colleges were once religious centers. It is important to realize that the need, facilities and possibilities of research are all about us, retarded only by the inertia that is in us.

Every chemist, even in his freshman days, handles the identical substances with which all material advances will be made. Because he cannot always handle them in the ways of the advanced industry, he is led to imagine that research is closed to him. Yet so much useful pioneer work in all fields has been done with simple material equipment coupled with good mental equipment, that it almost seems as though this was the rule. The telegraph and telephone started with a few little pieces of wire wound by hand with paper insulation. The basic work on heredity was carried out by an Austrian monk with a few garden peas. The steam engine came from the kitchen fire, and wireless from the tricks of a little spark gap. There was, however, the same general kind of mind behind each one of these discoveries—the mind of the inquisitive thinker.

### ADVANCED TRAINING NECESSARY FOR SCIENTIFIC SERVICE

Exactly the opposite belief is also quite common—that great advances are made by sudden flashes of thought through the mind of some lucky and presumably *unoccupied* individual. If this were so, there would be little need for the high degree of training which is necessary for almost any scientific service in our day. We may find a simple illustration of this point in organic chemistry. We know that the artificial production of important chemical compounds, such as indigo and rubber, has been accomplished. But how many of us realize the training that was necessary and the research that had to be done before success could be claimed. The Badische Company spent seventeen years completing the indigo work after the first synthesis, and expended about \$5,000,000 before a pound was put on the market. I might say that without at least fifty years of work by thousands of research chemists, neither problem could have been solved.

In my study I have a photograph of about thirty young research men grouped about Wöhler. This is the chemist of Göttingen who first discovered that an organic compound could be produced in a laboratory. It was he also who made the first metallic aluminum. The picture was taken in 1856, about as early as decent photographs were possible. Every year since 1856, that Göttingen laboratory, among others, has been training chemists in research. They have gone into fields of infinite chemical variety. Each man has



been a center in some distant place, and around this center there had often been built some kind of growing chemical structure. Many became teachers, and their students in turn became experimenters and teachers. Many followed industrial chemistry and extended the field of the ever-increasing army of chemists. In my particular photograph is one man who in 1866 became the Professor Goessman of the Rensselaer Polytechnic Institute and was later professor at Amherst and very prominent for years in the Massachusetts State Board of Agriculture.

Since 1836 the same seeking for knowledge by renewed groups of such men has been continually going on in many foreign laboratories. It is only slowly being taken up in our country. Is it not time that we awakened to the fact that, as research chemists, we are still in our infancy? If we are ever to be a leading country in industrial chemistry, research is absolutely necessary. If such research is done elsewhere, then the major part of the advantage will lie elsewhere also.

Scientific research, or research in the natural sciences and in the industries, might be defined as the pioneer work of the *developed* country. In this light it is easy to see that our turn has come. Not long ago our pioneer work was of another kind. It was opening up the undeveloped land. It was actively and well done. But the work must change because our requirements have altered.

Carl Helfferich, Director of the Deutsche Bank and now Secretary of the Treasury of Germany, writing before the war, said:

"All economic labor aims at making external nature contribute to the needs of man. It is as true of the primitive gathering of roots and berries as of the production of cyanamide or calcium nitrate. The enormous progress of modern economic technique is due to the splendid development of the natural sciences and the systematic application of scientific knowledge to economic labor. Physics, chemistry and electricity have outvied each other in their influence upon economic technique."

Speaking of the scientists, he says:

"Our hermit poets and thinkers converted themselves more and more during the past century into practical creative workers, and an enormous expansion of activity has resulted from the progress of the pure and applied natural sciences."

American chemists have had German chemists pointed to as examples almost long enough, but there is some value in concrete examples, and I cannot refrain from comparing our own impoverished condition in the matter of fixed nitrogen to that of Germany.

Excepting one or two minor attempts, we Americans have made almost no study of the fixation of atmospheric nitrogen. I want you to realize the varied and expensive researches, mostly carried on abroad, which were required to reach the present position of the nitrogen question. There were in Germany and, by German capital, in Scandinavia, several direct oxidation processes, carried through the experimental to the practical commercial stage. The Schoenherr process is one of these, the Birkeland and Eyde process another. The direct combination of nitrogen and hydrogen to form ammonia has been successfully developed in the German Haber process, and the cyanamide process, with all its products from carbide

to ammonium nitrate, was developed in Germany. There they used not only the peculiar reactions of calcium carbide with nitrogen, but the production of the nitrogen from liquid air, the reaction between water and cyanamide to form ammonia, and then an oxidation process for obtaining the nitric acid. The oxidation of ammonia to nitric acid by such methods as the Ostwald process has been studied by many investigators since 1830, and several different schemes are now in use abroad.

At the time most of this research work was under way it was not at all clear what use was to be made of it. Much of it was *purely academic* research, but it was clear that without the knowledge itself, certainly no use at all would be made of it.

I do not want you to look at research as an old, established utility. I want you to see it as I do: a powerful factor proved by the advance of the industrial welfare of the foremost countries, and a world-experiment of less than a century's trial, but something still unappreciated in America. It is true that the earliest man and many of the lower animals accomplished ends by research, but I refer now to research in the natural sciences and to the research which in our day is necessary to our desired activities. These sciences are already very highly developed, and advanced education is demanded by them. For example, if I wish to cure physical ills, I cannot expect to do it by reciting ancient incantations, nor by using roots and herbs, as was once customary. I must first familiarize myself with an accumulation of previous experience. I must study anatomy, physiology, chemistry, bacteriology, etc. This is a relatively recent world-condition. Conditions are similar in all the applied sciences. The accumulated knowledge in any field is already very considerable, and to get into the firing line of useful work one must go up past the baggage train of knowledge and experience. There is something in the blood which makes an American naturally hate preliminaries. It will be a great day when we see how important preliminaries are. The hospital surgeon well knows how much more willing the young interne is to actually handle cases, if it is only to administer the ether or the iodine, which any nurse can do, than he is to study the theory of ether as an anesthetic, or of iodine as an antiseptic, which perhaps no nurse could understand. The young student of mechanics thinks he could have devised the steam turbine if it had not been done before his day, but when he comes to study the problem as it has actually been developed, he finds the same old kinetic theories, differentials and integrations which he spurned as too theoretical when he sought a short road to engineering.

#### AMERICAN PROGRESS PROPORTIONAL TO PREPARATION BY RESEARCH

I want you to realize that in America we are going ahead in the future at a rate dependent *entirely* upon our preparation. Laboratories are a relatively modern thing. In most of the sciences they are a development within the lives of men now living. I want you

to see that we must be foremost in systematic, organized research, or we shall be distanced by other countries which already well recognize the value of *new knowledge*.

When so much of our material welfare, the condition and extent of our manufactures, the quality of our agricultural efforts, and the health of our people, depend upon the rate of our acquirement of *new knowledge*, there ought to be much greater effort made along the lines of research than is at present the case. We call knowledge power, but we need to see that *new knowledge* is the second power of power.

I would rather be a little Moses than a big Jeremiah. I would much rather point a way to a promised land, however remote, than talk about our lamentable conditions. But we Americans are not sufficiently imbued with the spirit of active and efficient service. We are a preliminary experiment on the possibility of operating a competitive nation in a democratic manner, but we don't care enough about it. We have about as little interest in the wonder and elasticity of nature, the laws of materials (except where they affect our stomachs and our health) as had Darwin's starving Patagonians. With us the spirit of the hive is confined to the bees. Germans and Japanese make better scholars than we do, and a Chinese laundryman sticks longer to his daily job and talks less about it. We are living in the Garden of the Gods, but we are still eating grass.

Is there no significance in the fact that many American colleges are better known through their foot work than their head work? Is it not significant that the Y. M. C. A.'s dotting our land are as strong in bowling alleys as in education, and that most of our religious training goes to the heathen? Is it a sign of health that so large a portion of our newspapers are paid to feed us with results of useless experiments between prize fighters? I think the stadium should be the accessory of the laboratory, not the temple of the oracle; and that in reality a research laboratory is more compatible with the object of a university than is the more common training table. I do not mean to be too insistent as a critic or too pressing as an advocate, but I hate to see my own country such a trailer as it now is. I hope the conditions are changing, but I know they are not changing fast enough. Probably Moses and Jeremiah were both right.

All service is based on knowledge, and knowledge is an ever augmenting thing which almost anyone may increase. If the stock is *eternally* useful, as it is, how great must be the value of the *indestructible* increments which *anyone* may produce. I do not think due reverence is given to *new knowledge*. I want to illustrate.

#### SERVICE OF RESEARCH

Sometime, somewhere, centuries ago, the slag of a fireside appeared transparent; someone tried to learn more about it, and so ultimately, glass was made. Research is still under way on that very material, and countless numbers of men have slowly added to the knowledge. Glass has kept the cold from the house. It has let in the light. It has renewed our eyes as they have worn out. Through

telescope and microscope it has shown us the greatest and the smallest things of the universe. It has bottled our drinks and held our lights. Every year still adds new service, just in proportion as experiments add new knowledge. To-day we hear of a new glass permeable to ultraviolet light, glass opaque to X-rays, and glass for cooking utensils. Not one of these little increments will ever be lost, but will continue in use, so how highly should we value them? Why did we delay so long in coming thus far, and how far or fast may we still go?

Research is preparation. It is preparing in one decade for the problems and the necessary work of the next. There are various kinds of preparedness. We are hearing a great deal about one of them nowadays—immediate preparedness for national defense. But there is a more far-sighted preparedness that no one has adequately described and of which the building of new laboratories is a token. This type is the very best kind of preparedness for national defense, if begun in time. The continued study of the secrets of nature, the uncovering of buried treasures which always seem buried just deeply enough to develop the diggers—these are the criteria of a strengthening nation.

Research presents a way, and the only certain one, of insuring peace, of preparing successfully for defense, and of being successful in war. It is the lasting, undeviating factor which has always dominated. This may sound bold and entirely inconsistent in itself. It is all true. Can we learn to see it? From the military expert to the anthropologist, thinking men recognize that for over 100,000 years war has been almost continuous on the earth. The inventors of chipped flint successfully fought those inferiors who had *not experimented* with flint. There were then no better arms. These also got their game even when it was scarce and other means failed, and so they continued to survive. This little and early example of survival was repeated a great many times before our present complex world conditions were reached, and will as surely continue to be repeated. The fundamentals were always the same. A 42 cm. gun is only a better flint. Trinitrotoluol is only a more modern sling. Arms and ammunition have changed, but just so have also changed the myriads of other important accessories to survival. This is the important point. Good guns go with good clothes, and niter is good for fertilizers and for guncotton. The signs that we are improving in our civilization will also indicate that we are growing in our powers of national defense, but this should come rather as a consequence than as an object. The world has always been improving, and the real growth and development has come to those nations which have been responsible for the original research work and not for the mere storage or conservation of the knowledge.

The first or fundamental discovery in any series is not the only important one, so I am going to take an extreme view and say, it is only the continuation of research which is of any considerable importance to us. The fundamental discoveries may be like seeds, but the values are like growing plants. An acorn



may correspond to the work of a Henry or a Faraday, but the great and growing tree of electrical or chemical work corresponds more nearly to the living state of the oak to which we are much more interested in what is to come than in what has already been accomplished.

#### PROBLEMS FOR RESEARCH

I realize that I ought to illustrate this appeal for research by concrete examples of chemical things to study. I know the feeling of the chemist who is mentally compressed by the mass of investigation work which has already been done and by the known facts which seem already to cover entirely all possibilities; but I know, too, that the future will make use of knowledge for which we now have *no vocabulary* and no powers for comprehension, and so could not possibly *anticipate*. If, then, I try to illustrate the search for new knowledge, you may be sure my illustrations will be inadequate.

In the first place, I cannot be reckless enough. This I learn from looking backward. I would not have dared suggest that a dozen good men should study the little hydrogen generator of the freshman laboratory, to see what was in it. If I had, I suppose I should have suggested a research on pipe organs, because of the singing hydrogen flame, or on bombs, because of the explosions. But someone tried synthetic ammonia, others Zeppelins, and others the cutting and welding of iron. When I see in our own factory the three score men now using oxyhydrogen all day for this latter use, I am impressed with the eternal proximity of new and useful knowledge. A very few years ago, two or three times as many men would have been necessary to do this work in the old, more difficult and less satisfactory manner.

The most natural suggestions for research are those simple ones referring to chemical elements. There are still plenty of "unknowns" among the elements, and of one thing we may be sure, there are certainly no two alike. Any chemist who wants to add to chemical knowledge need not go beyond the list of elements for his subject. The properties he discloses will every one of them be sometime a help to his science and of service to his country. As far as possible also, his country will reward him with patents if he asks them.

We ought to begin at the points where others left off, and continue the research of the chemical elements. One reason why this appeals to me is that I have seen so many recent applications of entirely new knowledge of elements in my own work. I merely mention tungsten, molybdenum, boron, argon, silicon, magnesium, titanium, thallium, vanadium and chromium, which, because of properties not known until recently, are nevertheless already doing commercial service in our restricted electrical field. Surely we know still far too little about these elements, but we know less about many others.

If now, the chemist, still neglecting the infinite compounds and narrowed in his researches to the elements, and then perhaps to the metals, and finally to a single element, still asks, "What shall I do?" I would refer him to the isotopes of his element. Our American Richards, supporting the researches resulting from the studies of radioactivity, has shown that there

are two leads. They are somewhat different, but cannot be separated easily. Of course someone ought to separate all isotopes, and then there is plenty of room for research on the single isotope.

One of the great needs of the country which reflects on us chemists and calls for immediate research, is that for American potash. There is no supply in sight which is nearly comparable with the German deposits, and our fertilizer and other industries will certainly suffer because of this difference. We have plenty of feldspar calling for a simple process for removing the potash it contains. We have oceans of sea-water carrying plenty of potash. We don't know how to extract it. Don't say it can't be done, for it is being done by miles of seaweed. Why should we confine ourselves to trying to take it away from the seaweed, instead of learning what the seaweed knows about getting it from the water? You may look supercilious, but until a large number of chemists have studied semipermeable membranes, there will always be this lack of understanding of those simple reactions of living matter going on around us. There will always seem to me a possibility of doing such physical and chemical things more nearly as we may wish to do them, when we know how they operate.

When nothing new is being done by us it will be a sure token of our decay. When we stop increasing our experimental activities or fall for a considerable time behind the activities of other countries, we may expect to see our light become merely a memory, like that of Greece or Rome. Thus far we Americans have not reached a fair average as investigators in natural sciences, and yet we have incomparably superior conditions for the growth of research. I cannot look beyond the period when research shall cease in a country and still imagine that country a power in the world.

There are no sharp lines to be drawn through research to separate pure from applied, scientific from practical, useful from useless. If one attempts to divide past research in such a manner, he finds that time entirely rubs out his lines of demarcation. At this particular time, however, one may imagine a more or less zigzag zone which serves to divide research in a commonly accepted way. I will illustrate. In a manufactory the price of a new product should include the cost of research. No matter how complicated the system, this is always true. Otherwise the industry would ultimately commit suicide. In practice it is common to apportion to particular products the cost of their separate development, and to fix the price so that within a reasonable time, or by a reasonable volume of sales, the so-called development cost may be wiped out. Thereafter the product may be sold on the basis of the continuing cost of actual production. While this system is extensive, it does not cover the cost of many of those original researches which may have been absolutely necessary. The argon tungsten lamp, in its development cost, did not carry the expenses of Rayleigh and Ramsay's work, and there will probably always be such classification of research work necessary.



FIG. 1—THE CHEMISTRY BUILDING, UNIVERSITY OF ILLINOIS

#### "UNPAID RESEARCH" NEEDS APPRECIATION

Under such a classification, the part of research I am most interested in promoting is what we may call the *unpaid* kind, not because it is cheapest, but because it is the most valuable. It is most neglected, most poorly understood, most in need of appreciative support in America.

The separate industries do not need encouragement in research nearly so much as the nation needs it. The industries can be depended on to estimate its value to them, for they take annual inventories. But a country which keeps no books, seems to have to depend on accident for its most valuable research work.

It seems to me that many of our American colleges have been shortsighted in this respect. This may be explained by the rapidly increasing demand in our growing industries for analytical chemists and chemical engineers, who could at once meet the existing industrial requirements. This demand has kept the chemical departments of our colleges and technical schools very busy with the elementary and analytical side of chemistry and left little room for the synthetical or experimental side. It has also naturally tended toward the development of highly efficient organizations, equipments and corps of instructors for the preparation of the one type of chemist, but this very success seems frequently to make impracticable the training of men for research. The conscientious American professor has usually devoted his life to bringing his students up to a certain promising stage of interest in science and experiment, only to see them scatter before they have had any experience in questioning Nature, or have tried any unbeaten path of chemical byway.

While I am greatly interested in what might be

done for science by technical research laboratories in the industries, I am sure that the university must be the important factor in guiding the pioneer work if we are to be a sufficiently advancing nation.

Let me recall recent words of President Wilson:

"I know I reflect your feeling and the feeling of all our citizens when I say the only thing I am afraid of is not being ready to perform our duty. I am afraid of the danger of shame. I am afraid of the danger of inadequacy. I am afraid of the danger of not being able to express the correct character of the country with tremendous might and effectiveness whenever we are called upon to act in the field of the world's affairs."

These words ring true. The American spirit is characterized by them. But think further a moment. They refer to a fear based upon an entirely corrigible defect. The cure is in our hands. The time when we are called upon to act in the field of the world's affairs is *now*; but it was yesterday, and it will be tomorrow. I maintain that no nation can effectively act in that field at odd or selected moments. It is either doing it much of the time, or it is likely to be unable to do it any of the time.

GENERAL ELECTRIC COMPANY, SCHENECTADY, N. Y.

#### DESCRIPTION OF THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS<sup>1</sup>

By B. S. HOPKINS

In 1901 the legislature of the State of Illinois appropriated \$100,000 for the erection of a chemical laboratory upon the campus of the University of Illinois. With this sum available, plans were drawn

<sup>1</sup> In compiling the data for this article the author has received the kindly assistance of members of the chemical staff, the supervising architect's office, and the contractors; he is under special obligation to Professor W. A. Noyes, Professor E. W. Washburn, and Dr. D. F. McFarland of the chemical faculty, Mr. E. R. Math, Superintendent of Construction, and the general contracting firm of Freeman and Brooks



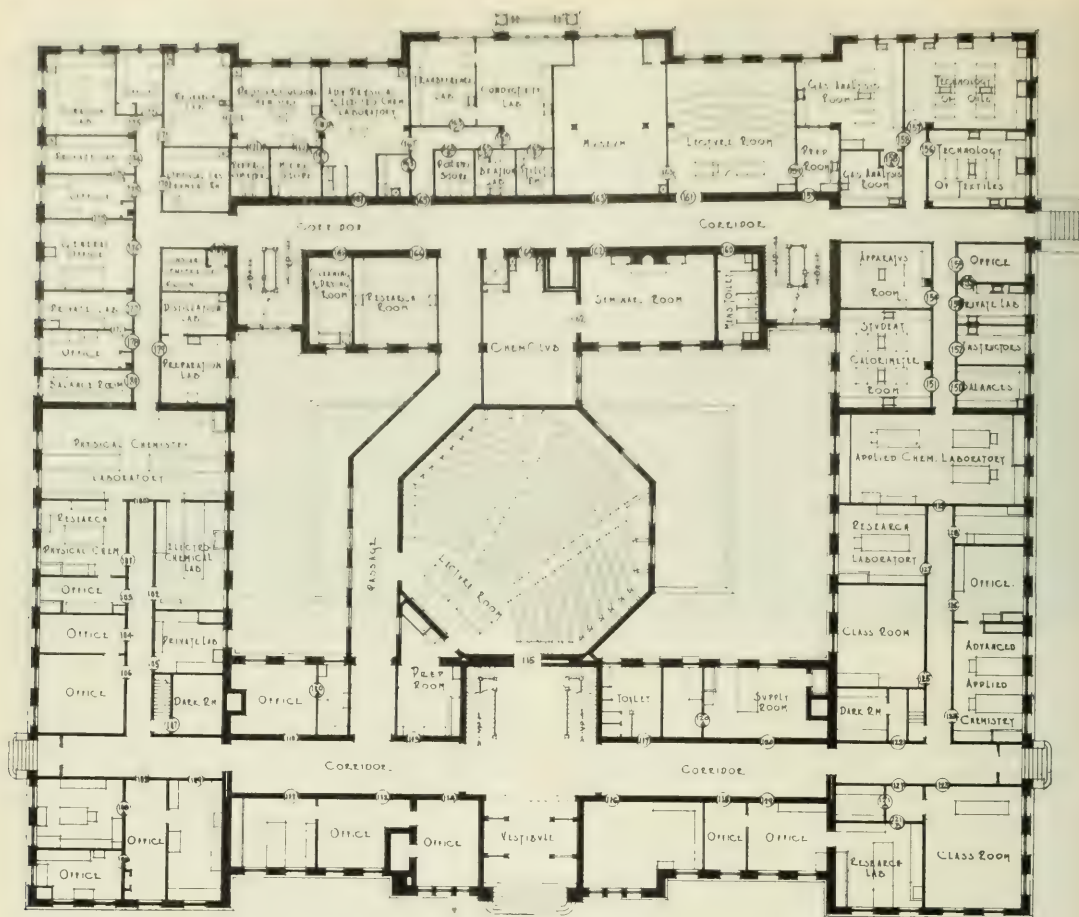


FIG. II.—PLAN OF FIRST FLOOR—CHEMISTRY BUILDING

for a building which it was expected would provide for the needs of the department for a period of twenty-five years. The smallness of the appropriation made it necessary to select a style of construction which entailed considerable risk from fire. It is built of red brick with Bedford limestone trimmings. It consists of three stories and basement, and is shaped like the letter "E," with a frontage of 230 feet and a depth of 116 feet along the wings. The middle rear portion contains the lecture room and the wings were largely given over to routine laboratories. The plans for this building were principally the work of the late Professor A. W. Palmer, to whose wise foresight and untiring energy this building stands as a fitting memorial.

The growth of the department of chemistry was much more rapid than was expected and it became evident that more room was needed before half of the twenty-five year period of usefulness had passed. Plans were formulated for the erection of an addition to the original building in such a manner that the completed building would form a hollow square, with the lecture amphitheatre in the center. The style of

architecture conforms in essential features with that used in the old building but the new part is built entirely of fire-proof material. The dimensions of the complete building are 230 feet by 202 feet, and there are available 164,288 square feet (3.77 acres) of working space. Plans for the new building are the result of the cooperation of the Supervising Architect's office with the heads of divisions of the department of chemistry under the able leadership of Professor W. A. Noyes, Director of the Laboratory. By this cooperative development of the plans, the special needs of each line of work are provided for, while the building as a whole possesses uniformity of design without needless duplication of equipment.

The new building joins the old at the extremities of the rear wings, where fire walls make it possible to shut off either side completely. The fire walls project above the roof and may be seen in the accompanying cut of the building. The liberal use of white enamel brick in the court makes the inner rooms light and attractive. Passage between the old and the new portions of the building may be effected through the

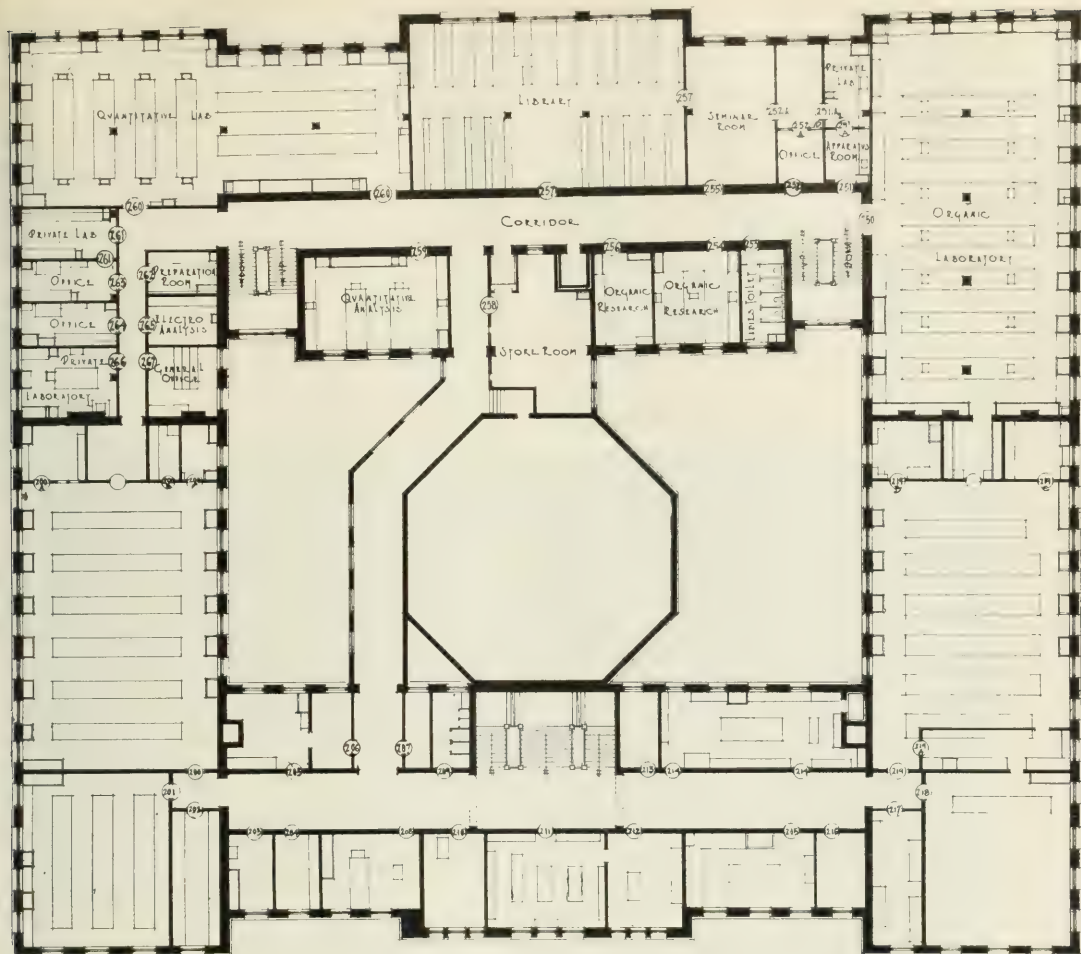


FIG. III.—PLAN OF SECOND FLOOR—CHEMISTRY BUILDING

wings or by a corridor which connects the center portions upon the first and second floors. Although the new part of the building covers a smaller area than the old, it furnishes a larger working space for the reason that five entire floors are available for laboratory purposes. The general plan of space distribution places the research laboratories, offices, library and museum in the new building while the routine laboratories are chiefly in the old building. It is expected that considerable remodeling of the old part will be done during the coming summer in accordance with this plan. The offices of the director of the laboratory and of the division of applied chemistry remain in the old part near the main entrance on the west front.

The building is a part of the quadrangle of university buildings and is conveniently located with respect to the College of Liberal Arts and Sciences, the College of Commerce and Business Administration, the College of Engineering, the College of Agriculture, and the Graduate School, from all of which the de-

partment of chemistry draws students. The main entrance is in the center of the west front, which faces the quadrangle. Two smaller entrances are located upon both the north and the south sides of the building, while in the center of the east front is located the service door, which is conveniently placed with respect to the main stockroom, the elevator and the shipping rooms.

#### THE NEW BUILDING

The framework of the new building is of structural steel, the major partitions and walls are brick, the minor partitions of pyrobar and the floors are composed of alternate rows of hollow tile and joists of reinforced concrete. The concrete covers the hollow tile to a depth of two inches, thus producing a continuous T-effect, giving strength and lightness. Upon the concrete, electric conduits for the wiring system are laid and a top layer of concrete covers the conduits. The final layer upon the floor is a coat of "rezilite mastic" which is about an eighth of an inch thick.



This last layer is acid-proof and gives considerable resiliency to the floors without making them soft enough to yield to heavy pressure. Some of the floors in the offices and seminar rooms are covered with battleship linoleum, while the library is provided with heavy cork carpet. The halls and stairs have Terrazzo finish.

The roof is of reinforced concrete which is made in large sections and supported by steel rafters. The concrete is covered by wood sheeting in order to give an air space for insulation purposes. The sheeting is covered with building paper and this in turn by slate or sixteen ounce copper plates. The skilful use of dormer windows makes the fourth-floor laboratories light and attractive and adds much to the architectural beauty of the building.

Very little wood is used in the building itself. The furniture is oak with a two-tone dull finish; the table tops and shelves are made of alberene, which material is used generally for window sills, open drains and sinks. The window sills in the halls, library and offices are white Alabama marble; the shelves in some of the rooms are made of milk glass.

Hoods are conveniently placed in all the laboratories. The frame of the hood is wood, the floor of alberene, the lining of white tile and the sides and top of reinforced plate glass. The doors are counterpoised by weights attached by means of a creosoted hemp rope. The pulleys and axles, which are wooden, are exposed, making repairs easy. Each hood has a separate flue running to the top of the building independent of other flues.

Ventilation is accomplished by means of forced draft. Two large ventilation fans with heating coils are housed in the court just outside the walls of the lecture room. This location is central and relieves the laboratories of the vibration of the fans. The fans have a capacity of 74,000 cubic feet of air per minute, which is driven to all parts of the building, entering the rooms through conduits at the ceiling. Foul air is forced out through the opening in the hood flues. The air is changed six times per hour, the temperature being controlled by automatic regulators. A small exhaust fan in the attic removes the air from the toilet rooms. There are also four chemical exhaust fans, each capable of handling 10,000 cubic feet of air per minute, which are used to remove the impure atmosphere from some of the laboratories and hoods.

Special attention has been given to the electrical equipment of the laboratories, five systems being available in all parts of the building: 10, 110, and 220 volt direct current and 110 and 220 volt alternating current. Besides these many of the laboratories are supplied with current from the storage battery system of 35 cells. Scattered through the building there are 150 wall plugs, 160 experimental plug boxes and 16 motor boxes, making electrical current available in all places. The lighting is the indirect system, there being 730 lighting outlets and 300 wall switches. The total electrical load of the building is 130 kilowatts, there being in use three transformers of 50 K. W. each.

The type of construction and the completeness of the equipment of the new building may be inferred from the following tabulation of materials used:

Structural steel.....	402 tons
Reinforcing steel.....	135 tons
Cement.....	75,000 barrels
Sand and gravel.....	6,000 cubic yards
Lime.....	3,000 barrels
Brick.....	2,000,000
Pyrobar.....	65,000 square feet
Hollow tile for floors.....	50,000 square feet
Sewer tile.....	5,600 feet
Cut stone.....	5,000 cubic feet
Terrazzo steps and risers.....	2,700 feet
Plastering.....	33,000 square yards
Sheet copper.....	30,000 pounds
Skylight glass.....	2,500 square feet
Radiating surface—181 radiators.....	11,000 square feet
Steam pipe.....	10,600 feet
Covering for steam pipe.....	4,330 feet
Pipe for temperature control.....	4,000 feet
Conduits, for electric system.....	8.32 miles
Electric wiring.....	12.78 miles
Iron pipe <sup>(a)</sup> for water, gas, vacuum, etc.....	3.6 miles
Block-tin pipe for distilled water.....	2,500 feet
Alberene (21,500 square feet).....	214 tons

(a) Excluding table fittings.

#### THE LABORATORY EQUIPMENT

THE DIVISION OF INORGANIC CHEMISTRY AND QUALITATIVE ANALYSIS occupies one laboratory on the fourth floor and the entire third floor with the exception of the rooms used temporarily by the guests of the department. Provision is made for the accommodation of about 1300 students, 400 of whom may work at any one time. In the new laboratories there are two special features worthy of mention, (1) the ventilation and (2) the commanding view of the entire room which is afforded an instructor in charge. In addition to the usual system of ventilation an independent suction system is used in these laboratories. Upon each student desk there is a 6-in. conduit which rises 8 in. above the table; a cap closes the opening when not in use. The conduits are made of canvass-coated fiber which has been thoroughly treated to make it a non-conductor, as well as water-proof and acid-proof. The exhaust fans draw the offensive gases downwards from the student tables and discharge them into a separate flue in the main ventilating stack. By this means the air in the laboratory may be changed eleven times per hour. Hoods of the regular type are also conveniently located for special experiments, and for the use of hydrogen sulfide.

An uninterrupted view of the laboratory is obtained by placing the ventilation flues and plumbing beneath the table top and omitting the usual reagent rack. Each student has at his own desk a set of reagent bottles, gas, suction, tap water, a sink and an open down-draft hood, while within easy reach there are also supplied compressed air, distilled water, steam, hydrogen sulfide, the electrical circuits and the regular hood system. An ingenious device is in use to permit the student to use his sink as a pneumatic trough. A piece of lead pipe 6 in. long is tapered to fit tightly into the outlet for the sink, the upper end of the pipe being closed with a perforated cone. In this way a depth of four inches of water is obtainable

with no danger of overflow. The sink is quickly drained by removing the lead pipe. These lead risers in the sinks as well as the ventilating conduits are plainly visible on the table in the foreground of the accompanying illustration of the inorganic laboratory.

Besides the large student laboratories, there are twelve small laboratories available for research problems and for private laboratories of the teaching staff. There are three balance rooms for student use and one for research workers, the latter room being insulated with cork. There is also a dark room for spectroscopic work.

THE DIVISION OF QUANTITATIVE ANALYSIS occupies the entire north end of the second floor. There are laboratories for beginning quantitative courses, advanced courses and food analysis accommodating in all 400 students. A large working space is assured to

a thermostat and other equipment needed for work of this type. An electrolytic laboratory is fully equipped for various types of electro-analysis. There are eight well-equipped smaller laboratories, which are used for research and private laboratories.

THE DIVISION OF ORGANIC CHEMISTRY occupies the second floor at the south end of the building. Two large laboratories accommodating 280 students are used for the undergraduate course. In the new laboratory each student's desk is supplied with gas, water, waste, suction and live steam. The latter is available either as a jet for steam distillation or in a cone for distilling inflammable materials. In this way the amount of gas consumed is greatly decreased and greater safety is assured. Special attention is given in this laboratory to the electrical equipment for synthetic work and an unusually large amount



FIG. IV.—A CLASS IN QUALITATIVE ANALYSIS IN THE INORGANIC LABORATORY

every student and double-length drawers are provided for condensers, burettes and other lengthy apparatus. The student desks are equipped with gas, water, waste and suction, while in the hoods compressed air, hydrogen sulfide, high pressure steam and electrical connections are supplied. In the hoods are also placed specially constructed steam baths, the tops of which are terraced with three levels in order to make the rear openings more accessible and to decrease as far as possible danger of accident to dishes on the front row of openings. There are three conveniently located balance rooms, containing 53 balances for student use. A Kjeldahl room is provided with equipment such that 150 digestions may be carried on at one time and the distillation apparatus has room for 50 flasks. A separate ventilation system is provided for this room. A dark room contains a polariscope, a refractometer,

of hood space is provided. On the side shelves connection may be made with the high vacuum pump; blast lamps are conveniently placed at the sides; and near the entrance to the laboratory is located a fire shower for use in emergencies.

In addition to the large laboratories there are several smaller rooms equipped for special lines of work. One room, the atmosphere of which is kept pure, is reserved for accurate physical measurements, such as determinations of conductivity and molecular weight. Accurate instruments, hung from a special solid wall, are in use. A dark room is provided for the study of reactions in the absence of light and two dark rooms are equipped for work with the refractometer, polariscope and spectroscope. A special feature is a collection of organic preparations from various



ness of investigation in the laboratory. This collection is kept in a separate room, and is indexed for ready reference. The research and private laboratories have adequate equipment for the problems under investigation. The division is rapidly accumulating permanent equipment for the manufacture of the chemicals needed in the usual organic courses.

THE DIVISION OF PHYSIOLOGICAL CHEMISTRY occupies the greater part of the fourth floor. The main laboratory has desks for 108 students, the equipment being similar to that in the organic laboratory. There is an advanced laboratory for 16 students and two smaller private research laboratories. An instrument room is equipped with high-speed electric centrifuges, thermostats, apparatus for accurate titration, etc. The following special rooms are also equipped for their particular needs: a metabolism room,

adjoining room is furnished with apparatus for precipitation, crystallization, filtration, centrifuging, drying, cooling, etc.

The cleaning room is equipped with a steam drying closet; an iron vat which is surrounded by steam coils and is filled with chromic acid cleaning solution; and a deep roomy sink with glass drain boards. The titration laboratory has a white tile floor and the walls, ceiling and furniture are finished with white enamel laboratory paint. The room has a north and east exposure and its four windows are fitted with ground glass panes. The equipment includes qualitative reagents and indicator solutions, weight and volume burettes, pipettes, volumetric flasks, cells for electrolytic titration, colorimeters with sets of color standards and suitable balances.

The constant temperature room has walls, floor and



FIG. V—THE ORGANIC LABORATORY

an operating room, refrigerator room, and a dark room.

THE DIVISION OF PHYSICAL CHEMISTRY occupies the north end of the first floor and in addition has a calorimetric laboratory and an electric furnace laboratory in the basement. The space devoted to undergraduate work is in the old building except one optical laboratory and a balance room. The large undergraduate laboratory has working space for 50 students.

A feature of the arrangement of space in the new building is the segregation of certain kinds of work in rooms designed for special purposes. The preparation and purification of all chemicals will be carried out in the two preparation laboratories. One contains various types of distilling and subliming apparatus, vacuum pumps, electrical furnaces, and generators furnishing a variety of pure gases. The

ceilings insulated with a layer of cork board. The room contains a pier, which is insulated from the earth by a layer of the same material. The temperature of the air in the room is controlled by an electric thermostat and heater, and the air is kept in motion by an electric fan. Provision is made for a future installation of brine coils for low temperature work.

Along the east side of the building is a series of research laboratories and dark rooms. Two rooms are designed for electrical conductivity and transference investigations. A large constant temperature bath in the doorway between the two rooms serves both of them. The electrical conductance room contains a large sound-proof booth, resting on a thick layer of felt. An adjoining room contains the apparatus for producing and controlling the high frequency alternating current and a still for the production of conductivity water. In this series is to be found also the

following special rooms: for the calibration of electrical measuring instruments; for the polarimeter; for the purification, storage and handling of mercury; for investigations in colloid or photochemistry; a dark room for ultramicroscopic investigations and another dark room for photographic work and refractometric measurements.

A large laboratory is equipped for the use of students in advanced physical and electrochemistry. In



FIG. VI.—LABORATORY FOR STUDY OF PAINTS, OILS AND TARS

this room is also situated the electrical distribution board for the division. In addition to the regular currents found in other parts of the building this distributing board is provided with 250 volt a. c. and d. c. connections.

There are several offices and private laboratories for the instructional staff; the general office of the division is provided with a collection of books and reprints and a large plotting table with drafting equipment. Opening off this room is the office and private laboratory of the professor in charge of the division. Two other offices with private laboratories are advantageously placed. An ingenious device permits some of these rooms to be used either as offices or as laboratories. A narrow ledge is placed against the wall at the height of an ordinary table. Upon this ledge is arranged a system of service supplies usually required in a laboratory. By placing a table against the ledge a convenient laboratory desk is obtained and by removing the table the room is quickly transformed into an office.

The work tables and laboratory desks are in most instances constructed with built-up birch wood tops, treated with aniline black. In some of the rooms, however, alberene stone has been used. Many of the lockers in the desks are fitted with wire-glass doors.

THE DIVISION OF APPLIED CHEMISTRY occupies the south end of the building upon the basement and first floor. The equipment of this division provides for work in all lines of industrial chemistry and metallurgy excepting water chemistry and electrochemistry.

The large general industrial laboratory in the base-

ment has desks for about fifty students in advanced industrial and metallurgical courses. The desks are of a special design with high sanitary base. The west half of the room is used for the installation of larger scale apparatus and machinery for both instruction and research. Supply pipes for gas, compressed air, high pressure steam, vacuum, etc., are conveniently placed, as well as switchboards with outlets for the power circuits. A room for fine balances and an instructor's office and record room are adjacent to this room.

METALLURGICAL WORK is provided for in a suite of rooms. For assaying and furnace work of all kinds a large room contains permanent installations of coal-, oil- and gas-fired muffle and crucible furnaces, a large roasting furnace, besides various experimental furnaces of special design. A fuel storage room is on the east side while oil supply is kept in a large underground reservoir located outside the building and designed for convenient filling from the street. From this tank the oil is forced to a constant-level distributing tank in the fuel room. The pyrometer laboratory located opposite the furnace room is designed for calibration and use of pyrometers, cooling curve work and preparation of metal specimens. Adjacent to this is the metallography laboratory with a pier for supporting two large metallurgical microscopes with cameras. A third microscope will be supported on the firm wall of the vault stack on one side of the room. A large dark room opens from this laboratory with ample facilities for the photographic work of metallography. All of the rooms of this suite have suitable electrical circuits for small experimental furnaces and electro-



FIG. VII.—TYPICAL PRIVATE LABORATORY FOR RESEARCH

lytic work. A large storeroom and an ore sampling room are placed near the furnace room.

In the basement of the older portion of the building several smaller research rooms are equipped for the study of various problems. Here also are shop facilities for work in connection with industrial courses and investigations; a coal grinding and sampling room, and other rooms for special purposes.



On the first floor are laboratories for gas and fuel analysis, calorimetry, technology of gases, paints, oils, asphalts, paper, textiles, etc., as well as the laboratories for the chemical work of the Engineering Experiment Station and the State Board of Administration.

The laboratory for gas and fuel analysis accommodates 120 students working in sections. The student calorimeter room permits the use of 15 calorimeters at once. A balance room is adjacent to this laboratory.

Three laboratories for advanced work in fuels, oils, road materials, tars, paints, etc., are fitted with the standard equipment of the new laboratory as well as for steam and electrical distillation. A large dark room is provided for photometric and optical testing.

The suite of rooms in the older portion of the building devoted to state chemical work is of especial interest. Here the chemical work for the Engineering Experiment Station, the State Geological Survey and for various university departments is done, and here is carried out the chemical work connected with fuel inspection for the university and for the State



FIG. VIII—LABORATORY FOR ELECTROCHEMICAL RESEARCH

Board of Administration. All coal used in the various state institutions is purchased upon the basis of analyses and calorimetric determinations made by this laboratory.

Several rooms devoted to offices and research laboratories complete the space allotted to this division.

THE DIVISION OF SANITARY CHEMISTRY AND THE STATE WATER SURVEY occupy the ground floor at the north end of the building. Offices are provided for the director, the chief engineer, the assistant engineers and draftsmen. In the drafting room is a special library of sanitary chemistry. Separate laboratories are provided for sanitary chemical analysis, bacteriological examination, and mineral analysis. These laboratories are separated from each other by glass partitions, making a particularly light and attractive

environment. There are two incubator rooms, one kept at  $20^{\circ}$  and the other at  $37.5^{\circ}$ , heating and regulation being accomplished by accurate electrical devices. In the wash room there are large sinks and drain boards; the permutit water-softening apparatus; a hot air sterilizer with an insulated oven; and a roomy new-model autoclave which is operated by high pressure steam. There is also provided a laboratory for research on special problems; a private laboratory for the director; a conference room; a special fireproof vault and a well-located shipping room.

The student laboratories for instruction in water analysis contain 48 desks as well as rooms for ammonia distillations, technical experiments, incubators and balance cases.

#### THE GENERAL SERVICE EQUIPMENT

STOREROOMS are placed conveniently about the building, one on the second floor, two on the third floor, and one on the fourth floor. The main stock room is in the basement, under the lecture room. An electric elevator facilitates the distribution of supplies to all floors.

THE WORK SHOPS are three in number. The *mechanician's* shop is equipped with lathe, power-saw, emery wheels, drill press, oxyacetylene outfit and tools needed for the manufacture and repair of apparatus. The *glass blower's* equipment includes 13 blowpipes, a small lathe, and a motor for grinding glass apparatus; a small laboratory is also equipped for instruction in glass blowing. The *plumber's* shop contains tools and materials needed for making repairs to the plumbing of the building.

FIREPROOF VAULTS AND THE ELEVATOR are available from all floors.

DISTILLED WATER is produced by two special stills designed by Professor Noyes. The new still, located in the attic of the new building, is shown in detail in Fig. X. The boiler, Fig. 1, is 36 in. high and 24 in. in diameter and is made of heavy copper. The heating coil *A* is a  $\frac{3}{4}$ -in. copper pipe, 15 ft. in length and connected with the high pressure steam, *G* is a drain cock, *D* an 8-in. manhole, *C* a constant level valve and *B* is a glass gauge. The head *E* is 20 in. high and 8 in. in diameter and contains 8 shelves shown at *O* each with a two-inch opening arranged alternately to allow steam to pass upward. The edge of each shelf is turned up  $\frac{1}{2}$  in.; condensed water runs back into the boiler through a tube, *H*, which rises  $\frac{1}{4}$  in. above the shelf and extends within  $\frac{1}{8}$  in. of the next lower shelf. The head is lined with pure tin and all soldering is done with pure tin.

The condenser box, shown in Fig. 3, is 12 in. deep, on the bottom of which is placed the  $1\frac{1}{4}$ -in. tin condensing tube *AB*. The end *LE* is 4 in. higher than the end *GF* to give proper drainage. The successive partitions from *HE* to *FG* have a space of two inches at alternate ends, while *FG* is solid. The compartment *LHGK* is designed as a flue to carry off gases and steam to a ventilator with a strong draft. The sides *HG* and *EF*, shown in Figs. 2 and

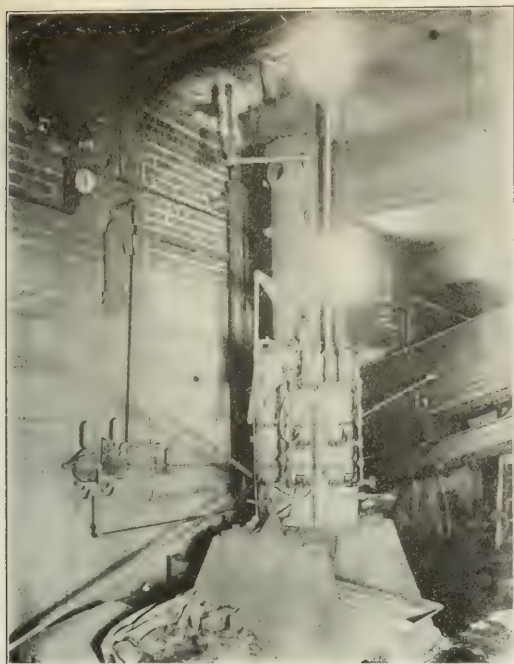


FIG. IX.—LOW TEMPERATURE COKING APPARATUS

4, have windows to facilitate the ventilation. *O* and the opening near *K* are drains. The box *LEFK* is covered, but the small compartment below *FG* is open. Feed water enters at *K'* through a constant level valve set to give a depth of 8 in. at *FG* and 4 in. at *HE*. As it passes back and forth across the box it is warmed by the condensation within the tube *AB*. The single coil *CD* is a 3-in. copper tube connected with the high-pressure steam permitting more thorough preheating of the feed water. The exit *I* is raised two inches above the bottom of the condenser box in order to leave behind any sediment. From *I* the feed water passes to *C* (Fig. 1). The final condensation of the steam is effected in the compartment below *FG*, into which cold water passes through *P*. The overflow *S* rises 8 inches from the bottom. The distilled water leaves the apparatus at *B* and is stored in a heavily tinned copper tank which has a capacity of 2800 liters.

The feed water used is rain water from cisterns when this is available; at other times use is made of the water from the university wells which has been softened by the permutit process. An amount of alkaline permanganate is added which is slightly in excess of the amount required by the oxygen consuming power of the feed water. The capacity of the still is 80–100 liters per hour but when running at full capacity the product contains somewhat more ammonia than is desirable. When running at the rate of 60 liters per hour the nitrogen in the form of ammonia may be reduced to 0.06 part per million or less. The original water contains 2.0 parts per

million of nitrogen in the form of ammonia and 0.15 part as albuminoid ammonia.

HYDROGEN SULFIDE is to be generated in an attic room which is thoroughly ventilated and completely shut off from the rest of the building. It is planned to install a generator patterned after the one in use at the University of Wisconsin. Distribution is to be made through a 500-gallon gas tank in order that the pressure of the gas may be as constant as possible.

STEAM is supplied from the university power house, through the service tunnel. The heating system is run under four pounds pressure; the supply for the steam baths and laboratories is under a pressure of 15 lbs.; the high-pressure system is run at 30 lbs.

VACUUM is furnished by a 14 × 8 in. vacuum pump in the machine room, which gives a vacuum equal to from 16 to 20 in. of mercury. In many of the research rooms and some of the student laboratories a special vacuum system is available which produces an exhaustion equivalent to 1 millimeter of mercury.

COMPRESSED AIR is also supplied from the machine room in which is placed an air compressor capable of supplying a pressure up to 80 lbs. per square inch.

THE LIBRARY is located on the second floor at the east front in a room which is commodious, attractive, fireproof and easily accessible from all parts of the building. The library contains 3500 books selected to cover all branches of pure and applied chemistry and 6500 bound volumes of chemical periodicals. An important part of the library equipment is the *Palmer Memorial Library*, which consists of the private collection of chemical works of the late Professor Arthur W. Palmer. In addition to the bound volumes the library receives 105 current periodicals.

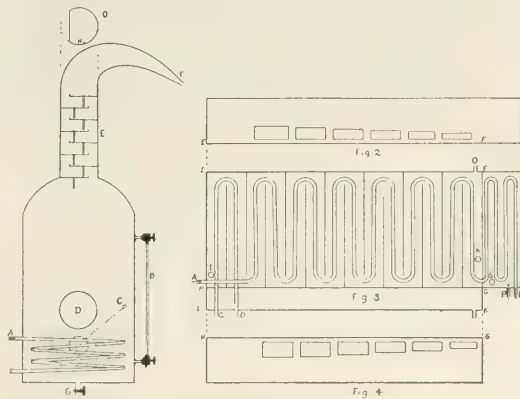


FIG. X.—DISTILLED WATER APPARATUS

At present the book stacks contain 1500 linear feet of shelving; the plans provide for doubling this amount. Further expansion of both the library and reading room is possible by the use of an adjoining seminar room. The card catalogue lists under both author and subject all literature of interest to chemists which is to be found upon the university campus. The



library is open daily (except Sunday) from 7:45 A.M. to 10:00 P.M.

THE LECTURE ROOM is an amphitheatre of hexagonal shape situated in the court at the center of the building. It was erected in 1902, but was remodelled in 1914, making it fireproof. The seats, of which there are 390, are elevated upon tiers of concrete benches, affording a good view of the lecture table from all parts of the room. It may be entered from the first floor directly opposite the main entrance or from the connecting corridor and from the second-floor corridor. The lighting is mainly by skylight, provision being made for darkening the room for the use of the lantern.

Three other smaller lecture rooms seating 100, 75 and 60, respectively, are in use for smaller classes. Each lecture room has a preparation room and is sup-

furnishing delightful social quarters. An open grate, appropriate decorations and comfortable furniture make these rooms homelike and popular.

#### GUESTS OF THE DEPARTMENT

THE DIVISION OF BACTERIOLOGY OF THE DEPARTMENT OF BOTANY occupies temporary quarters on the third floor. The large laboratory, which accommodates the students in elementary bacteriology, has 108 lockers. There are two smaller laboratories, one for applied bacteriology with locker provision for 34 students and the other for research with accommodations for 44 graduate students. Included in this suite are smaller rooms arranged and equipped as follows: a preparation room, a sterilization room, two constant temperature rooms which are kept at 37.5° and 20°, respectively, a seminar room, a supply



FIG. XI.—THE CHEMICAL LIBRARY

plied with the equipment needed for lecture demonstration. The lecture room used jointly by physical and applied chemistry has a lecture table with movable end sections, permitting experiments to be set up in the preparation room or displays to be arranged in the museum. In addition to these four rooms there are eight recitation rooms and three seminar rooms.

THE MUSEUM contains an extensive collection of mineral specimens, samples of manufactured products and other displays of interest to students of chemistry. Some cases containing specimens of general interest are placed in the connecting corridors in which are hung pictures of noted chemists.

THE CLUB ROOM is an attractive room on the first floor provided as a home for the Chemical Club and *The Illinois Chemist*. The adjoining seminar room may be thrown open by double doors, the two rooms

room, two offices and two private laboratories for use of the teaching force.

The furniture and arrangement of these rooms are in harmony with that in the other portions of the building. As future growth makes expansion necessary, these rooms are to be occupied by the department of chemistry.

THE BOARD OF TRUSTEES OF THE UNITED STATES PHARMACOPOEIAL CONVENTION is granted the use of an office and private laboratory upon the third floor which are occupied by its chairman, Dr. J. H. Beal. While the work done here is not strictly a part of the university curriculum, the presence of this laboratory is a great help to those students who are interested in pharmaceutical chemistry. Dr. Beal has consented to act as director of pharmaceutical research and accepts a limited number of graduate students for work upon special problems.

## THE VALUE OF THE BUILDING AND EQUIPMENT

The original cost of the building erected in 1902 was little short of the total appropriation which was \$100,000. For equipment a special appropriation of \$20,000 was made in 1903, and frequent additions to these amounts were made from time to time. In the following estimate of the present valuation of the entire plant of the department the items relating to the old building and the stock are taken from the report of the university comptroller June 30, 1915,

and the data concerning the new building were supplied by the office of the supervising architect April 25, 1916:

Chemistry building (old portion).....	\$ 80,200.00
Laboratory apparatus.....	32,095.08
Office equipment.....	1,241.95
Furniture.....	5,433.62
Small apparatus and chemicals .....	23,000.00
New building, including permanent equipment.....	\$400,000.00
TOTAL VALUATION.....	\$541,970.65

## ADDRESSES

THE WAR AND AMERICAN CHEMICAL INDUSTRY<sup>1</sup>By RAYMOND F. BACON<sup>2</sup>

The year 1915 will always be a notable one in the history of chemical manufacture in the United States. For fifty years several branches of chemical industry had been peering half-formed through the mists of chemical and political economics. For several decades other branches of manufacture had been affected by malnutrition and had failed to grow in strength. However, the present European war has exerted a reconstructive action, and since the beginning of last year chemical industry has borne rule over our other manufacturing activities. Indeed, the past year marked the commencement of a period of industrial transition, national in scope, and characterized by the serious endeavors of American enterprise and ingenuity to bridge the gap which has existed in the chemical industry of the United States as compared with that of Germany. In this stupendous undertaking, carried out so far with conspicuous success, the industrialists of to-day have not collected the materials for the structure, but they have designed it and have been active in the work of building. Although perhaps a weak bridge, and built upon shifting sands, it has provided at least a temporary channel of escape from European dominance, and it is constantly being reinforced and otherwise strengthened.

It has been indicated<sup>3</sup> that the measure of a country's appreciation of the value of chemistry in its material development and the extent to which it utilizes this science in its manufactures, generally measure quite accurately the industrial progress and prosperity of that country. Moreover, the quality and value of an industrial product are based upon the application of correct principles in its conception, preparation, and use, and the correct principles can result only from scientific research.<sup>4</sup> The wonderful headway made so far by our newer chemical industries has resulted largely from carefully organized research, but we are still far behind the pace which Germany has started. We must therefore strive for a greater recognition of the national value of industrial research.

## THE WAR AND ITS CHEMICAL INFLUENCES

At the expense of the unfortunate warring countries, the manufacturers of the United States have played a most important part in the markets of the world in the last thirteen months, and all possible efforts are being made through individual enterprise and through various commercial organizations to deal adequately with the export situation. Not only has the war opened the gates of world-wide commerce to the United States, but it has provided a tariff wall that has allowed our nation to develop its industries along broad lines.

<sup>1</sup> A general paper presented at the Urbana Meeting of the American Chemical Society, on April 18, 1916.

<sup>2</sup> Director of the Mellon Institute of Industrial Research, Pittsburgh, Pa.

<sup>3</sup> Bacon, *Science*, **40** (1914), 871-81.

<sup>4</sup> Bacon, *Sci. Am. Suppl.*, **80** (1915), 334.

While almost every branch of American industry has been directly or indirectly affected by the European war, its influences have been particularly felt upon all branches of chemical industry. It has operated detrimentally to many lines of manufacture, but in the business connected with the furnishing of war supplies there has naturally been a great stimulus to trade.

Two great interests in the United States have been especially acted upon by the prevailing war. The total cessation of the shipment of potassium salts from Germany to this country has seriously disabled the American fertilizer industry; this handicap has, in fact, resulted in material injury to the agricultural sections using fertilizers, particularly the cotton belt of the South.<sup>1</sup> Likewise the almost total stoppage of shipments of dyestuffs from the great German factories, which ensued with the opening of the war, over a year ago, has been seriously felt throughout the textile, paint, and other of our industries in which dyestuffs are consumed in large quantities.

As the result of international negotiations, there have been, from time to time, some transatlantic movements of dyestuffs and potassium salts, mostly, it is understood, through neutral ports adjacent to Germany. The United States has secured a share of these commodities, but the importations of potash have been very limited indeed, when compared with the shipments of dyestuffs which have occasionally reached the American markets. It has also been possible to obtain supplies of certain needed dyes through Swiss manufacturers, in exchange for intermediates shipped from the United States to Switzerland. Then, too, there have been importations of logwood and other vegetable dyestuffs from colonial possessions of several of the warring nations.

With such an acute situation confronting several of our leading industries, there has naturally been great activity to assist in meeting it, and especially to encourage the development of a domestic production of potash fertilizer material and dyestuffs within the nation; and material progress has been made in the production of dyes and chemicals from the increasing quantities of intermediates supplied from many new sources throughout the country. The present crisis has, in fact, evoked deep interest on the part of all concerned—tar distillers, manufacturers of chemicals, manufacturers of dyestuffs, the many users of dyes, and American economists. The producers of "by-product coke" have shown a gratifying readiness to multiply their recovery plants for the production of benzol and tar, and considerable capital and experience have been embarked in steps to build up a distinctly American coal-tar chemical industry.

## THE MANUFACTURE OF PRODUCTS FORMERLY IMPORTED FROM EUROPE

The developments which have recently taken place in the manufacture of products formerly imported largely or entirely

<sup>1</sup> The grand total of the world's sale of potassium salts by Germany amounted to 680,000 metric tons of actual K<sub>2</sub>O in 1915 as against 904,000 metric tons in 1914.



from Europe, are primarily instigated by the activity of those manufacturers who are interested in the industries discussed below.

**AMERICAN COAL PRODUCTS**—Under prevailing abnormal conditions, quite a large number of small plants have been erected for the production of products derived from coal. On the whole, these are now being operated at a pleasing profit; but at the end of the war many of them will probably fall like autumn leaves. While it is true that some of them may struggle on and pawn their war-bridal gifts in a hopeless endeavor to establish permanent business, only those which have been constructed on a sound economic basis will be numbered among the eventual survivors.

It is well known to chemists that the manufacture of products derived from coal is not an industry *per se*. It is, in fact, based upon, or rather an extension of, the manufacture of certain halogens, mineral acids, and alkalies. It follows from this dependence that a permanent coal products chemical industry cannot be created in America except by cooperation with or enlargement of the American acid and alkali manufacturing companies. The full realization of this basic consideration insures the long life of several of the large American producers in this field. These companies seem to be fully cognizant of the fact that with prices ten to fifteen times normal, it is now possible to manufacture some coal products with large profit in this country, but that with the return to normal conditions all processes must be combined with strict attention to rigid scientific methods.

Experience shows that the coal products chemical industry is vital to national defense—the basis of modern warcraft and hence the real source of military strength. Munitions cannot be manufactured in sufficient quantities during the exchange of diplomatic notes prior to the inception of hostilities; they must be produced and stored for future use long in advance of war. Under the aspect of our present international relations, none can doubt the propriety of increasing our means of defense. This can give no cause of offense nor increase the danger of a rupture. If, on the other hand, our Government should fold its arms in security and at last be involved in war for the maintenance of its rights without adequate preparation, the responsibility would be of the gravest character. Should collision be avoided, as we all sincerely hope it may be, the expenditures in making the preparations will not be lost. One main national defense is that great coal products chemical plants be established and operated continuously at commercial profits during peace, in order that they will be immediately available to produce unlimited ammunition during times of war. The establishment of a complete and profitable coal products industry is essential for the success of any program of national preparedness.

Such an industry must, however, be founded and operated on a basis to keep abreast with scientific progress. The steps essential to this progress are as follows:<sup>1</sup> The manufacture of nitric acid from the air on a scale which will render the nation entirely independent of supplies of foreign nitrates; a reasonable tariff which will divide coal products into classes according to their degree of advancement in manufacture and will levy duties proportionate to this degree; and the provision of an anti-dumping clause, to prevent unfair competition instituted for the purpose of destroying American industry.

It seems to be assured that a great coal products industry will result from the present activity and interest, but the degree to which this industry attains perfection will be proportionate to the extent with which the fundamental requirements for its profitable operations are provided.

**BENZOL**—During the past fifteen years the production of benzol has steadily increased in the United States. In fact, there was enough benzol at all times for the manufacture of

dyes, if a coal products industry had been established by the assistance of the Federal Government and by the sustained support of the American textile industrialists. Not only were both of these factors lacking, but, until they were obliged to alter their attitude, our textile manufacturers persistently gave preference to the products of English and German manufacturers instead of to corresponding dyes of American manufacture.

The annual production of benzol in the United States amounted to about 3,000,000 gallons before the war; by the end of 1915, however, it had increased to about 15,000,000 gallons. A heavy production (25,000,000 gallons) of American benzol is now assured,<sup>1</sup> and, when the war ends, the output from our plants will be so abundant that it may become available as an automobile motor fuel.

Table I gives the locations and capacities of the light oil plants in operation in the United States.

TABLE I—LIGHT OIL (50-60 PER CENT BENZOL) PLANTS IN THE UNITED STATES

COMPANIES	LOCATION OF PLANTS	Capacity Gallons per Day
Allegheny Coke Co.	Glassport, Pa.	1,800
Brier Hill Steel Co.	Youngstown, Ohio(a)	4,500
Cambria Steel Co.	Johnstown, Pa.	6,000
Camden Coke Co.	Camden, N. J.(a)	12,500
Citizens' Gas Co.	Indianapolis, Ind.	3,000
Gulf State Steel Co.	Gadsden, Ala.(a)	2,200
Inland Steel Co.	Indiana Harbor, Ind.	4,800
Lackawanna Iron and Steel Co.	Buffalo, N. Y.	6,500
	Lebanon, Pa.	1,600
Laclede Coke and Gas Co.	St. Louis, Mo.	1,800
Lehigh Coke Co.	South Bethlehem, Pa.	6,000
Maryland Steel Co.	Sparrows Point, Md.	2,500
Milwaukee Coke and Gas Co.	Milwaukee, Wis.	2,000
New England Gas and Coke Co.	Boston, Mass.	5,000
Republic Iron and Steel Co.	Youngstown, Ohio	5,500
River Furnace Co.	Cleveland, Ohio(a)	9,500
Solvay Process Co.	Birmingham, Chicago, Cleveland, Detroit, Holt, Ala., Philadelphia, Lebanon, Pa., and Syracuse	40,000(b)
Toledo Furnace Co.	Toledo, Ohio(a)	5,000
U. S. Steel Corporation	Fairfield, Ala.	15,000
	Farrell, Pa.	6,000
	Gary, Ind., and	16,000
	Joliet, Ill.(a)	9,000
Woodward Iron Co.	Woodward, Ala.	2,000
Youngstown Sheet and Tube Co.	Youngstown, Ohio(a)	11,000
Zenith Furnace Co.	Duluth, Minn.	600

(a) Not yet in operation.

(b) Approximate estimate.

**CARBOLIC ACID**—The production of carbolic acid has recently increased largely, mainly owing to the demand for picric acid for war purposes. With the exception that the production of the works of Thomas A. Edison—about 12,000 pounds per day—is used in the manufacture of phonographic records, the large quantities of carbolic acid which have been produced have not therefore become generally available for domestic use. However, a number of American plants have lately begun production which can be used for other commercial purposes to the advantage of the nation, and still other sources of supply will soon be ready. An annual production of 10,000,000 lbs. is needed to supply the national demand.

Carbolic acid was not produced in this country in large quantity until after the outbreak of the war, but synthetic carbolic acid was manufactured by the Smet-Solvay Company from benzol at Syracuse, N. Y., in 1900 and the following years, in quantities up to 2,500 lbs. per day. This carbolic acid was synthesized into picric acid, which was purchased by the United States Government.

**NAPHTHALENE**—The production of naphthalene has increased to an unprecedented extent during the past year. Before the war, the production in the United States amounted to about 2,500,000 lbs., but it is now over 7,000,000 lbs. The normal American consumption is about 9,000,000 lbs.; but by the end of this year, the output of the American plants will undoubtedly be sufficient to insure an adequate supply for all domestic

<sup>1</sup> About 10,000 gallons of light oil are produced daily by the distillers of coal tar; the remainder of the production comes from the light oil plants listed in Table I.

needs, with the result that England and Germany shall thereafter be unable to export naphthalene to this country.

**ANILINE PRODUCTS**—The five plants for the manufacture of aniline colors established in this country before the war, have, during the past fifteen months, extended their production to the utmost capacity in keeping with safety for the investments involved. Prior to the war these establishments produced a somewhat limited quantity of coal-tar colors, the annual output being about 3,300 short tons. For the purpose of their manufacture, intermediates were largely imported, principally from Germany. These were assembled into finished dyes by the aid of a few American chemicals and by the labor of about 400 workmen.

Before the war had continued a year, the output of American coal-tar colors had doubled, and at the present time it is, at least, three times the production before the war. This great increment involved an enormous increase in the production of coal-tar crudes, and it also induced the organization of companies for the manufacture of intermediates, especially of aniline.

The domestic supply of crudes has assumed quite large proportions. In December, 1915, the approximate monthly output, in short tons, was as follows: benzol, 7,500; toluol, 1,870; xylol, 950; naphthalene, 12,500; and carbolic acid, 10,000 tons. The demand for benzol, toluol and carbolic acid to be used in the manufacture of explosives is at present so abnormally high that there has been considerable difficulty in obtaining sufficient supplies for the manufacture of coal-tar intermediates. Nevertheless, the manufacture of these latter, especially of aniline, has suddenly grown to considerable proportions and it is constantly increasing. There are at least twenty concerns engaged in this branch of manufacture and one is constantly learning of others which are contemplating entrance into the field. Approximately an equal number of firms is now engaged in making finished coal-tar dyestuffs.<sup>1</sup> Synthetic indigo is being manufactured at Midland, Mich.

**POTASH**—During 1915, steps were finally taken to produce salts of potassium from mineral sources on a commercial scale in the United States. It is probable that Searles Lake in San Bernardino County, Cal., will be the most important American source of potash, but the war condition enabled other sources to be hastily developed.<sup>2</sup> The alunite deposits near Marysvale, Utah, thus became the first important producers of potash in this country. The production of potassium sulfate on a commercial basis was begun at Marysvale in October, 1915, by the Mineral Products Corporation, and this concern is contemplating doubling its present capacity.

The Searles Lake potassium-bearing brine will, in the near future, be treated for the commercial production of potassium salts and borax. Work has also been begun which will probably eventuate in the commercial recovery of potassium salts from the brine of the Great Salt Lake in Utah. In their present development, practically all of the producers of potassium salts are employing war-time processes which could not compete with the German producers on a pre-war basis. However, it is possible that potash will never be so cheap as it was before the war, for it is one of those commodities on which it will be most easy for Germany to levy and collect taxes in the future.

The scarcity of potash has caused a renewal of interest in the growths of kelp on the Pacific coast, regarding which much has appeared in the technical and popular press. Before this year most of the companies attempting to develop the kelp industry have been of limited capital. Recently, however, several concerns with, it is reported, adequate capital to carry their

developments through to a successful issue, have engaged in this industry, so that at the present time a limited amount of dried kelp is being produced and a considerable increase in this production is shortly expected. One of the prominent packing companies of Chicago has a kelp potash plant in operation at San Diego, Cal.

With the present high price of potash, it is said that the drying of kelp is a profitable business. It is predicted that such conditions will enable the industry to get a start and to work out its numerous problems. With normal prices of potash, kelp must be worked in plants of large capacity, well designed, with a minimum of labor, and every possible economy effected. All of the profitable by-products (iodine, algin, etc.) must be saved. Laucks<sup>3</sup> is of the opinion that if, even after the war, the price remains above \$35 per ton for 80 per cent muriate of potash, kelp can be worked at a profit in a properly designed plant.

Potash is now being recovered in the cement industry, and the manufacture of potassium salts from the refuse of molasses is to be begun in Colorado.

**BARIUM PRODUCTS**—Before the war about 40,000 tons of barite were annually shipped to the United States from Germany, and practically all of this considerable importation was used in the manufacture of lithopone, which was the only barium product made on a large scale in this country up to the time of the European conflict. It is said that there are now six manufacturers<sup>2</sup> engaged in the production of large quantities of lithopone from barite supplied from deposits in the states of Tennessee, Kentucky, Virginia and Missouri. Five American companies are also manufacturing barium compounds (chloride, carbonate, hydroxide, nitrate, and dioxide of barium<sup>3</sup>), thus giving still further production to American mines—possibly double the quantity of barite formerly imported. Stone<sup>4</sup> has stated that with the manufacture of barium salts we have a practically new industry which will make us independent of Europe in the future.

#### THE EFFECT OF THE WAR UPON CERTAIN ESTABLISHED INDUSTRIES

The war has had a salubrious effect on many of our well-established industries. It has, in fact, given rise to a general prosperity in certain lines which is most agreeable to those who live secure from the immediate calamities of it.

In particular, our munition plants have been hyper-active. It may be noted here, however, that four of the largest establishments are now turning out considerable orders for the United States, in spite of the enormous foreign orders which were reported to make work for our own Government entirely out of the question.

**MINERAL ACIDS**—There has never been any foreign competition on sulfuric, nitric and hydrochloric acids, mainly because of the heavy transportation charges, American manufacturers being able to make these acids at prices which render their importation unprofitable. Until about the middle of 1915, American manufacturers were entirely able to supply the needs of the country as usual; but as the war continued and the demand for munition purposes gradually increased, the requirement for acids became so urgent that the manufacturers thereof have found great difficulty in supplying them. As a consequence, many American consumers are unable to secure enough supplies to conduct their technochemical operations; or when they do get sufficient for their present business, they are unable to ob-

<sup>1</sup> *Met. Chem. Eng.*, **14** (1916), 308.

<sup>2</sup> Two of these are located in Tennessee: the Durex Chemical Works at Sweetwater and the Clinchfield Products Association at Johnson City.

<sup>3</sup> The consumption of "barium binoxide" is large, for the value of the hydrogen dioxide used annually in the United States amounts to \$8,000,000. Before the war, England supplied much of the barium dioxide used by the manufacturers of hydrogen dioxide.

<sup>4</sup> *THIS JOURNAL*, **7** (1915), 992; see also Toch, *Ibid.*, 993.

<sup>1</sup> Norton, *THIS JOURNAL*, **8** (1916), 167 and 287, has reviewed the dyestuff situation in the United States at the close of 1915. His report includes a list of the American dyestuff manufacturers.

<sup>2</sup> For example, the alkali lakes in Sheridan County, Nebraska, from which potassium salts are being produced by several companies.



tain any additional quantity for an increased business, so that the acid situation has been and is a very serious one indeed.

A prominent manufacturer of barium products stated several months ago that he has been unable to take contracts on barium chloride, nitrate or sulfate because it is absolutely out of the question to obtain the necessary acids. "The people with whom we have dealt for our acids for years are simply either refusing to give us any material or are supplying us with ridiculously small lots at enormous prices, for there are other channels which buy larger quantities and pay more than the peaceful manufacturer can afford."

War demands for sulfuric acid have stimulated the production of the great Tennessee acid plants to a maximum, copper being in reality only a by-product now. A number of important additions have been made to these and to numerous other sulfuric acid plants. The advance in both sulfuric acid and potash has put up the price of complete fertilizer and bulk acid phosphates, so that Tennessee phosphate properties have been stimulated both as to production and as to efforts to decrease metallurgical losses. Since the price of sulfuric acid began to advance, a number of the manufacturers of fertilizers have installed acid plants at their works, which indicates that the ruling quotations on sulfuric acid are more or less above the figure at which they think they themselves can produce it. For instance, one company producing superphosphate in Baltimore now has an output of 300,000 tons of acid per year.

Because of the large markets for sulfuric acid, its production from waste gases is now carried out at copper smelters in Arizona and California, as well as in Tennessee; and by-product acid from the sulfurous fumes of zinc smelters is being made at ten places in Colorado, Illinois, Indiana, Kansas, Ohio, and Pennsylvania. Liquefied sulfur dioxide is now being produced by the Virginia Smelting Company, of West Norfolk, Va., and the demands of the sulfate pulp industry may give rise to the recovery of sulfur dioxide at other metallurgical plants.

As indicated above, to insure the presence of our chemical self-containedness, it will be necessary to manufacture nitric acid from the air on a suitably large scale, and magnificent water power is available at a number of accessible points for the establishment of this industry. It was in the founding of electrochemical industries upon a grand scale at Niagara Falls that the United States first disclosed her latent power as a factor in the field of chemical industry; but we may derive much profit by careful study of the systematic and exhaustive manner in which the water power of Norway has been regulated, stored up, and pressed into the service of applied electrochemistry. Let us hope that industrialists will avail themselves of this opportunity and will enlist the services of our best technical talent. The Pauling process is in operation on a small scale (4 tons per day) at Great Falls, N. C., by the Southern Electrochemical Company, and the field invites the invasion by modern industrialism.

**AMMONIUM SULFATE**—The production of ammonia, calculated as ammonium sulfate, in the United States during 1915 is estimated to have been 212,000 tons, an increase of 17,000 tons upon the actual output in 1914. It is further estimated that approximately 80 per cent of the 1915 output was from by-product coke plants, and in view of the demand for coke and coal products chemicals it seems certain that a further substantial increase in output of ammonium sulfate in the United States must be counted on in 1916.

It is predicted that the question of sulfuric acid supplies will become more acute as the demand for ammonia for munition purposes increases, and there must therefore be some shrinkage in the production of ammonium sulfate; but munition manufacturers are able to use concentrated ammonia liquor instead of ammonium sulfate, so that no handicap will result.

**SODIUM COMPOUNDS**—About 1,500,000 tons of caustic soda,

soda ash, and bleaching powder are now being manufactured in the United States. For a short period after the war, American manufacturers were able to continue their supply of these products in the ordinary way, but the cessation of shipments of sodium compounds from European countries to other countries by reason of the war, eventuated in a demand for American products to supply this shortage. A large export business has thus been established by the American manufacturers and great prosperity has resulted.

In March, 1915, the stocks of soda ash in this country had accumulated to such an extent as to create a depressing sentiment among producers and to urge the most heroic measures of relief. Plans had been formulated to undertake the development of increased outlets in South America; but before the foreign trade campaign could be initiated, the market underwent a complete change. The importance of soda ash as a war munition factor was the turning development, and with England, normally the mainstay of foreign consumption, conserving home supplies for its own exigent needs, the export demand for the American product and the stimulus to the domestic manufacture of explosives soon made heavy inroads upon the holdings in this country. The effect of these factors has been emphasized during the last few months by the increased requirements in the fields of regular consumption, namely, the soap, paper, glass, textile and petroleum industries. Confidence has been expressed that a good share of the business in soda ash, directly or incidentally due to the war, will be retained upon the restoration of peace; but there are not known to have been undertaken any definite plans for additional equipment on the strength of enduring trade in the product on anything like the present volume. In March, 1915, soda ash was procurable at 57½ cents per 100 lbs., on the basis of 48 per cent; by the close of 1915, \$1.85 was in effect. The developments since the first of the year have resulted in a more stirring range of prices, principally through the control of the open market by second hands, who now maintain 4 to 8 cents per lb. flat, for a 58 per cent test.

Caustic soda has attracted much interest because of the part which it plays in the manufacture of picric acid; in fact, it is principally through this medium that the reformation of soda ash has been accomplished. At the present time, supplies of caustic soda are reported to be slightly freer than those of soda ash, but they are well controlled, with second hands dominating the market for prompt delivery. The question of increasing the production of caustic soda is involved in the difficulty and uncertainty of soda ash supplies. The premium on bleaching powder would prove an incentive to the production of caustic soda by the electrolytic process; but those manufacturers who employ the old method yielding straight caustic soda, are said to have the advantage of large supplies of soda ash.

Other products now manufactured in this country are ferrocyanides of sodium and potassium, sodium and potassium chlorates, and sodium and potassium dichromates; and the manufacturers of these salts hold the whole American trade, for there are practically no importations from abroad. The manufacture of potassium ferrocyanide has been limited, owing to the inability of American manufacturers to secure potassium salts from Germany; consequently, most of them are said to be working almost exclusively on soda, and the paint manufacturers, who are large users, have attempted to produce their Prussian blue from the sodium salt instead of that of potassium. At the present time the domestic output of sodium ferrocyanide is fully engaged without beginning to satisfy requirements; but relief to the prevailing stringency is expected upon the arrival of imports.

The manufacture of sodium chlorate and dichromate<sup>1</sup> has con-

<sup>1</sup> During 1915, the Natural Products Refining Company, of Jersey City, N. J., enlarged its dichromate plant at a cost of about \$50,000.

tinued in increasing quantity during the past year, but the production of potassium chlorate and dichromate has been limited, owing to the inability of the manufacturers thereof to secure proper quantities of potassium chloride from Germany. The sodium salts have been substituted wherever possible. Contracts for sodium dichromate are now being made on a basis of 20 to 22 cents, as against  $4\frac{1}{2}$  to  $4\frac{3}{4}$  cents for 1915, and the producers have withdrawn all offers for forwarding delivery. The heavy export trade has been the principal factor for the unusual position of the market, supplemented by the influence of chrome ore.

GLASS—A wonderful prosperity obtains in the American glass industry. This is mainly attributable to the war, which shut off importations from Belgium, France and Germany, and thus permitted American manufacturers to build up an export trade with neutral countries formerly supplied by the belligerents; but the domestic demand for glass products has also greatly increased—to such an extent, in fact, that selling agencies have withdrawn prices and the "hand" window glass plants may be operated during the coming summer months.

The following tables of imports and exports are clearly indicative of the effect of the war on this industry.

TABLE II—THE VALUE OF U. S. GLASS AND GLASSWARE TRADE DURING THE SEVEN MONTHS ENDING WITH JANUARY, 1916, COMPARED WITH THE PREVIOUS YEAR

ARTICLE	IMPORTS		EXPORTS	
	1915	1916	1915	1916
Bottles, plain.....	\$529,779	\$370,095	\$375,275	\$1,036,109
Bottles, ornamented.....	366,305	157,771		
Window glass.....	583,880	121,157	393,980	1,342,870
Plate glass.....	93,384	394	242,292	897,793
Optical, dutiable.....	233,585	90,546		
Optical, free.....	301,130	146,045		
All other.....	1,108,276	353,858	1,231,984	3,031,208
TOTAL.....	\$3,216,339	\$1,239,866	\$2,243,531	\$6,307,980

TABLE III—THE VALUE OF GLASS EXPORTS DURING JANUARY, 1916, COMPARED WITH JANUARY, 1915

ARTICLE	1915	1916
Bottles.....	\$ 47,083	\$178,884
Window glass.....	140,571	229,797
Plate glass.....	70,275	56,776
All other.....	156,761	505,668
TOTAL.....	\$414,690	\$971,125

CHLORIDES OF CARBON—The manufacture of carbon tetrachloride has greatly increased in this country since the war. At the inception of hostilities the American manufacturers were probably producing one-half of the national consumption. Since the war they have greatly enlarged their plants, so that they are said to be now supplying all of the American trade; the consumption of carbon tetrachloride is continually increasing, but those in touch with its manufacture state that even after the close of the war the whole consumption of the United States will be manufactured here.

At the present time the production of the chlorides of carbon is mainly dependent upon the availability of supplies of carbon disulfide.<sup>1</sup> Just as soon as an economic process for chlorinating natural gas rich in methane is available, the latter will probably supplant carbon disulfide.

OXALIC ACID—The manufacture of oxalic acid has been much developed in this country during the past two years. A plant was established a number of years ago at Bradford, Pa., but up to the time of the war it constantly experienced trouble in competing with the European product because of the reduction of duty in the last tariff. However, since the war practically stopped the importation of foreign acid, the whole American consumption is now reported to be taken care of. At the present time there is a considerable shortage in supply of oxalic acid and the price is therefore high; but eventually this product will be manufactured to the full extent of the American consumption and the business will be held here.<sup>2</sup>

<sup>1</sup> A plant for the manufacture of this compound has lately been erected in Monongahela, Pa.; but E. R. Taylor, of Penn Yan, N. Y., continues to be the leading producer.

<sup>2</sup> Stone, *loc. cit.*

STEEL INDUSTRY—The steel mills are being operated on an unprecedented scale, and the great demand for ferrous products has been aptly compared to the days of activity in Pittsburgh in Civil War times, when, however, the mills were fewer in number than they are at present and there was no Gary or Birmingham to increase the nation's output of steel products. During the past year numerous lines of steel have more than doubled in value, but nation-wide buying still goes on apace.

The annual report of the Bethlehem Steel Corporation for 1915—the first full year of the war—illustrates the turgid prosperity obtaining in the field of ferrous metallurgy. The net income of the year amounted to \$17,762,812.61, as compared with \$5,590,020.18 for 1914. The orders on hand on December 31, 1915, amounted to \$175,432,895.19 against \$46,513,189.95 on the corresponding date in 1914. The average number of employees in the United States in 1915 was 22,064 against 15,586 in 1914.

During March, 1916, the Carnegie Steel Company, with its equipment of 59 blast furnaces, was operating all but four of them. These four were being repaired, but the Company, in operating 93.38 per cent of its total furnaces, surpassed all former records. It may be mentioned here that all of the active stacks of the Carnegie Steel Company have been modernized and are now producing more than 120 per cent of their original capacity as a whole.

The total number of American furnaces in blast at the close of 1915 was 310, against 236 reported at the end of the first half-year. The production of pig-iron in 1915 (29,916,213 gross tons) was the largest ever reported in the United States, with the one exception of 1913; it amounted to nearly twice that of fifteen years ago. Increasing numbers of inquiries are constantly coming in from foreign buyers, mainly in Italy, for large lots of Bessemer pig-iron.

At the present time a famine exists in the ferro-alloy market, owing to the fact that the war has excluded much manganese from English sources and all the German supplies. Ferro-manganese, which sold at \$38 a ton when the war broke out, is now being sold at steel centers for spot shipment at \$350 a ton and on contract sale covering a certain period of delivery at \$175 a ton; but willing buyers are unable to purchase much even at these fabulous figures. Next to carbon, manganese is the most important ingredient of steel; hence, with its price increased from 1.9 cents a pound to 8.75 cents a pound, its influence on the rising cost of steel is clearly apparent. War-time conditions have made the demand in this country for manganese ore the greatest in history, causing the searching out and the development of the limited domestic deposits as never before in the economic history of the nation.

Tungsten has also advanced to high levels, and consequently its ores are in very strong demand. As high as \$90 per unit has been paid for prompt delivery of ore carrying 60 per cent of  $\text{WO}_3$ , and \$110 per unit has been offered for 65 per cent concentrates, but even such high prices have apparently failed to bring out new supplies.<sup>1</sup> Of interest is the advertisement of the largest producer as well as consumer of tungsten ores in this country, that the highest prices will be offered for all kinds of tungsteniferous minerals. Perhaps tungsten ore from South American sources may solve the problem of increasing the supply.

The tremendous activity which obtains in the shipbuilding of the United States has advanced steel plate prices up 147 per cent since the war began. Then, too, carbuilders are operating their plants to capacity whenever it is possible to obtain steel. In one case, a prominent car construction company

<sup>1</sup> Owing to the high price of tungsten during 1915, there was a scramble among prospectors in Colorado, and several minor discoveries were reported over a widely scattered area. Two new mills to treat tungsten ores were erected during the year.



was obliged to withdraw its bid on 4,000 steel freight cars because it was totally unable to obtain steel for them under the contract time of delivery. The war devastating Europe has also been responsible for considerable of the activity enjoyed by the manufacturers of wire products.

California magnesite is being calcined for use in open-hearth steel furnaces; but at the close of the war this will probably be discontinued, and the Austrian supply will be resumed.

**ZINC**—Perhaps the most important commercial feature in connection with zinc smelting since the commencement of the war, was the expansion of the United States Steel Corporation, through its subsidiary, the Edgar Zinc Company, into the zinc-producing field. The new Donora, Pa., plant of this Corporation has a smelting capacity of 100,000 tons of zinc ore annually and a productive capacity of about 40,000 tons of spelter.

The total production of spelter by ore smelters in 1915 was 507,142 tons, against 370,312 tons in 1914. The production by quarters showed a steady increase, especially in the second quarter, when the important new plants of 1914—Rose Lake and Langeloth—began to strike their gait, when several of the older smelters began to start new furnaces, and when the resumption of work in several previously idle plants—particularly Caney, Dearing, and Altoona—began to count largely in the production. In the third quarter several of the small coal smelteries of earlier times, one or two new ones, and some of the older natural gas plants began operation.

**TIN SMELTING IN THE UNITED STATES**—The United States imports normally about 45,000 tons of tin annually, and of this quantity about 90 per cent is Straits tin, which is largely consumed in the manufacture of tin plate. The Straits Settlements impose a protective export duty on tin ores, thus

TABLE IV—THE PAST AND PRESENT MARKET VALUES OF VARIOUS STOCKS (a)

"ORDNANCE STOCKS"	Prices of Common Stock			
	July 30, 1914	June 4, 1915	April 10, 1916	
Bethlehem Steel.....	30	149	465	
Bliss (E. W.).....	85	340	420	
Canadian Explosives.....	88	330	350	
Colts Patent Fire Arms.....	165	360	825	
Du Pont (E. I.) Powder.....	120	410	352	
Electric Boat.....	15	80	370	
Hercules Powder.....	120	231	390	
Savage Arms.....	120	172		
Winchester Arms.....	1,190	1,570	2,000	

OTHER "WAR STOCKS"	Prices of Common Stock			
	July 30, 1914	June 4, 1915	April 12, 1916	
Allis Chalmers.....	6	17	28½/s	
American Car & Foundry.....	44½	53	71½	
American Can.....	19¼	43	60¼	
American Locomotive.....	20¼	50	76¼/s	
Baldwin Locomotive.....	41	52	104½/s	
Crucible Steel.....	14½	32	92	
New York Air Brake.....	60	88	141	
Pressed Steel Car.....	34	49	51	
Westinghouse Air Brake.....	120	129	137	

(a) It is impossible to furnish a complete list of the quotations on "chemical stocks" prior to the war, for many of these issues were traded in only through the secretaries or directors of the companies between stockholders and no official records are available. However, the following information was supplied by Messrs. Gilbert Elliott & Co., of New York, on March 20, 1916:

"The tremendous rise in 'powder stocks' since the war commenced has been closely paralleled by the advance in 'chemical stocks.'

"General Chemical, for instance, has advanced from a low of 163 last year to 310 at present. On February 1 the Company paid extra dividends of 15 per cent on the common stock. Semet-Solvay, which was selling around 90 early in 1915, is now selling at 325-350, after having increased its capitalization by a stock dividend of 100 per cent. This is equivalent to 650-700, or a sixfold increase. Dow Chemical sold around 135-140 a year ago, and recently reached \$500 per share. The Company declared a dividend a few days ago of 60 per cent on the common stock, payable two-thirds in preferred stock and one-third in cash. Grasse Chemical sold at about 120 in 1913, compared with a present price of nearly \$300. Last year the company paid a 10 per cent stock dividend. Many of the chemical stocks reaping the benefit from war prices for chemicals, which in some cases represent a 1000 per cent increase over normal, have hitherto been so closely held that a comparison of prices is impracticable. However, it is interesting to note the high prices which are at present bid for representative stocks of this character, viz.: Union Sulphur, 4400; National Aniline & Chemical, 490; Dow Chemical, common, 465; Freeport Texas Sulphur, 400; Solvay Process, 300; and Smith Chemical, 225."

compelling the reduction to metal in the country in which it is produced. Several years ago a tin smelter was built at Bayonne, New Jersey, but about the time it was completed this duty was imposed, so the works was never operated.

Apart from the Straits Settlements, Bolivia is the largest producer of tin ore, but Bolivian ore contains impurities which, with the established method of smelting, do not permit the production of a tin suitable for tin plate. During 1915, however, the American Smelting and Refining Company began the erection of a plant at Perth Amboy, New Jersey, which is not only to smelt the impure ores from Bolivia and elsewhere, but is also to refine the product by an electrolytic process.<sup>1</sup>

The tin plate capacity of certain of the companies in the Pittsburgh district was increased during 1915 and the early part of 1916. The Standard Tin Plate Company, of Canonsburg, Pa., completed 10 new mills; the McKeesport Tin Plate Company, of McKeesport, Pa., built 20 new mills; and the Phillips Sheet and Tin Plate Company, of Weirton, W. Va., the Wheeling Steel and Iron Company, of Yorkville, Ohio, and several other companies added mills to their plants. While the price of all commodities entering into the manufacture of tin plate, including steel, pig tin, palm oil and sulfuric acid, advanced considerably during the past year, and certain of the companies have at times experienced difficulty in securing supplies of these materials, the market is strong and the outlook is generally regarded as satisfactory.

**ALUMINUM**—The Aluminum Company of America has enjoyed much prosperity during the past two years, and it has in consequence greatly increased its capacity. A big water power, estimated at 800,000 h. p., is being developed on the St. Lawrence River, and the plant of the Southern Aluminum Company at Whitney, North Carolina, which was taken over during the past year, is being completed. The Aluminum Company of America is said to be bending every energy to increase its output, and it is thought that when its new works are finished whatever pressure now exists for an additional supply of aluminum will be relieved. This Company is proceeding on other substantial enlargements for 1917 and the following years. While it is said that it has not sold any aluminum for munition or for war purposes, nevertheless considerable resold aluminum has gone out of the United States for this purpose, being derived partly from aluminum transmission wires which have been replaced by those of copper.

The extreme demand for aluminum from Europe arose partly from the increase in the use of ammonal, a mixture of ammonium nitrate and powdered aluminum, which is used in large quantities as an explosive by the European belligerents.

**ANTIMONY**—For a number of years the consumers of this country have been accustomed to buying Cookson's and Hallitt's antimony to the exclusion of nearly every other brand. With the outbreak of the war, however, Great Britain required all the antimony its smelters could produce; and although shipments have been reaching this country from England, they are made under special permit, difficult to obtain. During 1915, Chinese antimony<sup>2</sup> was introduced to the American market, and next to China, Japan now sends the largest quantities of antimony here.

The high prices for antimony in 1915 induced several American concerns to engage in the smelting of its ores. Among the most important of these are the Western Metals Company, of Los Angeles, Cal., which is managed by persons who were previously connected with Cookson & Company, Newcastle-on-Tyne, England; and the Merchants Finance Company, of Harbor Industrial City, Cal. Antimony smelting has also been started on the Atlantic coast, the Magnolia Metal Company having inaugurated smelting in Brooklyn during 1915. Great difficulty has been experienced in securing suitable ores. China

<sup>1</sup> Several American companies, among them the National Lead Company, have carried out experimental work on the smelting of Bolivian ore.

<sup>2</sup> The Wah Chang Mining and Smelting Company, of Changsha, China, has been especially active in introducing Chinese antimony to American consumers.

no longer ships antimony ore, Australia has put an embargo upon its shipment, and competition for the South American ore has been very acute. Transportation difficulties in Alaska are the main obstacles to obtaining the supplies of antimony ore from there, although the Alaskan ore is of exceedingly good quality. During 1915, antimony mines in all parts of the United States were therefore rejuvenated and several small furnaces were built. Stibnite deposits are being worked north of Neualia, in Kern County, California, and also at Wild Rose Spring, northeast of Trona, California. While several smelters operated in Mexico during the past year, no attempt has been made to exploit the great deposit of jamesonite which exists there; however, this deposit will undoubtedly be drawn upon in the future.

It is said that approximately  $12\frac{1}{2}$  per cent of the present production of antimony is used in the manufacture of war supplies.

**MERCURY**—The production of mercury in the United States in 1915 amounted to 20,681 flasks, compared with 16,548 flasks in 1914. This production was chiefly derived from California.

The mining of quicksilver was at one time an important industry in California and may become so again if the investor is given reasonable assurance of a tariff which will permit him to operate in fair competition with European producers after the embargo is lifted and conditions again become normal. It is said that a reasonable import duty to compensate for the different labor conditions would probably double the California production within a period of two years. This production may not be of great importance outside of California, provided the United States can always be certain of obtaining adequate supplies for Government uses in times of emergency. However, for the time being, we are cut off from foreign supplies, and the state of the market indicates that it might be a difficult matter for even the Government to accumulate any considerable reserve stock for the manufacture of fulminates and antiseptics. The production, not only of California, but of all North America, is now far short of the ordinary requirements of the United States in times of peace. These requirements are in the neighborhood of 25,000 flasks per year and seem to be increasing.

During 1915 the output of California amounted to 13,916 flasks. The remainder of the small American production came from Nevada and Texas; but with the active prospecting and development which have continued in these states since the beginning of 1915, it is probable that their total outputs will constantly increase. Then, too, the California State Mining Bureau has under investigation the concentration of and the application of flotation to cinnabar, and the results of this inquiry may serve to encourage additional development.

#### INDUSTRIAL PREPAREDNESS

A prevailing illusion, especially among people living outside the "big prison," as the economist Naumann refers to the "self-contained commercial state," is that, when the military resources of the European contestants are exhausted, and peace is established owing to the depletion of their martial energies, war is to cease. It is conceded that as a military enterprise it will be concluded when one or the other side perceives that it is hopeless to gain anything further, and will, in consequence of this forced attitude, be desirous of making concessions for the sake of peace; but it is certain that the great economic contest, waged with such vigor for several decades, will be resumed with renewed intensity. This world battle will be fought by trained men in laboratories, mills and commerce, just as the present war has been fought by trained men who have behind them superior capacity in shop and office.

Germany, the "big prison," is arming for this new war, which will be not merely a struggle for the existence of her economic

power, but rather a fight for the full development for the future of her inheritance of science, technical ability and organizing capacity. In her efforts for industrial and commercial recuperation, Germany will therefore be strenuous to find markets for her enormous capacity of chemical production. Great Britain and Russia, former great customers, will be lost to her, and other belligerent countries may close their ports to her. The inquiry therefore arises, where is Germany to market her surplus manufactures?

In the past Germany has demonstrated not only a marvelous industrial efficiency but a remarkable capacity for intimate and effective commercial partnership between private initiative and government support. In 1870, her export trade amounted to only \$350,000,000 per year. At the outbreak of the present war she was the possessor of a world trade of \$2,500,000,000 per year. At the present time her industrial structure is intact and she has acquired possession of land of great natural wealth. She has already lost custom, and it seems probable that for some time the bitterness engendered by the present conflict will not make "made in Germany" a recommendation among the allied powers and their colonial possessions. To what market will Germany therefore turn under the stimulus of her necessity? One can only conclude that she will endeavor to establish herself in South America and in our own alluring domestic market.

This is not, however, the entire problem. The present antagonists of Germany will, in their battle for rehabilitation, have heavy debts to pay. In consequence whereof, they will be in every market her active rivals, and will enter into this competition not only with new and greatly intensified motives, but with increased efficiency. To quote an English statesman, "We have introduced scores of millions worth of automatic machinery which will have an enormous effect upon our industries when the war is over." It follows, therefore, that the United States shall have much to face, and this realization brings us to the consideration of our industrial defenses.

Economists urge that we do not base our expectations upon the present commercial tumidity, which is essentially abnormal. Moreover, every month of the continuance of the war must enormously inflate present prices and consequently increase the risks of the inevitable reaction. It is true that in the amount of our exports we are at present leading the world, and it is agreed on all hands that for some time after the war a great demand must continue for certain of our products, as, for example, structural materials; but there are obvious reasons. If it were not for the alimental influences of the war, we should be to-day as we were at the beginning of 1915, limiting our enterprises and endeavoring to provide for idle workmen.

It is clear from the conditions obtaining in Europe that when the present belligerents once enter upon the struggle for industrial and commercial recuperation, they will lower their prices to a point which will enable them to procure ready markets. Their governments will urge upon the people, as an obligation of patriotism, the extension of the laboring day, the acceptance of lower wages, and the reduction of the profits of business for the purpose of securing markets for their products. We must therefore actively prepare for this coming commercial war. At this time, when expert knowledge and trained skill constitute the chief buttress of national defense, it is our industrialists who must lead in the great work of preparation. Provided they are extended reasonable guarantee for the future and are permitted to solve in their own way the great problem of world competition on the basis of a secure home market, American manufacturers shall be able to get our industrial defense in readiness; but prompt action is required if we are to avoid the dire consequences of the coming contest.

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HISTORY AND PRESENT METHODS OF FLUORSPAR MINING IN ILLINOIS<sup>1</sup>

BY CARL C. LUEBKE

The Fluorspar mines of Illinois lie along the Ohio River in Pope and Hardin Counties. Hardin County, however, produces practically all of the fluorspar in this section, and for that matter in the United States.

In 1839 William Anderson, a settler, sinking a well near Fairview Landing, Hardin County, Illinois, discovered a bright ore which he took to be silver, but which on analysis turned out to be lead. Another well in 1841 also encountered the ore, and lead mining on a small scale was begun. The fluorspar which occurred with the lead was at that time valueless and was dumped out with the rest of the waste. Up until the early seventies the mining here was only desultory but with the discovery of the value of fluorspar as a flux in basic open hearth steel furnaces, fluorspar mining began and reports were turned in each year to the U. S. Geological Survey.

Many small surface prospects occasionally operated by farmers when prices are high dot the counties of Pope and Hardin. Four-fifths of the spar produced in the United States, however, comes from the Fairview and Rosiclare Mines of Hardin County, Illinois. The Kentucky mines across the river ship about a tenth of the total output and the remaining tenth comes from Colorado and New Mexico.

Fluorspar or fluorite, chemically calcium fluoride ( $\text{CaF}_2$ ) consists of 51 per cent calcium and 49 per cent fluorine. It is at times crystalline, but more often amorphous. It crystallizes in the isometric system and is slightly harder than calcite. The ore occurs in irregular lenticulated masses, usually a dull semi-opaque white, but often crystals are found, usually imperfectly formed in clusters and varying in color from bluish, or green glasslike through various other brilliant colors to dark purple. Associated intimately with the spar is calcite or calc spar as it is known locally together with the sulfides of lead and zinc in minor quantities. Experience shows that the galena and zinc blends decrease with depth, while the calc spar increases.

The method for analysis or valuation of fluorspar has been worked out by Dr. E. Bidtel<sup>2</sup> of our company. The method follows with a few revisions made by Dr. Bidtel in 1914, and gives excellent results for industrial purposes. Qualitative tests show the absence of barium. The carbonates are dissolved out by acetic acid and calcium fluoride also being slightly soluble in acetic acid, this solubility is reduced to a factor. The silica is determined by volatilization with hydrofluoric acid. The iron oxide is transformed into iron fluoride and together with lead and zinc is extracted by a solution of ammonium acetate containing ammonium citrate, leaving the pure calcium fluoride behind.

In the Fairview-Rosiclare district there are three principal veins known, the Daisy, Blue Diggings and Rosiclare-Good Hope. The Rosiclare-Good Hope vein was the first to be exploited and was operated as a lead mine from 1862 to 1874 on the property now owned by the Fairview Fluorspar and Lead Company. The Blue Diggings Vein, which is parallel and about 800 ft. west of the main or Rosiclare-Good Hope vein was opened up only a few years ago to any extent by the Fairview Fluorspar and Lead Company, and the showings of ore here are excellent. Very little is known of the Daisy vein, as no mining of any extent has ever taken place on it, but it is generally supposed to be the north extension of Blue Diggings. The general strike of the veins is approximately North and South. The vein deposits occur along fault fissure planes, and the veins are known as fault fissure, or contact veins and dip from 40° to vertical.

Where the dip is more than 70° little fluorspar has been found, but where it is less than 70° the largest bodies have been discovered. The veins vary in thickness from a mere slip to an extreme width of 35 ft.

Mining is carried on by means of vertical shafts with cross-cuts driven approximately every hundred feet to the vein. The depths of these shafts, of course, vary. The main shaft at Rosiclare mine is now 520 ft. deep. The Blue Diggings mine of the Fairview Company has been sunk to the 500 ft. level, and Mines No. 1 and 2 of the same company have each been sunk to the 200 ft. level. The method of ore recovery used in these mines is a shrinkage system, locally known as back or fill stoping. Drifts about 14 ft. high are driven in the vein and stulls placed at a height of about 7 ft. above the track rails, and poled over with lag poles, the stulls being placed about 6 ft. centers. Ore chutes are placed about every second or third opening between stulls, and the ore drawn from the stopes into ton cars which are trammed by hand or by mule to the shaft. The walls in these veins are usually good and square setting is never resorted to, being too expensive. Occasionally slabs on the wall are held in position by lags or light stulls, but the quantity of timber used is very small compared to the tonnage extracted. The methods of hoisting differ in the two mines: the Rosiclare mine using a cage and the Fairview, a skip. In the former case, the mill is placed over the shaft while in the latter, the mill is situated some little distance between the mines. This necessitates surface haulage by a standard gauge railroad.

After long years of experimenting the present process of milling has been evolved. The ore passes from the storage bin through either a shaking or revolving washer onto a conveyor belt. The highest grade, used in the manufacture of hydrofluoric acid, is picked by special men, part of it being shipped in lump form, and a portion dried and ground. This is the highest grade of fluorspar known, and analyzes from 98.5 to 99.5 per cent calcium fluoride with less than 1 per cent silica, is pure white in color and is known to the trade as Keystone. The second grade is also hand-picked in the same manner as first grade, and this is all ground before leaving the mill. This spar is known to the trade as A-1, analyzes 96 to 98 per cent calcium fluoride, with less than 3 per cent silica, is used in various enameling processes, and in the manufacture of opalescent glass. The next grade picked off, known as No. 2 Lump, is used in cupola furnaces by manufacturers of high-grade castings. The spar remaining on the belt passes through a crusher, thence through rolls and is then delivered after sizing to about one-half inch through a revolving trommel onto jigs. At Fairview the lead is all recovered on the jigs, while at Rosiclare tables are also employed, both mills making about the same grade of concentrates. The percentage of lead recovered is about 0.8 per cent of the ore treated. No zinc is recovered since the amounts occurring are practically negligible. Tailings or waste from the jigs is practically all sandstone, limestone and calc spar, and varies from 10 to 20 per cent of the amount of ore treated. The fluorspar product of the jigs, known as Gravel spar, varies from 85 to 90 per cent calcium fluoride, constitutes the greater tonnage of the mine and is consumed as a flux in the basic open-hearth steel furnaces. The market then for fluorspar depends almost entirely on the steel industry.

In 1914 the mines of Hardin County produced 70,000 of the 78,000 tons of fluorspar consumed by this country. In 1915 they produced 115,000 tons. This year the rate of production shows a considerable increase over that of 1915, but the demands are more than keeping pace with the increase of production. What the future is, no one can predict, but the mining of fluorspar is now taking its place among the important industries of the United States.

<sup>1</sup> Presented at the 52nd Meeting of the American Chemical Society, Urbana-Champaign, April 18-21, 1916.

<sup>2</sup> THIS JOURNAL, 4, 1912.

## CURRENT INDUSTRIAL NEWS

### MAMMOTH OIL-USING SETTLEMENT

According to *Gas and Oil Power*, an arrangement is said to have been entered into by certain British shipping companies, including the Cunard, White Star, Atlantic Transport, Dominion and Leyland Lines with the Mexican Petroleum Co. whereby the latter has undertaken to supply all the oil required by the former during a period of twenty-five years. The shipping companies will equip all their new vessels as oil-burners and also, as soon as possible, convert those now using coal, and there are to be formed out of the combined interests two British concerns which will build tank steamers for the transport from Tampico of the liquid fuel.—McMILLAN.

### STRING SUBSTITUTE IN ENGLAND

The supplies of ordinary string and twine have become so scarce that efforts are being made to find a suitable substitute and an enterprising engineering firm appears to have solved the problem by manufacturing a string from paper. In appearance, says the *London Standard*, the new string exactly resembles the genuine article and it is difficult to detect any difference. The string, which is strong and suitable for tying parcels, has so far been produced of only one thickness but other varieties are to follow. According to reliable sources, the usual kinds of string are unobtainable and, as this substitute can be sold at less than the real article, it bids fair to come into general use both for cheapness and necessity.—M.

### MINING IN VENEZUELA

According to a report in the *Mining World*, Venezuela seems to have vast resources of mineral wealth. The country abounds in asphalt, coal, petroleum, salt and sulfur as well as in ores of copper, silver, gold, iron and lead. No statistics seem to be available as to the number of men employed in the mining industry but at least 1,200 men are employed in washing gold, chiefly from alluvial washings. Asphalt is annually exported to the extent of 61,000 metric tons which has a value of \$350,000. The greater part of this goes to the Bermudez Asphalt Co., an American company formed to exploit the Bermudez Lake in the State of Sucre. Coal deposits are found at El Isiro near Coro and also at Naricular near Barcelona in the State of Bermudez. The coal mines, which are worked on a small scale, belong to the government and all the coal mined is consumed locally. As regards copper, work is being carried on at the Aroa copper mines, situated between Barquisimeto Tucacas and Villa de Cura, with the result that 15,000 metric tons of copper are annually exported. The quantity of fine gold produced annually is nearly 1000 kilograms. Hematite iron containing from 55 to 70 per cent of iron exists in large quantities at Manoa near the river Amacuro. There are also important iron ore deposits to be found at Imataca in the lower Orinoco. Boring for petroleum has been carried on extensively, notably in the peninsula of Manicare.—M.

### HYDROSULFITE OF SODA IN ENGLAND

Hydrosulfite of soda ( $\text{Na}_2\text{S}_2\text{O}_4$ ) was, previous to the war, sold as "Blankit" and, being a powerful bleaching agent, has been of late much used in the sugar industry. It is, however, at present practically unobtainable and its want is much felt. The *Intern. Sugar Journal* announces that M. Louis Deschamps, a well known French chemist, has, after some years of experimenting, discovered a process which can be installed in a sugar factory for the manufacture of the above bleaching agent in

the form of a solution ready for use. The plant is simple and need require only one workman to attend it. The process involves, in the first instance, the preparation of the hydrosulfite of zinc by acting on metallic zinc with sulfurous acid. The hydrosulfite of zinc is then acted on by caustic soda when a solution of hydrosulfite of soda is obtained. Liquid sulfur dioxide is now not indispensable to the process as was the case formerly. M. Deschamps has further devised a special oven for the production of sulfurous acid gas entirely free from oxygen though containing nitrogen, which does not interfere with the subsequent reaction. It is this invention which renders this process of making the hydrosulfite a practical one in the tropics, since it obviates the necessity of using liquefied sulfur dioxide, the transport of which in cylinders was both costly and difficult.—M.

### SOUTH AFRICAN ANTIMONY

The South African *Mining Journal* suggests that there is a possibility that profitable results may attend the working of the well known Murchison range which is rich in antimony. The reef is located in schistose rocks, which dip almost vertically towards the north, and is made up of lenticular bodies of quartz mingled with calcite, dolomite and iron carbonates. The ore occurs in bunches and masses of some size and can also be followed occasionally over long distances. The reef varies in thickness but the average width in many places is between 3 and 10 feet and, in one particular place, a width of 20 feet has been measured. The deposit seems to be of large dimensions and, at the present time, the ore may be profitably worked for the base metals contained in it as well as for the antimony. No great difficulties regarding mode of transport seem to present themselves as a line of railway is connected both with the Pretoria Delagoa main line at Kumati and with the Pretoria Messina line at Zokmakaar. The principal difficulty is the want of water, but the government has considered this and, doubtless, would be quite willing to remedy it if they are satisfied that the needs of a rising industry warrant the expenditure.—M.

### BRITISH UTILIZATION OF PITCH IN COKE OVENS

The stocks of coal-tar pitch, says the *Chemical Trade Journal*, have reached such enormous proportions and the prices, owing to war conditions, have become so low that its utilization in coke ovens has been suggested as a remedy which is, at the same time, most ready in application and immediate in effect. Experiments have been carried out in which coke and pitch have been carbonized according to ordinary coke-oven practice. These tests have had a threefold object: (1) to find the best percentage mixture; (2) to study the effect upon the physical conditions of the coke; (3) to estimate the effect on accumulated stocks of coke. According to an article in the *Iron and Coal Trade Review*, mixtures varying from 2 to 6 per cent of pitch have been tried, but a considerable increase in the percentage of tar was noticed at the higher percentages, owing to some of the pitch being kept in circulation. With a 3 per cent mixture, no trouble was experienced but the quality of the coke was improved, being denser and harder. Further, the ash and sulfur contents were decreased and the percentage of breeze reduced. No difficulty was experienced in working the mixture in the ovens, the pitch being first ground up and mixed with the slack at the elevator hopper. The oven charge could be worked off in the usual time and the coke pushed easily. The yield of coke was from 55 to 60 per cent, the balance being made up approximately as follows: tar, 23 per cent; gas, 14 per cent; loss, 3 per cent.—M.



# SULFATE OF AMMONIA AS A FERTILIZER

Special reference is given to the use of sulfate of ammonia as a fertilizing agent for various crops, in a pamphlet recently issued by the Department of Agriculture of Leeds University, England. The supplies of sodium nitrate not being available this year, farmers must rely on sulfate of ammonia for nitrogenous manure. Experiments have been conducted in the East and West Ridings of Yorkshire on land varying in character. In the case of barley, the yield was increased from  $3\frac{3}{4}$  bushels per acre to  $7\frac{1}{2}$  bushels by a moderate application of sulfate of ammonia, the experiments being carried out in different classes of soil and under varying climatic conditions of different years. The effect on oats was more marked, the increase in one case being  $9\frac{1}{4}$  bushels of grain and  $4\frac{1}{2}$  cwt. of straw per acre. For potatoes, sulfate of ammonia has been in great favor. In combination with farmyard manure and artificial manures containing superphosphate and sulfate of potash, an application of 1 per cent has increased the crop by  $15\frac{3}{4}$  cwt. per acre, this being the average of 29 experiments conducted over a period of six years. In the case of turnips, it was found as a result of 44 trials over a period of eight years, that an application of  $1\frac{1}{2}$  cwt. of sulfate of ammonia in addition to dung and superphosphate increased the yield of swedes by 12 cwt., while 130 lbs. of sulfate gave an average increase, taken over 4 years, of  $6\frac{3}{4}$  cwt. per acre, in the case of meadow hay.—M.

# STEEL AND MALLEABLE IRON

The choice between steel and malleable iron castings, says the *Engineer* (Vol. 121, No. 3145), is dictated by respective properties, partly by price and partly by the limitations of the processes by which malleable iron is made. Steel seems to be a more homogeneous metal and, therefore, tougher and stronger. Again, castings of malleable iron are somewhat prone to be more porous and spongy at the center, especially in certain portions of irregular castings so that, for this reason, a steel casting is stronger and more reliable. Finally, malleable iron can be made only into castings of quite light sections, whereas there is no limit as to size and weight of steel castings. However, for light castings where only fair strength and toughness are required, it pays to buy malleable iron castings since they are cheaper than steel ones.—M.

# OCCURRENCE OF HYDROCARBON OILS IN FISH-LIVER OILS

Recently, says the *Pharmaceutical Journal*, a shipment of fish-liver oil to London was condemned as being adulterated with mineral oil. A portion of the oil was afterwards examined and found to contain 83 per cent of unsaponified fat. Endeavoring to find the source of this, the analyst himself extracted the oils from the livers of fresh samples of Mediterranean fish and found that the oil obtained from two distinct species, *centrophorus granulosus*, and *scymnus lichia*, contains no less than 80 to 90 per cent of unsaponifiable liquid hydrocarbon having all the characters of a mineral oil. This fact seems to confirm the theory that petroleum is of animal origin.—M.

# BRITISH GLASS INDUSTRY

The annual report of the Barnsley Chamber of Commerce, England, states that there is considerable activity in the glass-bottle making trade and that the prospects are good. The supply of labor, however, tends to become scarcer. The manufacture of fine kinds of glassware, such as electric lamp bulbs, has been taken up by local firms and, in particular, one firm, by the special request of the Government, is producing chemical laboratory glassware in the ordinary quality and also in a very

high resistance quality for the finest analytical and research work. The material produced is said to be as good as anything on the market. It is hoped that this kind of business will be developed, so that British chemical laboratories may become entirely independent of Germany for special glassware.—M.

# EXHAUST FROM LIQUID-FUEL ENGINES

According to a report in *Nature*, the composition of the exhaust from liquid fuel engines has been studied by Mr. R. W. Fenning and a paper on the subject was recently read before the Institution of Mechanical Engineers, London. Various fuels were employed in the investigation, the considerations affecting their choice being volatility, purity and general suitability for use as motor spirit: hexane and benzene were taken as standard, high-grade petrol and benzol as commercial fuels. Mixtures with air were exploded in a small glass vessel and a complete chemical analysis was made of the products. Exhaust samples were also taken from the engine fitted with Dr. Watson's apparatus for measuring air and fuel and these samples were analyzed. In each case a set of curves was plotted, taking as abscissae ratios of the fuel to air by weight and, as ordinates, percentages of each of the products of combustion in turn, such a set of curves being termed an exhaust-gas chart. The author draws the conclusion that with volatile fuels there seems to be little difference in the composition of the products of combustion from air-fuel mixtures in a small explosion vessel or in an engine cylinder in spite of the conditions being so dissimilar and, further, that there is only a very small quantity, if any, of unsaturated or saturated hydrocarbons present in engine-exhaust gases; this latter conclusion is, of course, based upon the results obtained in gas analysis by the method adopted and described.—M.

# BRITISH BOARD OF TRADE

During the month of April the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply of the following articles. Firms which may be able to supply information regarding these things are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall Street, London, E. C.

Bones burnt, used bone	Jars, stoneware
Brass, "Neptunes," for evaporating	Laces, shoe, artificial silk
sea-water for salt	Lamp burners
Briquettes, coal, egg-shaped	Lithographic stones, size 49 $\frac{1}{2}$ in.
Buttons	by 67 in.
Caseln	Locks, 3 in. brass for fiber cases
Celluloid substitute	MACHINERY FOR
CHEMICALS:	Cutting teeth of combs
Barium carbonate, powdered, for	Embossing leather
making case-hardening mixture	Making chocolate
Recovered precipitated oxide of	Making boot laces
manganese	Making fancy chains
Red lead, pure	Making fishing nets
Resin compound	Making tinued sheets
Sulfuric acid	Making wood-wool
Tartaric acid	Plant for making phosphoric acid
Thallium salts or material con-	Preparation of tapioca
taining thallium residues	Spinning and carding goats' hair
Thorium nitrate	Magnets
Zinc oxide, guaranteed absolutely	Mantles, incandescent
leadless	Metallic ends for boot laces
Combs	Millinery buckram
Clocks, small, for fixing in wooden	Nickel wire
cases	Pins, hair
Elastic webbing	Pins, iron plated
Elastic loom	Ploughs, agricultural wheel type
Fiberboards, for cheap attaché cases	Rings, rods and nozzles for in-
Fiberboard, vulcanized for suit cases	candescent mantles
Fireclay, ground for fireproof cook-	Rubber strip for electrical purposes
ing ware	and for golf balls
Glass bulbs and tubing, leadless, for	Spring clips, small steel
X-ray tubes	Spring motors for gramophones
Glass tubing for hypodermic	Sheets, iron, black malleable
syringes	Silk, artificial
Glove fabrics	Typewriter ribbons
Glue, cold, for tin labeling ma-	Vegetable down
chines	Washers, copper, asbestos
Hinges, brassed $\frac{3}{4}$ in. to $1\frac{1}{2}$ in.	Weighing machines, dormant—
for fiber suit cases	platform, automatic
Ink, writing, in 1st and 2nd bottles	Wheels for tinder lighters

—M.

### BRITISH EXPORT PROHIBITION

By an order in Council, the exportation of the following goods is prohibited to all destinations: Acetic acid, cinematograph films, ferro-molybdenum, ferro-silicon, ferro-tungsten, platinum (salts of), radium and tungsten; further, that on and after March 27th, the exportation of "manufactured fuel" should be prohibited to all countries except British possessions; that the exportation of the following be prohibited to all European countries except France, Russia (except through the Baltic), Italy, Spain and Portugal; Barium sulfate, calcium sulfate, iron sulfates, sodium sulfate and bisulfate (including niter cake), strontium sulfate, glucose and malt sugar, salt (rock and white except table salt).—M.

### SILVER-PALLADIUM ALLOY

A description of a silver-palladium alloy which has been introduced for use in contact and spark devices to replace platinum is given in a recent number of the *Electrical World*. The proportions of silver and palladium vary according to the conditions under which the alloy is to be used, one with only 2 per cent palladium giving satisfactory results under many circumstances. Where the contacts or spark points are exposed to sulfur compounds, 5 per cent at least of palladium should be used. The alloy which was found to give the greatest resistance to spark erosion was that of 60 per cent palladium and 40 per cent silver. Palladium has a higher melting point and lower thermal conductivity than silver so that when it is mixed with the latter, the melting point is raised and the thermal conductivity lowered. Experiment, however, has shown that the heat from the spark is conducted away fast enough to prevent the silver being melted, and, on this account, alloys containing very large percentages of silver and relatively small ones of palladium can be used in many cases with entire success.—M.

### CHANGES IN BRONZE BY ANNEALING

A research has just been completed by the Bureau of Standards, Department of Commerce, London, on the annealing of bronze. The alloy used was the commercially important zinc bronze (Cu 88, Sn 10, Zn 2) and the results have been published in *Technologic Paper*, No. 60, recently issued. The properties of cast iron may be greatly improved by proper annealing and the changes occurring in cast brasses and bronzes upon annealing are by many metal workers regarded in the same light. The results of the Bureau's research show that bronze is very different in its behavior from steel and shows no recrystallization "grain refining" unless it has previously been cold-worked, as by rolling or hammering.—M.

### CADMIUM VAPOR LAMP

At a recent meeting of the Physical Society, London, Dr. H. J. S. Sands exhibited a specimen of an enclosed cadmium vapor arc lamp similar to the well known mercury lamp in general principle. It is constructed of quartz glass. To start the lamp, the metal is melted by means of a Bunsen burner and the arc struck by tilting. The metal, before being introduced into the lamp, is freed from oxide and dissolved gases by a special process of filtration while at the pump. It is prevented from adhering to the glass, which might lead to fracture, by the presence of a loose powder in the lamp. The lamp once started gives a powerful light and continues burning indefinitely.—M.

### DISINFECTANT SOAPS

According to a paper recently published by Dr. K. Rulke, the products of oil of turpentine that exercise an acid effect consist, besides carbohydrates, principally of bornyl esters and fenchyl esters. The borneol, which is produced by the saponification of the bornyl ester, is a solid melting at 203° C. If it is desired,

therefore, to produce a disinfectant soap with borneol as the effective principle from bornyl esters with soap employing an excess of alkali, the borneol will crystallize out, lose its effect and render the soap useless. It would seem that this might occur when not pure bornyl ester but the acid-effect producing product of oil of turpentine is treated with soap and alkali. It has been found, however, that, contrary to expectations, this does not happen. The borneol after saponification of the acid-effect product does not crystallize out but remains in solution in the soap and renders it effective. Hence, by the new process, it is possible to obtain in a very simple manner a disinfectant soap containing borneol as active agent. The soap has a pleasant odor, the unpleasantness of the fenchyl alcohol being overcome by the more agreeable borneol.—M.

### NEW ASBESTOS DEPOSIT

It is announced from the Transvaal that a discovery of fibrous asbestos occurring in rock formation has recently been made. It is of a new and superior quality and one which, it is thought, may have important bearing on the asbestos industry. The material available is said to be considerable and of a new color, mostly golden brown. The fiber is said to be of greater length than any mineral fiber previously found, and also to be of good weaving strength.—M.

### EFFICACY OF NATURAL DYES

The shortage of synthetic dyes, says the *Chemical Trade Journal*, has led the Indian authorities to experiment with indigenous vegetable dyes, especially upon cotton goods. Dr. F. Marsden, the tinctorial expert to the Government of Madras, found that the cultivation of the plants he wanted had practically ceased and only scattered lots, found in the wild state, were available. Before the introduction of alizarine, chay root was the chief material in use but it is thought that the roots now found contain only about 50 per cent of the dye which they contained when the material was in general demand. Dr. Marsden gives it, as his opinion, that the scarcity of materials, the extreme cost of the process and the change in the tastes of the public who have now acquired the habit of buying bright colors, make it useless to persist in the use of vegetable dyes on cotton.—M.

### THE SCOTCH KELP INDUSTRY

It would seem that the outlook of the kelp industry in the Outer Hebrides, Scotland, is, at the present time, somewhat promising. In North and South Uist, a market is found for the manufactured kelp, the purchasers being the British Chemical Company. The annual output of kelp and ash for South Uist alone is close upon 1000 tons and the prices paid last year were 80 per cent higher than formerly. There is a probability that the Board of Agriculture will erect storing sheds at the various ports to facilitate transport.—M.

### PRODUCTION OF VEGETABLE DYES IN CHINA

The Acting British Consul in Szechuan has forwarded a copy of a memorandum on the production and uses of vegetable dyes in that province of China. The various Szechuan dyestuffs are enumerated and the methods of preparing and employing them are described. The memorandum may be consulted at the Board of Trade Offices, London, where specimens of the dyes are on view.—M.

### ZEPPELIN SEARCHLIGHTS

Reference was recently made in many of the London papers to Dussaud's invention of the so-called "cold light" which, it was being suggested, was used for the searchlights mounted on Zeppelins. So far as we have been able to ascertain, says *Nature*



(Vol. 97, No. 2420), the device tests on the plan of overrunning a metallic filament lamp at anything from 50 to 150 per cent higher voltage than the normal. The candle power of a filament lamp has been reckoned to progress approximately as the 3/6th power of the voltage and the efficiency of an overrun lamp is high. The safety of the filament is secured by applying the current only momentarily, and the flicker of the light is avoided by employing a nest of lamps which are lighted in succession by the use of a motor-driven rotary switch provided with the appropriate number of contacts. The British patent specification speaks of "low-voltage" lamps (less than 25 volts) which restriction may be conditioned by the length of time required to raise the filament to incandescence. The device has been applied to cinematograph lanterns, the interval between the excitation of two successive lamps being arranged to correspond with the interval between successive pictures.—M.

### ELECTRICALLY CONDUCTING PAINT

In a recent issue of the *Electrical World*, a method for the production of an electrically conducting paint is described. The method consists essentially in the treatment of a bronze paint with hydrochloric acid. Bronze powder does not conduct of itself, probably because each particle is covered with oxide or fat. If, however, a bronze paint is made, containing equal parts of amyl acetate and acetone and 4 per cent of transparent celluloid, it can be rendered capable of conducting electricity by rubbing the slightly moistened surface with concentrated hydrochloric acid or by exposing a freshly painted surface to the acid fumes. A ready-made conducting paint can be obtained by mixing bronze powder with amyl acetate solution and adding concentrated hydrochloric acid. The mixture is stirred until a paste is obtained and afterwards washed by decantation with water, and alcohol. The residue, which consists of a paste, is mixed with amyl acetate. The paint should be used as soon as it is made and gives a paint film with an appearance of gold-foil. The resistance of the film increases with time and, if exposed to sunlight, the increase takes place at a very rapid rate.—M.

### HYDROGEN GAS FOR HEATING AND LIGHTING

The use of hydrogen gas, as a heating and lighting agent, either as a substitute for, or mixed with coal gas, is advocated in a recent issue of *Elettrotecnica*. The gas is to be obtained by electrolysis. The main difficulties attending its use are the means of distribution but, even after taking these into account, it would seem that its utilization for heating and cooking is easier of realization than the replacement of coal gas by electricity.—M.

### NOTES ON AUTOMATICS

According to the *Engineering Review*, it seems to have been shown by experience that automatic metal-working machines can be made profitable only when they can be made to run smoothly for as long a time as possible and with one setting of tools. If there is considerable variation of hardness in the bars thus worked up, an automatic machine often produces variations in the size for the reason that the harder the metal the more pressure is required on the tools. The extra pressure causes enough spring in the machine or give in the tool to cause variation in size while an abnormally hard bar will often destroy the keen edges of the rigidly set tools so that a general regrinding will be necessary. Therefore, it has become the practice to keep a line in the uniformity of the hardness in the stock which is thus used up whenever necessary. On the other hand, it often does not pay to set up an automatic machine unless the best tools are used and in which, of course, the hardness is a prime factor.—M.

### BRITISH ORGANIZATION OF SCIENTIFIC EFFORT

At the Royal Society, London, a conference of representatives from engineering and scientific institutions was recently held to consider the desirability of establishing a committee to organize scientific effort in the British Isles. The following resolution was passed and the committee was asked to give effect to it and report to a future meeting: that this meeting considers that it is desirable to establish a conjoint Board of Scientific Societies for the purpose of (1) promoting the coöperation of those interested in pure and applied science; (2) supplying means for scientific opinion on matters relating to science, industry and education finding effective expression; (3) taking such action as may be necessary to promote the application of science to our industries and to the service of the nation; (4) discussing scientific questions in which scientific coöperation seems advisable.—M.

### RUST PREVENTION

Experiments are continually in progress, says a contemporary, at one place or another with the object of discovering the best kind of paint or varnish for protecting iron and steel from corrosion. From the latest investigation on the subject, it would appear that a single coat of paint or varnish is more effective than several coats of the same material, the explanation adduced being that subsequent coats tend to loosen and increase the porosity of the preceding coat. Experience shows that the only way of using steel without risk of corrosion is to apply it as reinforcement in ferro-concrete, a material possessing marked advantages over structural steel work and having none of its disadvantages. An anti-corrosive coating composition intended especially for machinery, but said to be applicable generally, has been patented by the Carter Suspension Bridge, Chemical Works, Leeds, England. It consists of a solution of 100 oz. common resin or colophony in 100 oz. of petroleum spirit with addition of 5 oz. liquid drier and 1/4 to 1/2 dram solid spirit-soluble red.—M.

### RUSSIAN PERFUMERY TRADE

All the Moscow perfumery firms have once more raised their prices for perfumes, owing to the continued rise in the cost of the necessary ingredients. They have issued circulars saying that all orders sent them will be considered as accepted at the prices that may be ruling when they are executed and the goods dispatched. Further, orders will be accepted without engagement to execute them and without guarantee or date, and will be executed in the order of their arrival. For the reasons named above, many of the large firms of Moscow have added 100 per cent to their list prices, inclusive of increased excise in spirit.—M.

### ALUMINUM PRODUCTION IN NORWAY

It is reported from Stockholm that a large plant for smelting aluminum is to be erected at Höyanfjord, Norway, where there is a waterfall which may furnish 60,000 H. P. It is proposed to develop 20,000 H. P. at once to provide for the production of 4,000 tons aluminum per year.—M.

### MINERAL OUTPUT OF CANADA FOR 1915

The figures for the metal output of Canada for 1915 are given as follows:

Gold.....	916,076 fine ozs.
Silver.....	28,401,735 fine ozs.
Copper.....	51,306 short tons
Lead.....	21,689 short tons
Nickel.....	34,039 short tons
Zinc ore.....	15,553 short tons
Pig iron.....	913,719 short tons

The output of gold is considerably higher than is generally realized.—M.

## WILLARD GIBBS MEDAL AWARD

The Willard Gibbs Medal for the year 1916 was conferred upon Dr. Willis Rodney Whitney, director of the research laboratory of the General Electric Company, and member of the U. S. Naval Board, at the meeting of the Chicago Section of the American Chemical Society, held May 19, 1916, in the Louis XVI Room of the Hotel Sherman.

Dr. W. D. Harkins, Chairman of the Section, opened the meeting with a short résumé of the conditions which prompted the institution of the Willard Gibbs Medal Award. Mr. Harkins introduced Mr. Gustav Thurnauer, Vice-President and Treasurer of the Aurora Metal Company, Aurora, Ill., who made the presentation address. Following the receipt of the medal, Dr. Whitney thanked the Section in an informal and very sincere manner for the honor indicated in the bestowal of the medal, and then delivered his address on "Incidents in Applied Research." The presentation address and the medal address are printed in full below.

The Willard Gibbs Medal was founded in 1910 by William A. Converse, of the Chicago Section, and is bestowed annually in recognition and encouragement of eminent research in theoretical or applied chemistry. The medal has now been conferred upon six great chemists:

SVANTE A. ARRHENIUS	1911
THEODORE W. RICHARDS	1912
LEO H. BACKELAND	1913
IRA REMSEN	1914
ARTHUR A. NOYES	1915
WILLIS R. WHITNEY	1916

Willis Rodney Whitney was born in Jamestown, N. Y., August 22, 1868. He received his bachelor's degree from the Massachusetts Institute of Technology and his Ph.D. degree at Leipzig. On returning to this country he became an instructor in chemistry in his alma mater, and was afterward associated, in the Research Laboratory of Physical Chemistry at the Institute, with A. A. Noyes, who by an odd coincidence was granted this same medal last year. During this time he did some technical work, and was associated with Dr. Noyes in an investigation which resulted in the saving of very considerable amounts of solvents by a great concern engaged in the manufacture of photographic supplies. In 1904 he was engaged by the General Electric Company to start for them what was at that time a pioneer undertaking in this country, a real research laboratory to carry out investigations for the benefit of a great industrial corporation. Here he showed his broad-mindedness by employing as his assistants men of broad theoretical training, with the result

that his laboratory is now the leader in this field in the whole world. Under Mr. Whitney's direction many remarkable industrial developments have been perfected, and many scientific discoveries of value made. Thus there need only be suggested the names ductile tungsten, pure boron, the Coolidge X-ray tube, the nitrogen-filled incandescent lamp, the work of Langmuir on the reactions of gases at low pressures in heterogeneous systems, to indicate that the work of the laboratory is directed by a man of considerable breadth of view. Mr. Whitney's own work has been carried out in such lines as solubility, the corrosion of iron, the nature of colloids and suspensions.—[EDITOR.]



WILLIS RODNEY WHITNEY—WILLARD GIBBS MEDALIST, 1916

### PRESENTATION ADDRESS

BY GUSTAV THURNAUER

MR. CHAIRMAN, DR. WHITNEY, LADIES AND GENTLEMEN:

It would be difficult to find in the realm of modern industries any one which does not overlap in some way into the domain of chemistry. The recognition of this fact has brought about the wonderful development of continental industrial progress in Europe, during the last sixty years, by the systematic encouragement and development of chemical research with industrial ends in view. However, in the United States the value of chemical research has begun to be appreciated only during the last decade of the past century.

Our large industrial corporations were the first to show the clear foresight of attaching to their manufacturing plants research laboratories in which work has been done, regardless of immediate financial returns. This, however, in the end has turned out to be a mine, not only of wonderful additions to knowledge, but also of golden remuneration.

To appreciate this statement, it is only necessary to

call your attention to the work of the Standard Oil Company on the "cracking" of mineral oils, which has not only yielded lower hydrocarbons for use as gasoline, but also the valuable aromatic derivatives of the benzol and toluol groups.

The study of condensation products by the third Willard Gibbs medalist, Leo Backeland, and others, has given us varnishes and plastics of heretofore undreamt-of qualities and applications.

To mention only the name of Thomas Alva Edison's research laboratories suggests wide vistas of exceedingly interesting and useful labors.

The investigations in the research laboratories of the General



Electric Company, of which Dr. Whitney is the director, are a particularly beautiful example of the value of such work to science, as well as to the industry which it serves.

The achievements of Dr. Whitney and his associates are so variegated and numerous that it would be impossible to mention them all in this short space of time, and I shall confine myself to some of the most important ones only.

It was of course quite natural that among the work of primary interest to Dr. Whitney, should be the matter of artificial light, and this subject has been pursued with particular attention in his laboratory.

The fact that artificial light, no matter of what origin, wastes considerable energy by production of heat has led to the development of filament lamps in which an ever increasing amount of energy has been turned into light and an ever decreasing amount of energy into heat. The steps from the carbon filament incandescent lamp to graphitized filament, tungsten filament and finally nitrogen-filled tungsten filament lamps mark the stages in which these results have been achieved. Though the ideal light of the firefly, which turns energy into light with a negligible formation of heat, has not yet been achieved, a great approach towards this goal has been made.

Incidental to this work, Fink, in Dr. Whitney's laboratory, made his classical research on ductile tungsten and molybdenum (two metals heretofore known as hard and brittle), showed how they can be drawn to wire of less than  $1/1000$  of an inch diameter and that working not only increases the tensile strength of these metals, but also their hardness to such a point that they will cut glass.

In the same laboratory, Irving Langmuir and J. A. Orange developed by their researches the nitrogen-filled tungsten lamp and Mr. Langmuir also enriched science by his wonderful investigations on reactions of gases at low pressure in heterogeneous systems, as well as by the discovery of the highly reactive atomic hydrogen—probably the "nascent hydrogen" long suspected but never before realized by chemistry.

By modifying the Roentgen tube and using tungsten terminals and a molybdenum mirror, W. D. Coolidge obtained an X-ray tube which emits pure electrons and differs from the lamps made heretofore in sharpness of focus, in that intensity and penetration are under complete control of the operator and that there occurs no fluorescence and no local heating.

Of other work done in the research laboratory of the General Electric Company, I wish to mention only in passing Mr. Weintraub's investigations on boron and its uses in making sound castings of pure copper, also the development of a carbon resistance furnace for studying at high temperature, under high and low pressures, the melting points and other qualities of different materials, and furthermore the use of this furnace for manufacturing, under controllable conditions, high resistance elements.

It also might be stated that constant researches are carried on in reference to the rare elements of the air—argon, krypton, neon, helium—that plastic condensation products of the Bakelite type have been developed by the reaction of glycerin and citric, phthalic and other acids. This is only mentioned, without any attempt on my part to cover the field completely, to show the wide range of work done under Dr. Whitney's guidance.

TO DR. WHITNEY:

In recognition therefore of the great and meritorious work done by you, Dr. Willis Rodney Whitney, and under your able and inspiring direction, the Chicago Section of the American Chemical Society has decided to bestow upon you its highest honor, the Willard Gibbs Medal, founded by our fellow member, William A. Converse.

In the name of the Section I have the honor to present to you this, the sixth Willard Gibbs Medal, with the wish and confi-

dence that the beacon light by which you have been guided early and late, "Chemical Research," will ever burn brightly in your life, and that your achievements will continue to approach within constantly decreasing limits, and finally emulate the efficiency of the light of the firefly.

## INCIDENTS OF APPLIED RESEARCH

### MEDAL ADDRESS

By WILLIS R. WHITNEY

Previous recipients of the Willard Gibbs medal have properly and interestingly described their own contributions to the advance of chemistry, and usually those particular scientific contributions which stood for the individuality of the man himself. How fitting it was, for example, that Arrhenius should have presented that intimate and conversational address on the birth of the dissociation theory, describing its hard struggles for air and light and recognition in just those places where such a theory should have been most eagerly sought.

As for myself, I cannot describe constructive chemical work of personal accomplishment. But if I can combine a little of my experience in a modern research organization with some suggestions drawn from the work of others in a way that may be helpful to my profession, I shall be content.

Any chemist, whether he be an appreciative artist of the profession, or one of the greater number of chemical artisans who revere the memory of the great Gibbs without being able to understand his writings, must thrill with brother feeling when he recalls the history of Gibbs' work, or the stories told by Arrhenius of his own personal experiences. Both accounts show us how new knowledge is made every day, that it often looks too new to be true, and is not generally anticipated, even by the experts who ought to know. Such stories should encourage us to believe in ourselves and in our own ideas. We might almost conclude that we should believe in ourselves the more when no one can understand us, as in the case of Gibbs, nor can agree with us when they do understand, as in the case of Arrhenius. It took a quarter of a century for anyone to comprehend what Gibbs had written.

When Arrhenius had his dissociation theory perfectly clear to himself, he admits that he did not dare include it in his doctor's thesis, for fear he would thereby lose the hoped-for doctor's degree. At that time those chemists and physicists who were certainly best fitted to understand, were also slowest to accept the new theory. Arrhenius mentions Cleve, Ostwald, Thomson, Kohlrausch, van't Hoff, Planck, Helmholtz and Wiedemann as not accepting his ideas of electrolytic ions, for a long time, at least. This was a galaxy of experts. Meanwhile, objections to the theory were brought forward by the score, and not by untrained, but by trained thinkers. They were exactly the same kind of objections you and I advance so strongly when a new idea crops up and we have a perfectly reasoned theory of its impossibility. But we apparently never learn the lesson that growth of knowledge is the only existing perpetual motion and must be considered in every forecast.

Because of the examples set by my forerunners, I am going to be personal. I wish first to say that to attempt to express properly my appreciation of the honor of being awarded the Gibbs medal would be entirely futile. I studied his papers in the "Connecticut Transactions," and could not then grasp their significance. I know the value of such a trail-blazer, however, and I realize that we shall never get beyond the applications of the principles he enunciated. I am thankful that some of these principles may become instinctive to chemists through continual contact and reminder, even though they are not capable of easy assimilation at a single effort.

My own contributions to science are mostly the work of others. As a chemist I was developed at a time when the rapidly growing technical industries of our country began to need chemists in cooperating groups, and while I might claim that for a few weeks I was the chemical research portion of a large manufacturing company, it was soon evident that I was not sufficient, and an organization began to grow about me. I have always felt that organized research is what our country needs, and that, as manufacturing companies grow in size and expand in interests, very much greater extension of research will be warranted. I feel this much more now than ever before, since I have seen how every nation is being forced to study and apply research to the things which determine national preservation and success in an advancing world.

Those who have followed the history of useful chemistry have seen how much has depended on pure research. All our industrial activities can be traced back of that time when they first promised utility, into that important period when they were simply natural inquisitiveness concerning Nature.

#### STATUS OF APPLIED RESEARCH

One of the results of the great modern era of education in natural science in Germany has been the extensive application of the discoveries of pure research. While this has not been confined to Germany, it was there most extensively realized. Our own country, less hampered by tradition than England, but limited in advanced teaching in natural sciences and particularly in pure research, seems destined to take a position in chemical activities intermediate between those countries.

On the part of the American Manufacturer there was, a few years ago, a perfectly reasonable feeling of fear that academically trained chemists constituted a pure speculation. At this very time the corresponding German chemists were building up some of Germany's greatest industries, and the English chemists were being kept out of British plants because, "knowing something about the business, they might influence it some way."

On the part of some American scientists there was the feeling that making a utility of the God-given discoveries of the truly beautiful phenomena of Nature was a prostitution to be deprecated, and that research could only be pure when it was sterile.

In the midst of these various points of view has come the development which seems to show that no knowledge can be counted as permanently useless. Cooperation between the forces which selfishly develop the useful and those which produce new knowledge seems always brought about by the gentle hand of time.

It may be of interest to others similarly placed, to give an account of the alteration of mind involved in my own change from pure to industrial research. I was at the time teaching at the Massachusetts Institute of Technology, and while the salary was very small, it was compensated by the feeling that I might be contributing something to science by the investigation of colloids. This field seemed to me then, as it does now, much more important than is generally realized. In spite of the fact that it is concerned in all the reactions of life, it still has more historians than workers. Such work appeared to me much more altruistic than did the opening in industrial research, and so I explained to the officers of the Company that I could not agree to give up teaching and pure research, but would give half-time to their research laboratory. After three years of this double, or rather half-service (for it was not over half-service altogether), I found that I had accomplished very little research on colloids, but had developed a desire to

take part in more extensive research than could be accomplished by my personal efforts alone. I would have been glad to be one of a large group of coöperators in colloid research, but the greater rate of possible accomplishment in industry decided the case for me. The desire for doing research work of an unselfish sort has actuated many men and the instinct, adhered to, accounts for many of the greatest discoveries of our science.

Dr. Coolidge experienced a similar change of ideal. He joined our research corps on the condition that half of his time should be devoted to research on the electrical conductivity of aqueous solutions at high temperatures and pressures, a subject upon which he had already done excellent work with A. A. Noyes. For a while he devoted himself religiously to perfecting his resistance bomb, but ultimately presented it to the Institute of Technology, because he wanted to devote all his time to other research. What Dr. Coolidge might have done with the resistance of electrolytes is unknown, but what he has accomplished by the application of extensive efforts and with many assistants to a forced research on ductile tungsten is well known. In practically every city, village and residence in the world where electric wiring has found its way, the work of Dr. Coolidge has helped contribute the lamp.

#### SCOPE OF GENERAL ELECTRIC COMPANY RESEARCHES

The varied interests of the General Electric Company made complex intercoöperation possible between widely diversified needs and equally diversified lines of knowledge, and I find on a rough survey that we have worked in some way on such a long list of subjects that even the list itself is tiresome. It extends from paints, oils and varnishes, to irons, steels and alloys; from the production of copper and zinc to molybdenum and magnesium; from thermions in plotrons to X-Rays in beetles; from carbon and tungsten incandescents to luminous arcs and searchlights; from the mica in the commutator of a railway motor and the brush that wears it away, to the electric solder on the bars and the insulation on the wires; from the composition of the turbine blade to the corrosive action of the boiler feed water; from atomic hydrogen in lamps to molecular layers in catalyzers; from silicon in transformer iron to silica in fuse-fillers; in elements from lithium and boron to uranium and thorium; in substitutes for rubber and for platinum, in the insulating body of the aero magneto, and the contact of the automobile vibrator; from Sherardizing to Calorizing; and from condenser and boiler tubes to special pyrometer tubes; and always, through prosaic past experience, to the exciting new outcome.

Through all I see the same interesting fact. It is the desired unforeseen which frequently eventuates, and our constant need is for faith that this will happen again. The regularity with which we conclude that further advances in a particular field are impossible seems equalled only by the regularity with which events prove that we are of too limited vision. And it seems always to be those who have the fullest opportunity to know who are the most limited in view. What, then, is the trouble? I think that one answer should be: we do not realize sufficiently that the unknown is absolutely infinite and that new knowledge is always being produced. The thing which has been impossible will be accomplished by new knowledge which cannot now be accurately preinventoried.

#### THE UNEXPECTEDNESS OF NEW KNOWLEDGE

I recall that the great geologist, Le Conte, probably delayed the development of aeroplanes for years by pointing out certain facts relating to the maximum sizes of fossil birds. Larger than his maximum fossils, no future creation of God or man might fly. Even a layman would instinctively hesitate to predict future impossibilities on the basis of fossils.



In the development of mechanical flight there have been hundreds of just such impeding arguments. In aeronautics everybody was expert, poets and mechanics, bible students and governments.

Some of you may recall that when dirigible balloons were lusty infants, Itham Maxim, the greatest living expert and a man who had actually done more on mechanical flight in England than anyone else, said: "I think we may therefore conclude that, as far as balloons are concerned, it will not be possible to improve greatly upon what Mr. Santos Dumont has already accomplished." Dumont had then been able to make short excursions and return to the point of departure even in the face of a slight wind. Could you blame a Zeppelin pilot on a thousand-mile trip in winter for wanting to drop a bomb on Mr. Maxim's English Experiment Station? Maxim said: "In all nature, we do not find a single balloon," and "Nature has not yet developed a bird that can feed on petroleum." Scintillating statements, yet Nature has done both of these things in ten years, and not even by new knowledge, but by a little higher degree of refinement of the old.

At the risk of excessive digression, I want to add another aero illustration. The well-known American astronomer, Simon Newcomb, tried to give the future all possible latitude and still he fell into the pit. In his own words, he put faith aside, and listened to no "evidence of things not seen." Reasoning exclusively on what had already been done, though he must have known that the arts continually progress and that some allowance must be made for this progress, he said:

"All should admit that if any hope for the flying machine can be entertained, it must be based more on general faith in what mankind is going to do than upon either reasoning or experience. \* \* \* \* \* But, as I have already intimated, there is another great fact of progress which should limit this hope. As an almost universal rule we have never solved a problem at which our predecessors have worked in vain, unless through the discovery of some agency of which they have had no conception. The demonstration that no possible combination of known substances, known forms of machinery, and known forms of force can be united in a practicable machine by which men shall fly long distances through the air, seems to the writer as *complete as it is possible for the demonstration of any physical fact to be*. But let us discover a substance a hundred times as strong as steel, and with that, some form of force hitherto unsuspected which will enable us to utilize this strength, or let us discover some way of reversing the law of gravitation, so that matter may be repelled by the earth instead of attracted—*then* we may have a flying machine. But we have every reason to believe that more ingenious contrivances with our present means and forms of force will be as vain in the future as they have been in the past."

Professor Newcomb was a representative expert, and I think that the suffering this chapter of his book may have brought to the real experimenter and searcher, Professor Langley, who, under the derision of the less inquisitive scientists, laid the foundations of aeronautics, ought to make us discourage the scientific knocker, no matter who he is. No less a physical authority than Lord Kelvin wrote, in 1896, to Colonel Baden Powell:

"I have not the *smallest molecule* of faith in aerial navigation other than ballooning, or of expectation of good results from any of the trials we hear of. So you will understand that I would not care to be a member of the aeronautical society." He, too, the greatest English physicist, did not care to make any allowances for a single new step beyond the beaten path fully known to him.

#### ARC RESEARCH

I remember the timidity with which, in the early days of my

own interest in arc lamps, I tried a few experiments to see whether in reality the migration of the material of the carbon electrode was coupled quantitatively with the passage of current. I believed it was, and recalled being taught that positively charged carbon particles passed across the arc gap, but, having read and imperfectly understood J. J. Thomson, I secretly expected in some way to show that the current was in reality due to motion of weighable *negative* particles moving in the opposite direction. By operating a direct current arc between one stationary electrode and an electrode which was rapidly rotated in a lathe, I soon learned that there was no simple quantitative relationship, at least, between the positive carbon loss and the current, as this loss became negligible when the carbon was kept cool. The negative electrode always lost a little in weight, and for a short time this looked like the coulomb equivalence to be expected. Perhaps it was, but I never proved it, and still doubt it in spite of a recent publication to this effect.

We talked freely of negative carbon ions in carbon arcs, but were still surprised to find that in other arcs, such as the magnetite, the negative electrode was the only one consumed. The consumption in both of these cases is probably not the primary result of carrying the current at all, but a secondary effect following oxidation and vaporization, due to local heating.

It was quite in accord with experience and with the aims of my present argument for preparedness for unexpectedness that something yet unexpected was to be found on further investigation of this simple phenomenon. What the world has since learned about electronic emission, from Richardson, Langmuir and others, and the ionization of vapors or gases between electrodes, is very far from being the logical interpretation of the available data we had before the days of the negative corpuscle of Thomson. So here again we see the creative effect of the unexpected. Our entire views on arcs have been revised in a very few years and there is more to follow.

Skipping the history of the ions, let me touch just one or two points of experience which emphasize to me the rapid growth of the unexpected.

Instead of weighable positive particles of matter carrying the current across highly evacuated space, we now recognize only negative corpuscles moving in the opposite direction. Instead of finding that they involve a loss of weight at their source, we find the weight of the electrodes unaltered. Surely these two conclusions were as improbable a few years ago as any relevant conclusion could possibly have been. That these intangible corpuscles, while within that vacuum gap, should constitute an essential part of several of the devices of wireless telegraphy and telephony was of course also among the unexpected by-products.

I shall not describe Dr. Langmuir's pliotron nor Dr. Hull's dynatron. They have been described in the literature by the discoverers, but I will use one more illustration in this field to continue my argument that we ought to expect the unexpected, and search for it.

#### THE SURPRISES OF HIGH VACUUM RESEARCH

When, in a very high vacuum, the velocity at which negative corpuscles impinge upon a plate exceeds a certain value, the surface in turn sends off negative corpuscles and in greater numbers, though at a reduced velocity, than those which are received. As the velocity of the primary corpuscles is proportional to the voltage, increase of voltage thus produces a diminished current to the plate and the contrivance then fulfills the conditions of a negative electrical resistance. This is quite an unexpected outcome, and to call the apparatus a nega-

tive resistance, as is done, is in keeping with this unexpectedness.

When one of the men of the laboratory recently showed me a new alloy which was pyrophoric, I was not surprised because I had already been surprised by that phenomenon in the well known cerium alloys.

But when another brought me a small solid rod of alloy which persisted in growing hot on standing, even after repeatedly being cooled off in water, I was surprised. If someone had first asked me if it were possible to make such a thing, I should have said "No." Apparently certain alloys may undergo a slow oxidation sufficient to warm them up, without showing any visible alteration for a considerable time.

You may have heard it said that the first steam-propelled vessel to cross the Atlantic brought to these shores the first copies of a book in which was explained the impossibility of transoceanic steam propulsion. Doubtless, too, the real sailors of the day were the surest of all people on this point.

#### INCANDESCENT LAMPS

It almost seems as though more useful discoveries come as surprises than arrive in accord with our well-laid plans. I recall that in the case of the carbon incandescent lamp we had what we thought was a splendid theory for the decay of the filament during burning, and we had a sure cure for it. This was all based on the residual ash of the carbon and its subsequent slow reaction with the filament during the life of the lamp. To get rid of the ash before making the lamp, it seemed necessary only to preheat the filaments in an electric furnace at the vaporizing temperature of the foreign matter. Fortunately, we used composite filaments; that is, those which had, besides the carbon base or core, also a thin shell of graphite which had been deposited from benzine, as was the custom at that time. High preheating of these filaments produced the great improvement in the lamp known as the metallized, or GEM lamp, but it was not at all in accord with our theory as experts, but because of another one of those entirely unforeseen novelties of Nature which make experimentation so attractive. The graphite shell of these filaments was changed by the high temperature into a new kind of carbon. We called it metallized graphite because it reacted chemically like pure graphite, and, like the metals, it had a higher electrical resistance hot than cold. Ordinary graphite has a coefficient of the opposite sign. Had we ever imagined such a form of graphite we would doubtless have thought it too improbable to warrant experiment.

We passed through the time when such an expert as Welsbach said that pure osmium, under incandescent lamp conditions, is probably "the most refractory and unalterable body known to science and which at high temperatures emits the greatest amount of light." This was very generally believed, but under the same conditions it was later found that tungsten was still better. I have often thought that possibly the very commonness of tungsten may have made its successful use in lamps seem improbable. To Auer von Welsbach, at least, it must have been as easy to test as was osmium, which for several years made the best incandescent lamp. The unforeseen possibilities were just as surely there as was the possibility of some one climbing Pike's Peak after Zebulon Pike's diary predicted that no human being would ever be able to scale its rocky heights.

We had the great pleasure of living through the period when the work of Dr. Coolidge, of the laboratory, made brittle tungsten ductile. We talked with some of the world's greatest chemists on this work, even while it was under way, and learned how sure all the experts were that tungsten was forever a brittle element. We knew it only as a finely divided powder or as hard grains. Filaments of it had been made for several years

by a paste process, and these were so brittle that they could not be bent cold at all, and broke into pieces if dropped on the floor.

For a year or more all sorts of experiments on the removal of impurities and the introduction of ductility-producing materials were tried without success. It is fair to say that everyone who could be called expert on tungsten considered it fully as nonductile as to-day's experts on chromium or silicon, for example, would pronounce these metals. But it was made ductile by a long series of undeviating experiments, to the incredulous surprise of our German competitors in the race.

For some time after tungsten wire had been drawn successfully, there were experts who pointed out that this could not be done cheaply enough to displace the older type filament, and I recall distinctly being nearly convinced of this myself, for we were drilling diamonds for draw plates for the wire. If I had had such a lesson every day, I fear the necessity for repetition would still remain.

It is a well known generality of nature that thermal and electrical conduction go hand in hand. Porcelain and glass are insulators and metals are good conductors, but the best thermal insulator made in our laboratory was found to be a good electrical conductor. This is one of those matted distillation products of the electric furnace, composed of silicon, carbon and oxygen. As the material seems transparent under the microscope, it is again paradoxical that it should conduct current.

Similarly unpredicted was the result which Dr. Weintraub obtained when he made pure boron as a possible lamp filament material. Here is a material unlike every other known product, for it passes through the entire range from high insulator to good electric conductor within a very narrow temperature range.

For years we in the laboratory worked in every conceivable way to remove the last traces of gas from incandescent lamps. We carefully determined the effect of the last molecule of every gas which could possibly enter a lamp and some which could not. As a result, Dr. Langmuir discovered the hitherto unsuspected fact that a better tungsten lamp can be made by filling the bulb with nitrogen or argon. There had been a long time when we felt we knew with certainty that the vacuum was necessary. But there were relevant things we did not know even then. New knowledge changed the looks of things. During the vacuum work I certainly lacked faith in the beneficial effect of gases. Nature was ready with the new facts when we made suitable inquiry.

I remember also that after we had tried to increase the resistance of our early tungsten filaments by introduction of rare oxides and other material which we hoped would remain in the filament when hot, and had seen them distill out at the temperature of operation, someone suggested adding traces of such oxides for the purpose of increasing the life of the filament. It seemed a futile experiment, but the traces served the new purpose, while greater quantities had failed.

Why should we force new knowledge to come by such difficult and circuitous routes? Can we not train ourselves to be more ready for it, more open-minded for its reception and more stunted in our satisfaction with present knowledge?

We seem to live in a rapidly changing environment so far as Nature's laws are concerned. Of a truth, we ourselves and our conception of things, are the variables, and when we have once realized this much, there comes the possibility of directing our hope and expectations, our visions and experiments along what we may call a pragmatic path. This means more care and respect for the contents of the future and more urgency in their development.



## AMERICAN NEED FOR STUDENTS AND EXPERIMENTERS IN PHYSICAL AND CHEMICAL SCIENCE

Your medal is bestowed for service in chemistry. Our greatest American need to day is not in cannon, nor yet in soldiers but is for students and experimenters in physical and chemical science. We in the United States have not really started on the way of doing our share of the new work of the world, except possibly in the field of biology. We have got to create an atmosphere. It must be an atmosphere in which the real searchers for material truth can grow and multiply. Instead of finding in a few of our colleges one or two teachers who do a little experimental work when they get time from their classes, there must be some arrangement by which those who are fitted by nature to contribute to new knowledge may do so. These men must not be confined to attempting to fill students with ancient knowledge, so that they in turn become repositories of stationary thought (to use Dr. Woodward's expression). If they are given a little support I am sure that we can produce in this country at least as large and active groups of scientific investigators as were so common in Germany before the war. This can perhaps be hastened by continued reminders that it is a necessary factor of any well-planned and sure system of national preparedness for defense or for peace.

Apparently we have become so accustomed to foreign degrees in science that we do not realize that we might become independent of them. A college which does not even permit its teachers to do experimental work still always favors the applicant teacher who has a degree for which research was required. How can we alter this narrow view of our opportunities? We can alter it by proper recognition of the value of new contributions to our store of knowledge. It was that thought which kept Willard Gibbs at work on his abstract generalizations, which, years later, were started on their tour of endless practical appreciation and application by Roozeboom. It was that thought which prompted William A. Converse to establish this medal fund and it is to that end that I wish to utilize this address.

We have never needed extensive scientific research so badly as we do now and we never have been in so fair a condition for its extension. The objection has been made, and it seems to be the only one, to grants of money from the government to the land grant colleges for research work, that there is no suitable system for insuring wise expenditure, especially in states where there has been little experience in research. This is a real objection and applies equally well to grants from other sources when they are made to little-known institutions and individuals. Yet these last are the very ones which most need encouragement to enter the field of research. Under the guidance of sympathetic and intelligent men, who are thoroughly in touch with the research and needs of the United States, this objection might be removed.

Practically all of our many scientific societies have for their object, as expressed in their constitutions, the advancement and diffusion of knowledge or the advancement of the theory and practice of the particular science. The American Chemical Society Constitution contains the words "the objects shall be the advancement of chemistry and the promotion of chemical research."

## OPPORTUNITY FOR NATIONAL RESEARCH "CLEARING-HOUSE"

We have in Washington a number of endowed and Federal research and scientific laboratories where chemistry is prominent as, for example, the Bureau of Standards of the Department of Commerce. We have the Bureau of Mines and the Geological Survey of the Department of the Interior, and the Bureau of Chemistry and the Bureau of Soils of the Department of Agriculture, all with extensive testing and industrial research labo-

raries. In the separate states are colleges and university laboratories, and a growing number of technical laboratories. These ought all to be cooperating in the advancement of knowledge. I believe the time is ripe for constructive work on the coordination of the various research organizations, existing and potential.

I think that the government difficulties, augmented by the present war, could be lightened by a system which involves the research experts of the country as coöperators. There is need for a central clearing-house in new scientific endeavor. This is well shown by such a condition as exists in relation to the question of a nitrate supply for explosives, dyes and fertilizers.

No single government office knows the main facts of all the various processes for nitrogen fixation. The Department of Agriculture is interested in any form of fixed nitrogen and is carrying on experiments for itself. The army and navy want only nitric acid or something from which it can be made. The Department of the Interior is interested in it as a mineral proposition and is doubtless drilling for it. Several industries are trying to produce nitrates or ammonia and many industries would use the product. The complete knowledge of such a subject should be in the hands of a central office from which reliable data could be easily obtained by Congress.

Such an office could foresee some of our general needs and by suggestions assist directors of government and college research in their activities. In this way and by other means this central office would ultimately know who in America was trying to do research, what his equipment was and how he might help or be helped. Its officers would be welcomed by government and college laboratories, so long as they actually kept in touch with the work and gave constructive advice upon it. They would help in encouraging the development of American research in more or less isolated laboratories and colleges by visits to them and acquaintanceship with their men. The importance of this personal contact can scarcely be overestimated. There would accumulate a great deal of new information and experience which could with propriety be passed from one laboratory to another. Coöperation could be effected in regard to the use of the special apparatus so common in research.

This work would demand the exclusive services of a few of our ablest scientists who would thus devote their entire energies to the orderly promotion of our country's interests in research. Unguided, misguided and duplicate research might be reduced. Unplanned work might be well planned and such steps taken as continuous systematic study of the subject showed to be warranted.

Such a function would constitute splendid work for our National Academy of Science, hitherto not particularly active, but made up of over a hundred of the very foremost American Scientists. It might warrant the Federal aid in the way of permanent building and support evidently desired by the Academy.

I would suggest that the American Chemical Society, possibly through instigation by the large and active Chicago Section, might start such a scheme into activity. It might advise the President of the United States that for the benefit of research it seemed desirable to have some such system by which greater coöperation could be attained in existing efforts and through which we could have assurance of active foresight and encouragement for the future research work of our country. Cannot the Chicago Section in this or some better way become the leader of a great advance?

RESEARCH LABORATORY  
GENERAL ELECTRIC COMPANY  
SCHENECTADY, N. Y.

# SCIENTIFIC SOCIETIES

## AMERICAN INSTITUTE OF CHEMICAL ENGINEERS EIGHTH SEMI-ANNUAL MEETING, CLEVELAND, OHIO, JUNE 14 TO 17, 1916

The eighth semi-annual meeting of the American Institute of Chemical Engineers will be held in Cleveland, Ohio, June 14 to 17, 1916, with headquarters at the Statler Hotel. The meeting will open on Wednesday morning, June 14th, at the Statler Hotel, with an Address of Welcome by Ralph L. Fuller, president of the Cleveland Chamber of Commerce. The business session will follow. The Wednesday evening session will be held at the University Club, followed by a smoker and entertainment given by the Local Committee.

On Thursday a complimentary luncheon will be given at the Students' Club of the Case School of Applied Science, with an Address of Welcome by President Charles C. Howe. The laboratories of the Case School are to be inspected.

The Subscription Dinner (\$3 per plate) will be held on Thursday evening at the Statler Hotel.

The Friday evening session will be a joint meeting with the Cleveland Section of the American Chemical Society.

### PROGRAM OF PAPERS

**The Production of the Rarer Metals.** JOSEPH W. RICHARDS.  
**The Effect of Storage on Mixed Paints.** E. E. WARE AND R. E. CHRISTMAN.  
**Recent Developments in the Production of Nitrocellulose.** EDWARD E. WORDEN.  
**The Utilization of American Clays.** ARTHUR S. WATTS.  
**Nitric Acid Sophistication—A Serious Production Menace.** JAMES R. WITHROW.  
**Sound (Illustrated lecture).** DAYTON C. MILLER.  
**Experimental Work for a Cleveland Sewage Disposal Plant.** R. R. PRATT.  
**The Purification of Sewage by Aeration in the Presence of Activated Sludge.** II. EDWARD BARTOW.  
**Water Powers of the United States.** HERMAN STABLER.  
**Acid-Resisting Alloys.** W. C. CARNELL.

### PROGRAM OF EXCURSIONS

The following places of interest will be visited: The Central Furnaces; Semet-Solvay Company; Biprodukt Coke Oven Plant of the Cleveland Furnace Company; Newburgh Plant of the American Steel & Wire Company (where pig iron, bessemer and open-hearth steel are drawn into all kinds of steel wire); Ore Docks of the Pennsylvania Railway Company; Cleveland Filtration Plant; National Carbon Company; Lamp Factory, Research and Engineering Laboratories and Glass Works of the National Lamp Works of the General Electric Company at Nela Park; Goodrich Rubber Company, Akron.

### COMMITTEES

Mr. F. Lee is *Chairman* of the Local Committee and Mrs. A. W. Smith is *Chairman* of the Ladies' Committee. A special program has been arranged for the ladies.

## NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES NEW YORK—SEPTEMBER 25 TO 30, 1916

The managers of the Second National Exposition of Chemical Industries to be held at the Grand Central Palace during the week of September 25th, report that practically every one of the exhibitors of last year has already contracted for space for this year. About 30 per cent more space is now contracted for than was contracted for last year, so that two floors of the building will evidently have to be used to accommodate the exhibits.

There is a bill now pending before Congress for an appropriation of \$10,000 to be used in the preparation of a governmental exhibit, and this promises to go through.

The Bureau of Commercial Economics is arranging the motion picture program, and new films never shown before will constitute the program. Last year too many films were shown, and many of the best were shown only once, and consequently were not seen by every one interested. This year, however, fewer films will be shown and these several times each.

Because of the general meetings of the American Chemical Society and the other scientific organizations which will be held in New York City during the week of the Chemical Show, the Exposition will offer no addresses or lectures.

The list of exhibitors to date (May 19th) is as follows:

Buffalo Foundry & Machine Co.	The Palo Company
Glens Falls Machine Co.	Uehling Instrument Co.
Lenz & Naumann, Inc.	Ruggles-Coles Engineering Co.
Metallurgical & Chemical Engineering	Emil Greiner Co.
The Pfaunder Co.	Scientific Materials Co.
Toch Bros.	International Glass Co.
Merck & Co.	Thermal Syndicate, Ltd.
Norton Co.	Leeds & Northrup Co.
Detroit Range Boiler Co.	Sweetland Filter Press Co.
Thos. A. Edison	De Laval Separator Co.
Shaples Specialty Co.	Valley Iron Works
Condensite Co. of America	Thwing Instrument Co.
Duriron Castings Co.	Celluloid Zapon Co.
United Lead Co.	Sturtevant Mill Co.
Raritan Copper Works	Great Western Power Co.
J. T. Baker Chemical Co.	E. B. Badger & Sons Co.
Benzol Products Co.	Huff Electrostatic Sep. Co.
Dorr Co.	Carborundum Co.
Schutte & Koerting	Semet-Solvay Co.
Schaeffer & Budenberg Mfg. Co.	Research Corporation
Sowers Mfg. Co.	Laboratory Supply Co.
Stamford Mfg. Co.	Monsanto Chemical Works
Verner & Pfeiderer Co.	Kieselsbuh Co. of America
Abbé Engineering Co.	Precision Instrument Co.
Tolhurst Machine Works	Williams Pat. Crusher & Pulv. Co.
Zarembo Co.	Union Sulfur Co.
Elyria Enamelled Products Co.	Schaum & Uhlinger, Inc.
Emil E. Lungwitz	Patterson-Allyn Eng. Co.
L. O. Koven & Bro.	Beckheim Fdry. & Machine Co.
E. I. DuPont de Nemours Co.	Footo Mineral Co.
Eimer & Amend	International Filtration Corp.
Swenson Evaporator Co.	American Cyanamid Co.
Dow Chemical Co.	E. R. Squibb & Son.
Hardinge-Conical Mill Co.	Weiller Mfg. Co.
Standard Aniline Products, Inc.	American Chemical Society
Lead Lined Iron Pipe Co.	Paper & Pulp Association
United States Smelting Co.	Niagara Falls Electrochemical Soc'y
J. L. Mott Iron Works	Society of Chemical Engineers
J. P. Devine Co.	American Electrochemical Society
General Chemical Co.	American Inst. Mining Engineers
General Bakelite Co.	Paul O. Abbe
The Barrett Company	German-American Stoneware Co.

### REPORT OF PATENT COMMITTEE

#### 52ND MEETING AMERICAN CHEMICAL SOCIETY

Since the last meeting of the American Chemical Society, nothing of real importance has occurred on the subject of patent legislation. The activities of the legislative bodies of the United States have been mostly concentrated on the subject of national preparedness. Up till now, their main attention has been given to the preparedness of our Army and Navy. However, it has become obvious that the industrial preparedness of our country is even more indispensable. This has been clearly set forth by the Subcommittee on Industrial Organization, Standardization and Manufacturing, of the United States Naval Consulting Board, which, through President Wilson, has enlisted the coöperation of the American Chemical Society and the principal engineering organizations of the country.

It is very probable that the question of patent reform will be taken up as soon as more urgent matters are disposed of. It seems hardly possible, however, to take up thoroughly the subject of patent reform during the present legislative session.

In the meantime, the so-called Paige Bill has again been presented for consideration before the House of Representatives. Although this bill is conceived with the best of intentions, its defects are such as to do incomparably more harm than good. The bill has been thoroughly discussed last year before the House Committee on Patents, and for a time, it seemed as if this bill were to be withdrawn. Aside from the arguments which



were presented against this bill by the representatives of your committee, there has been published by Dr. Bernhard C. Hess an exhaustive article on this subject in which all further data can be found. This article appeared in *THIS JOURNAL*, 7 (1915), 965.

The unfortunate part of all such bills is that they merely constitute patchwork devised without any comprehensive idea of the general situation and which, therefore, unknown to their authors, embody dangers which would tend to cripple our whole patent system and make it still worse than it is.

We fear that this situation will persist as long as the matter of systematic patent reform is not entrusted to a nonpartisan, non-political, technical commission of qualified men, including representatives of the public, the manufacturers, the inventors, the Federal Courts, and the patent bar.

This suggestion along the lines of efficiency, which seems simple enough to chemists and engineers, does not, however, appear to meet the views of our legislative bodies, which are overwhelmingly composed of lawyers. This once more brings out how a most democratically planned Republic may lead to inefficiency, if for some reason or another, the people prefer to elect, almost exclusively, lawyers to act as their representatives in Congress and in the Senate. This matter resolves itself simply to what is more desirable—government by lawyer-politicians, or government by experts?

A general plan of revision of our patent laws could hardly be carried out without taking into consideration treaties with foreign countries. The very fact that practically all important foreign industrial countries are now at war, makes it impossible to undertake anything of the kind at present.

Your committee holds itself ready to take the first opportunity, whenever conditions warrant it, to cooperate with similar committees of other societies for the advancement of any constructive patent legislation which will tend to bring our patent system up to the requirements of modern conditions.

It gives great satisfaction to the committee to mention that the present Patent Commissioner has done much to simplify and increase the efficiency and operation of the Patent Office; it should be stated also that the present Chairman of the House Committee on Patents has given considerable study to the patent situation and is unusually well prepared to investigate the merits of any subjects brought before his committee.

L. H. BAEKELAND, *Chairman*

#### BLOEDE SCHOLARSHIP IN CHEMICAL ENGINEERING

The Chemists' Club of New York announces the establishment of a scholarship fund, the income from which, approximately \$500 per year, is to be devoted to assisting financially deserving young men to obtain education in the field of Industrial Chemistry or Chemical Engineering. This scholarship has been endowed by Dr. Victor G. Bloede, a prominent manufacturing chemist of Baltimore. Its benefits will be open to properly qualified applicants without restriction as to residence, and may be effective at any institution in the United States which may be designated or approved by the Chemists' Club. Applicants must, as a minimum qualification, have completed a satisfactory High School training involving substantial work in elementary chemistry, physics and mathematics and present a certificate showing that they have passed the entrance examination requirements of the College Entrance Examination Board or its equivalent. Preference will be given to young men who have supplemented these minimum qualifications with additional academic work, especially in subjects which will form a suitable groundwork for the more advanced study of applied chemistry and chemical engineering. All inquiries should be addressed to the Bloede Scholarship Committee of the Chemists' Club, 50 East 41st Street, New York City. Applications for the academic year 1916-1917 should be in the hands of the committee

on or before June 1, 1916. The scholarship will be awarded and candidates selected and notified on or before July 1, 1916.

Dr. Victor G. Bloede, the founder of the Bloede Scholarship, was born in Dresden, Saxony, in 1849 and began his technical education at Cooper Institute in New York City and later established himself as a manufacturing chemist in Brooklyn. In 1873 he organized the Victor G. Bloede Co. of Baltimore, of which he is President. He has been prominent in philanthropic work for many years, having presented to the State of Maryland its first hospital for advanced consumptives. He is a member of the American Chemical Society, the Society of Chemical Industry, Johns Hopkins Club, the Baltimore City Club, and Chemists' Club of New York, of which latter institution he is now non resident vice-president.

#### HOFFMANN SCHOLARSHIP IN CHEMICAL ENGINEERING

The Chemists' Club of New York announces the establishment of a scholarship fund, the income from which, approximately \$400 per year, is to be devoted to assisting financially deserving young men to obtain education in the field of Industrial Chemistry or Chemical Engineering. This scholarship has been endowed by Mr. Wm. F. Hoffmann. Its benefits will be open to properly qualified applicants without restriction as to residence, and may be effective at any institution in the United States which may be designated or approved by the Chemists' Club. In accordance with the deed of trust applicants must, as a minimum qualification, have completed a satisfactory high school training involving substantially work in elementary chemistry, physics and mathematics and present a certificate showing that they have passed the entrance examination requirements of the College Entrance Examination Board or its equivalent. Preference will be given to young men who have supplemented these minimum qualifications with additional academic work, especially in subjects which will form a suitable foundation for the more advanced study of applied chemistry and chemical engineering. All inquiries should be addressed to the Hoffmann Scholarship Committee of the Chemists' Club, 50 East 41st Street, New York City. Applications for the academic year 1916-1917 should be in the hands of the committee on or before June 1, 1916. The scholarship will be awarded and candidates selected and notified on or before July 1, 1916.

Mr. Wm. F. Hoffmann, the founder of the Hoffmann Scholarship, is prominent in the industrial chemical profession, and is President of the American Oil and Supply Company, of Newark, N. J. He has always been active in the civic affairs of Newark and is well known for his philanthropic work. He is one of the founders of the Chemists' Club of New York, and has always been a leader in the activities of the chemical profession.

#### OBITUARY—CHARLES ALBERT CATLIN

By the death of Charles Albert Catlin chemical circles and society at large suffers a very real loss. For over forty years Mr. Catlin has been connected with the Rumford Chemical Works and there, as in every other circumstance, has served the interests of his profession with distinction and capacity.

His activities were not confined to chemical matters, however. He also took an active and effective part in many educational and philanthropic as well as social organizations, living in every relation the well-rounded life of a good citizen.

His genial personality will be missed in many places, but with especial keenness by those who have had the pleasure of working with him during his service of seventeen years on the Council of the American Chemical Society.

W. R. WHITNEY	} <i>Committee for Council American Chemical Society</i>
W. A. NOYES	
H. P. TALBOT	

## NOTES AND CORRESPONDENCE

### CHEMISTRY AND PUBLICITY

*Editor of the Journal of Industrial and Engineering Chemistry:*

In the *New York Tribune* of Sunday, May 14, 1916, in which the Preparedness Parade, held in New York City the day before, was appropriately and extensively treated, there appeared as a leading editorial "Water Power and Preparedness," based upon the Washington, D. C., meeting of the American Electrochemical Society and its symposium on Niagara water power. In the course of this editorial occurred the following statements:

"It is perhaps not unnatural that the public is ignorant of its interest in this vital question. Engineers and technical men are themselves largely responsible for the popular apathy since they have left the matter in the hands of ignorant legislators and met the restriction of power development with what could at best be described as passive resistance. \* \* \* Yet our only hope at present is in the scientific and technical men. They have been too easy-going and have not taken sufficient pains to explain their aims and purposes to the public. It is only by doing so that they can hope to bring pressure to bear on legislators. \* \* \* In the recent meeting of the American Electrochemical Society there were signs of a clearer realization among technical men of their public responsibility in this matter. This is all to the good, for it is only through their efforts that the public can be made to understand what they have a right to demand of their legislators."

Speaking from my own personal experience, I am convinced that the editors of our own daily papers are themselves in good measure responsible for the conditions referred to in the above quotation. In February, 1911, acting as Secretary of the 8th International Congress of Applied Chemistry, to be held in Washington and New York in September, 1912, I sent to the editors of the daily papers of New York, Philadelphia, Boston, Baltimore, Washington, D. C., Chicago, Pittsburgh, St. Paul, Minneapolis, Omaha, Kansas City, Denver, San Francisco, and other cities, a short history of the seven preceding Congresses and statistical information as to their labors, also copies of our first pamphlet describing our aims and purposes and organization; in all, 390 dailies all over the country were so approached. So far as I was able to learn, only two papers, in two different states, both west of the Mississippi, took any notice whatever. In June of that year I followed the February material up with more material and gave a short abstract of what we had accomplished and of what we hoped still to do, and sent that also to these same papers and about 150 boards of trade and chambers of commerce, and 8,000 manufacturers all over the country. At intervals thereafter I reported progress to the daily press in about the same way. Up to the summer of 1912, not one single New York daily took the slightest note of the matter sent to them. During that summer one daily did say something about the Congress, but only because we made very great personal efforts to arouse the interest of that paper.

During the summer of 1912 one other New York daily did give about a quarter column to the Congress, printing a clipping out of the Consular Reports; but this clipped matter reached the Consular Reports because our Consul at St. Petersburg, Russia, with whom I had been in very active correspondence about the Congress, sent this matter to Washington as a news item. I had sent precisely the same information to that same New York editor eight months before, but it had no value to his paper until he found it in the Consular Reports, even though it was then more than eight months old. When the Congress program was ready, I sent copies to every New York paper, and, as I recall it, only two took any notice during its sessions of what the Congress was trying to do. Towards the end of its session

they became a little more interested, but only in a lukewarm way. During this Congress two public lectures were given, whose combined attendance was something over 3,000; at the first of these lectures an exhaustive and illustrative treatment was given of the Norwegian process of making nitric acid from air; at the second lecture an experimental demonstration of the synthetic production of ammonia was given; these two things are probably as great achievements as have been accomplished within the last generation, yet the New York dailies took no note of it whatever, and it was not until a clever Chicago reporter lampooned it that the press took notice of it; the only way that synthetic nitric and synthetic ammonia could break into our daily papers was through such an extravagant statement, as, for instance, "Chemists Make Eggs Out of Air;" it certainly is a very long way from synthetic ammonia and synthetic nitric to synthetic eggs.

This Congress was by no means a negligible affair; 28 countries took part in it; 18 different countries had organizations for preparation for the Congress, and these foreign organizations comprised 573 individuals and 55 societies. The American organization numbered upwards of 1500 technical and scientific men whose purpose was to promote the interests of the Congress. We distributed our news service to 438 trade, technical and scientific publications the world over, and this exclusive of our news service to the daily press; altogether we sent out over 300,000 pieces of printed matter informing the public what our aims and purposes were; 151 public meetings were held in New York City during the week this Congress was in session.

At the New Orleans meeting of the American Chemical Society, in March and April, 1915, that is, after we had had eight months of the great war, there were nineteen short papers presented, each of them wholly in nontechnical language, on what the American chemists had done for nineteen American industries; advance proofs of each of these papers together with a short résumé of each of them, and all printed, were sent to the editors of about thirty prominent dailies inclusive of New York dailies; outside of New Orleans I could find but one daily that took any notice whatever of the matter and that was done by the simple process of "lifting" one of the articles as an editorial without giving any credit whatever to the American Chemical Society.

The first point of entry for publicity *must* be by way of the editors of our dailies; if they block the way nothing can be done. We must first educate our editors as to what the country should know, and then induce the editors to educate the public. The editors know better than any one else the mechanism for educating the public; if the editors will receive technical matter in a welcoming way, it is absolutely certain that the technical men will state their case in the language and form which the editors consider best fitted for instructing the public. I say this, even though it has happened to me that after spending nine hours with an efficient editorial writer of a large New York daily, in explaining technical matters to him and in going over his manuscript and his copy and had boiled down a very technical story into fewer than 1500 words, our combined effort was crowded out by the editor-in-chief because he needed the space for something else. However, I am not discouraged; I still believe that our editors can be educated up to the point of wanting technical matters, and if the editors will come only one-third the way, the technical men will gladly go the rest of the distance.

25 BROAD STREET, NEW YORK  
May 15, 1916

BERNHARD C. HESSE



## MATERIALS IN A TON OF KELP

Editor of the Journal of Industrial and Engineering Chemistry:

The seriousness of the current shortage of potash gives increased importance to a careful consideration of the American sources of it. The following table gives in pounds the quantities of the materials mentioned that are contained in a ton (2000 lbs.) of fresh kelp. The three species mentioned are the ones that are harvestable in commercial quantities along the Pacific coast of North America. The supply available on the California coast is mainly *Macrocytis*, that in the Puget Sound region is mainly *Nereocystis*, while that in Southern Alaska is *Nereocystis*, *Macrocytis* and *Alaria*. In Western Alaska the supply is *Nereocystis* and *Alaria*. The sources of information for the data given in this table are fully indicated in the notes.

	Water	Potassium Chloride	Other Salts	Iodine	Algin	Crude Nitro- fiber	gen
<i>Nereocystis</i> .....	1834	52.7	25.1 to 37.7	0.22	23.4	8.4	2.9
<i>Luetkeana</i> .....	(a)	(b)	(c)	(d)	(e)	(f)	(g)
<i>Macrocytis</i> .....	1736	52.5	26.7 to 55.7	0.61	44.4	19.3	4.3
<i>pyrifera</i> .....	(h)						
<i>Alaria fistulosa</i> .....	1726	39.3	27.6	Trace	No data	No data	7.1
	(i)	(j)	(k)				(k)

## LITERATURE CITED

- 1—F. K. Cameron, "Pacific Kelp Beds as a Source of Potassium Salts," U. S. Dept. Agr., *Rept.* 100 (1915), pp. 9-32.
- 2—T. C. Frye, "The Kelp Beds of Southeast Alaska," U. S. Dept. Agr., *Rept.* 100 (1915), pp. 60-104.
- 3—D. R. Hoagland, "Organic Constituents of Pacific Coast Kelps," *J. Agr. Res.*, 4 (1915), pp. 39-58.
- 4—G. B. Rigg, "The Kelp Beds of Puget Sound," U. S. Dept. Agr., *Rept.* 100 (1915), pp. 50-58.
- 5—J. W. Turrentine, "The Technology of the Seaweed Industry," Sen. Doc. 190, Sixty-second Congress, second session (1912), pp. 232-262.

## NOTES

(a)—Computed from an average of the per cent of moisture reported in (2) p. 63, (3) p. 43, and (4) p. 54. All other computations for *Nereocystis* are made on the basis of 166 lbs. of dry matter per ton of fresh kelp.

(b)—Computed according to the per cent given in (1), p. 17, using the factor 1.58 in figuring KCl from  $K_2O$ . No account is taken anywhere in this table of differences in content between stems and leaves. The samples of *Nereocystis* and *Macrocytis* from which the data here referred to were secured usually consisted of the harvestable portion, which comprises both leaves and stems. The samples of *Alaria* usually consisted of leaves only. In general there is more potash in stems than in leaves, and more nitrogen in leaves than in stems. See (1), pp. 26-27.

(c)—The minimum was computed as follows: The per cent of KCl was figured by multiplying the per cent of  $K_2O$  given in (1), p. 17, by 1.58. This per cent was then subtracted from the per cent given on the same page for "total soluble salts"  $[46.9 - (20.1 \times 1.58)] \times 166 = 25.1$ . The maximum was computed in the same way except that the "total salts" reported in (3), p. 43, was used  $[54.5 - (20.1 \times 1.58)] \times 166 = 37.7$ .

(d)—Computed according to the per cent of iodine given in (1), p. 17. For a discussion of the forms in which iodine is present in kelps see (3), p. 52.

(e)—Algin is the material that can be dissolved in sodium carbonate and precipitated with acids. Computed according to the per cent given in (3), p. 43. For a discussion of its properties see (3), pp. 47-50, and (5), pp. 249-253.

(f)—Computed according to (3), p. 43. The crude fiber reported was approximately half cellulose. See (3), p. 50.

(g)—Computed from an average of the percentages given in (1), p. 17 and (3), p. 43.

(h)—Computed according to the per cent of moisture given in (2), pp. 64-65, and (3), p. 43. All other computations for

*Macrocytis* are made on the basis of 264 pounds of dry matter per ton of fresh kelp. All computations for *Macrocytis* are made in the same manner as those for *Nereocystis*. The per cents are all taken from (1), p. 15, and (3), p. 43.

(i)—Computed on the basis of data given in (2), pp. 64-65. All other computations on *Alaria* are made on the basis of 274 lbs. of dry matter per ton of fresh kelp. All computations for *Alaria* are made in the same way as those for *Nereocystis* and *Macrocytis* except that (j) is figured for the minimum only, since no data in regard to *Alaria* are given in (3), and that (k) is based on (1), p. 18 only, for the same reason. All per cents for *Alaria* are from (1), p. 18.

UNIVERSITY OF WASHINGTON  
SEATTLE, March 23, 1916

G. B. RIGG

## SYNTHETIC PHENOL RESINS

Editor of the Journal of Industrial and Engineering Chemistry:

Permit me to adjust to their proper value some statements contained in a letter signed by Messrs. L. V. Redman, and his business partners, A. J. Weith and F. P. Brock, published on page 473 of the May number, 1916, of THIS JOURNAL:

Dr. Redman says: "One method of producing these resins was developed by Dr. Baekeland." The fact is that I developed and patented several methods; each of them is suited to special conditions and is preferred, in one case or another, according to the varying requirements or purposes of different technical applications.

One of these several methods refers to the use of bases, in small proportions, as a condensing agent, in the manufacture of infusible resinous phenolic condensation products. The action of bases under these restricted proportions makes it unnecessary to resort to counter-pressure during the hardening, and the last step of the process, which brings about final hardening through polymerization by heat, can then be carried out at relatively moderate temperatures. However, this still necessitates longer time than if higher temperatures are available. Slow methods are a great objection for most industrial processes. But the use of counter-pressure can be here called into service to excellent advantage, because it permits much higher temperatures and thus shortens considerably the hardening process and renders the method available for the majority of technical applications.

Ammonia, whether it be used directly as such, or combined to formaldehyde as hexamethylenetetramin, is still preferred over other bases for the great majority of phenolic, resinous condensation products now in the market. A careful search in the literature or in the prior art, which has been carried on now for about nine years by all my opponents, as well as by myself, has failed to disclose one single instance where ammonia has been used or recommended for the production of infusible synthetic resins from phenolic condensation products, prior to the time when I discovered and employed the eminently valuable properties of ammonia for this purpose. It is true that ammonia, or hexamethylenetetramin, had been used in some instances, but for entirely other purposes, for example in the manufacture of antiseptics derived from phenolic condensation products, and not for the production of infusible phenolic resins of the kind which have found, of late, so many industrial applications.

Dr. Redman should not overlook the important fact that the use of ammonia in the proportion of less than one-fifth of a molecule, is only one of the 34 U. S. patents which I obtained thus far in relation to phenolic condensation products. There are other ways of using ammonia, as such, or as hexamethylenetetramin in large proportions, which in some instances may answer the purpose; these I have covered by some pending patents.

As to the Luft process, it consisted in obtaining some kind of a phenolic condensation product by the use of strong acids. The latter have a tendency to produce the kind of condensa-

tion products which are not wanted, namely, condensation products of the Novolak type (permanently fusible); or, if by increasing considerably the amount of formaldehyde they may, under certain well defined conditions, produce *some kind of* infusible resins, the latter are so much contaminated by products of the Novolak type and some ill-defined substances, that they are practically worthless for technical purposes. If Luft recommended an alkali or alkali carbonate, *after* the condensation with strong acids has taken place, this was simply done in order to neutralize any remaining amounts of acid which otherwise are difficult to wash out of the mass. Luft, therefore, recommends thorough washing afterwards. So the statement of Dr. Redman that Luft "added a basic condensing agent to finally transform the resin," is decidedly misleading.

In the complicated reactions of these phenolic condensation products, where so many radically different results are obtained, according to slight modifications of the process, although starting from the same raw materials, it makes an enormous difference in the final technical result whether the base is added at the beginning or during the condensation process, or whether it is added *after* the condensation has already taken place *by the aid of an acid*, which has beforehand directed the reaction in the wrong way.

Dr. Redman states: "Luft's process is more rapid and gives the same type of insoluble resins." Why then, if you please, does not Dr. Redman, or others who seem eager to avoid my patents, utilize this Luft process, if it is better than mine or "just as good?"

If too much ammonia, introduced as such or as hexamethylenetetramin, remains in the mass at the step of the process where final heating for hardening is applied, ammonia gas tends to liberate and to cause porosity, and gives a worthless product. But I have indicated in my patents a sure way of coping with this difficulty by the joint use of heat and counter-pressure, and thereby it becomes possible to insure quick hardening at high temperatures even if a larger amount of ammonia is present, which, under ordinary conditions, would prove an obstacle in any rapid hardening process.

With quantities of ammonia less than one-fifth of a molecule, it is quite possible to harden without the use of counter-pressure, although then the process is decidedly slower.

Any chemist knows that hexamethylenetetramin, and ammonia and formaldehyde, are tweedledum and tweedledee. Therefore, Professor Chandler was entirely correct when he said: "The action of ammonia in presence of formaldehyde in the process, is entirely similar to that of the use of hexamethylenetetramin." Yet Dr. Redman says: "This cannot possibly be true." Now let us examine this denial. Is it true—yes or no—that if you add ammonia to a solution of formaldehyde, the latter is immediately transformed into an equivalent amount of hexamethylenetetramin?

Is it true that if instead of adding ammonia to formaldehyde, an equivalent amount of hexamethylenetetramin is substituted, the mixture will finally contain the same amount of hexa—never mind whether in presence of phenol or cresol, this hexa combines secondarily and makes addition compounds like hexamethylenetetramin-triphenol—or tricresol?

That ammonia and formaldehyde added together form immediately hexamethylenetetramin is such a well known fact in chemistry that one of the first things which were tried in my laboratory during my early research work, was to make sure that hexamethylenetetramin could be substituted in the reaction, and it was shown that it gave substantially the same infusible product. But in the preparation of some of my first patents, there was no need, nor advantage, of dwelling particularly on this subject, in view of the fact that in this patent, I tried to embody a general reaction which I had discovered and which included the use of all bases—including amines,

of which hexamethylenetetramin is a typical example. In a patent, it is not required, nor always advisable, to explain all possible theoretical reactions which may or may not occur. If this had been done for ammonia, then why not for caustic soda, where the side reactions on formaldehyde are again totally different? If I referred to hexa at all, I merely wanted to warn that if ammonia was added in very large amounts, all the formaldehyde would be transformed into hexa. I wanted to exclude the formation of such large amounts of hexa with its troublesome ammonia, *as far as this particular patent was concerned*. Later on, in subsequent patent applications, I described means which I had devised for handling the process even in presence of larger amounts of hexa or ammonia.

On this occasion, let me point out the fact that in my different patents, one process completes, or supplements, or replaces another, according to special uses or purposes. For instance, for some particular uses, dielectric properties are essential; for others, electric properties are of no importance whatsoever. For billiard balls, electric properties become decidedly objectionable, because while playing in dry weather, the balls attract the dust of the billiard table. There are numerous instances where strength, or appearance, are the paramount desirable qualities.

Dr. Redman filed his first patent on phenolic condensation products on June 17, 1910, and in the interference proceedings, he declared that he conceived his process on April 29, 1910. In this connection, it is interesting to note that the British patent of Wetter, published in July, 1908, about two years sooner, disclosed the following: "The 40 per cent formalin may be replaced by the polymerization products as well as by substances which yield formaldehyde such for example as hexamethylenetetramine," and Dr. H. Lebach, in his article published in the *Zeitschrift für angewandte Chemie*, in August, 1909—ten months before Dr. Redman's filing date—clearly pointed out that in my process the use of ammonia produces hexamethylenetetramin, which then further reacts as if it had been added at first. Aside from this reference, there are several other examples in the prior patent literature, where mixtures of formaldehyde and ammonia are declared equivalent to the use of hexa for various purposes.

The interference proceedings before the U. S. Patent Office, to which Dr. Redman refers, relate to only one of my many pending patent applications, and the ruling to which he alludes was not as to whether hexa is equivalent to a mixture of formaldehyde and ammonia, but was as to who was entitled to a "wet" or a "dry" process. Nor do we know, at this time, whether the "dry" claims will be awarded to Dr. Redman or to Mr. Byron Goldsmith, who was one of the several contestants in these interference proceedings, in as far as this case is still pending before the office. I did not claim, in this interference, a "dry" process, but simply wanted to bring out that it had no technical advantages which could not be obtained by the "wet" process. On the other hand, I claimed the use of hexa under certain specified conditions, and my claims directed to this method have recently been allowed to me by the U. S. Patent Office.

I rather applaud, as an act of loyalty to the dry State of Kansas, that her chemists should pin their faith and enthusiasm on a "dry" process, but may I be permitted to claim that I can do at least as well, if not better, with a "wet" process?

As to the arguments concerning the relative advantage of the "drys" and the "wets," this may seem very interesting from a theoretical standpoint. But here is another instance where a pretty theory and practical considerations have to part company before well established facts.

After all, this whole discussion simmers down to the presence of small amounts of water in the *final* product, which might depress the electrical qualities. But water can be eliminated not only before the reaction, but *after* or *during* the reaction,



regardless of whether you start with products containing water or not, and this explains why, in some of our own experiments, we have demonstrated that the highest dielectric properties in these phenolic resins have been obtained in processes which started from watery solutions.

Dr. Redman says: "This cannot possibly be true, as the formaldehyde and ammonia would leave 60 per cent of water present in the reaction, which is troublesome at any time." May I remind him of the plain fact that it does not matter at all whether 60 per cent of water—which worries him so much—is present at the beginning of the reaction, as long as it is not present in the end product; and, this is easy to take care of. His reasoning is about the same as if he would say that rubber cannot be made dry because it has been washed with water, or that shellac cannot be freed from water, after it has been dissolved, bleached and precipitated in aqueous solutions. He might extend this reasoning and say that saltpeter cannot be obtained anhydrous because it has been made from a watery solution.

Nor is it difficult to explain our practical results. For instance, the phenolic resin molding mixtures which have found the most extensive use on the market, on account of their great mechanical strength, as well as their dielectric properties, are all made with wood-fiber as a filler. This is covered by my U. S. Patents Nos. 942,852 and 949,671. It is a known fact that wood-fiber, in itself, even after drying, contains water, which can be set free by heating at somewhat higher temperatures. The same is true of cotton and paper; and yet, we know that all these products are excellent insulators. It all depends upon the condition in which the water is present. But there are other considerations. Unduly large amounts of ammonia in presence of wood-fiber act in some way to lessen its dielectric properties. Ammonia seems to fasten itself on the wood-fiber, perhaps decomposes some of the substances contained in the fiber, and thereby attracts some of the water which heretofore was tied and harmless. Furthermore, the presence or absence of free water is objectionable only for electrical purposes. But the presence of alcohol, glycerin, free cresol, or free phenol, is just as harmful for these purposes, because they all tend to lower the dielectric properties. In view of this fact, it is rather illogical that Dr. Redman, after being so emphatic about "dry" products, should be so lenient as to recommend glycerin, or alcohol, and as to use an excess of phenol or cresol, as indicated by the proportions specified in his patents—"Straining at a gnat and swallowing a camel."

As to his statement that "The use of free formaldehyde and a small amount of ammonia makes a resin with a blinding, stifling odor of formaldehyde, which cannot be used commercially," this is hard to reconcile with the plain fact that here and abroad, millions of pounds of articles made from such products have been successfully manufactured and sold, and their use is all the time increasing. If Dr. Redman will give himself the trouble of purchasing, for instance, in any store, a sample of a Bakelite cigar-holder, he can easily verify what everybody knows, but what he seems not to desire to know, that the product is absolutely tasteless and odorless.

I should like to submit the following questions to Dr. Redman: (1) Does he know of the existence of any industry here or abroad, based on infusible, insoluble products, before I had started publishing my results on this subject, and before I had shown what can be accomplished with this material?" And now let us come to "the test of the pudding: (2) Has he ever manufactured with his "dry" process—which he claims is so superior—molding mixtures containing wood-fiber as filler and which show any higher dielectric properties than, or as good dielectric properties, as those which we are able to obtain by the use of our "wet" processes? If so, can he give me

the name and address of anybody or any concern in New York City who uses this molding mixture?

I am willing to submit my samples for a comparative test before impartial, competent witnesses.

YONKERS, N. Y., MAY 19, 1916

L. H. BAEKELAND

## ON THE EFFICIENCY OF AIR-DRYERS

*Editor of the Journal of Industrial and Engineering Chemistry:*

In the 1909 and 1910 issues of the *Journal of Metallurgical and Chemical Engineering* appeared a series of articles on the efficiency of air dryers. This discussion apparently ended in a misunderstanding, and inasmuch as the fundamental factors involved were not developed during that discussion, it seems highly important that the matter should be taken up again.

The concept of efficiency always involves comparison with a perfect method for accomplishing the result desired. That this is true will be more readily granted if one will call to mind the fact that to designate the efficiency of an apparatus or process as greater than 100 per cent always arouses suspicion and leaves in the mind the impression that an error, either in the work or calculation, is unquestionably involved. It is undoubtedly true that efficiency can be defined in other ways than by involving this concept of perfection, but the fact quoted certainly indicates the close connection between this concept and our ordinary use of the word efficiency.

With this point in mind the following definition of efficiency is offered. The efficiency of a machine can be considered from either one or the other of two points of view: (1) the input can be considered as constant, in which case the efficiency is the output of that machine divided by its theoretical output; or, (2) the output of the machine may be considered as constant, the efficiency being the theoretical input divided by the actual input. That these two definitions are entirely equivalent will be evident without further explanation. With regard to the use of the word "theoretical" as applied to output and input in the above definitions, the theoretical performance of an apparatus must be considered as the performance of a perfect type of machine or process under conditions which eliminate all losses due to friction, radiation or other irreversible processes. It will always be impossible actually to realize such a theoretical apparatus or process because such losses as have been mentioned will always be present, and furthermore, such an apparatus will in general operate under substantially equilibrium conditions so that the driving forces will be infinitesimal, the rate of the reactions correspondingly small, and the capacity in consequence negligible. On the other hand, these idealized conditions must serve as the basis of our concept of efficiency.

When we come to test the efficiency of a steam boiler, of an electric motor, or of other such types of apparatus no disagreement in the application of our definition will be met. The reason for this is that everyone can agree as to the amount of both input and output of such a machine and as to exactly what a perfect machine should accomplish. For example, an electric generator should take the mechanical energy delivered to it in the form of work and convert it quantitatively into electrical energy. No electric generator does this, but knowing as we do the mechanical equivalent of electrical energy we can calculate the electrical work which should be obtained from a certain amount of mechanical energy, and thereby can immediately express the efficiency of any given generator. In the same way the perfect steam boiler should take the heat energy of the fuel and deliver it quantitatively as energy in the steam produced, and while no steam boiler does this, the actual amounts transferred are readily determinable and the heat efficiency of such a boiler is a thing on which all engineers readily agree.

On the other hand, certain types of apparatus are met concerning the efficiency of which agreement is not so easy. For

example, a steam engine takes energy in the form of heat in steam and converts a part of it into work. The fraction of this energy converted into work is small. This fraction is generally called the thermal efficiency of a steam engine and rarely exceeds 20 per cent. Every engineer realizes, however, that even the perfect steam engine could not possibly convert all of the energy of the steam consumed into work even under ideal conditions of operation, but when engineers attempt to calculate the fraction of the energy content of the steam which the perfect steam engine should be able to convert into work, misunderstandings develop as to conditions of operation, allowable assumptions, and similar points, which make it impossible for an agreement to be realized. As a result of this condition of affairs engineers have very wisely given up all attempt to express the efficiency of a steam engine in any terms comparable to those indicated by the above definition, agreeing to express efficiency by what is called performance, the pounds of steam consumed reduced to definite though hypothetical conditions—per horse-power-hour of mechanical energy produced.

With regard to the efficiency of hot air dryers, the question immediately presents itself: "Theoretically what is the minimum heat necessary for the removal of water from an inert material such, for example, as sand, rock, etc.?" The consideration of two methods for the evaporation of water from such material will enable us to answer this question. First, let us assume that the material is dried, not in an air dryer, but by introducing the material into an ordinary vacuum dryer. The steam coming from this dryer is to be utilized, not by sending it to a condenser, but as the source of heat in the heating surface of another vacuum dryer of the same type. The steam from this dryer is to be utilized for evaporating more water in another similar apparatus and so on. In an ideal apparatus only a differential temperature difference between the steam condensed in any dryer and the material being dried in that same apparatus will be required. In other words, with any finite temperature difference between the heat supply at one end of the series of dryers and the temperature corresponding to the vacuum maintained at the other end, an indefinitely large number of effects may be interposed. If now the heat contained in the dried material from each one of these effects be utilized to preheat the material entering that particular effect in a suitably designed counter-current preheater, it is evident the heat supplied to the first dryer can be re-utilized an indefinitely large number of times. In other words, the heat consumption necessary to evaporate a pound of water under such conditions can, theoretically at least, be reduced to any desired quantity, however small. Since this theoretical heat consumption is negligibly small, but since the actual heat consumption in any real apparatus cannot possibly be reduced indefinitely, the efficiency of any actual dryer of this type as compared with the theoretical performance of a perfect machine is zero, or at least indefinitely small.

It may be objected that this argument applies only to the use of a dryer of the vacuum type and not of an air dryer. This, however, is not the case. The second way to accomplish air drying with a minimum expenditure of energy is to spread the material out under a shed and let the wind blow over it. The material can be dried perfectly in this way, at least provided the material is really inert toward water; and while heat has been consumed in the process, this heat is obtained from the inexhaustible supply available in our surroundings and need not be furnished from any exterior source. While the actual energy consumption of such an operation is finite, it can be carried on if desired to an unlimited extent, and the fuel consumption required would, of course, be zero.

This outline will convince the reader that the theoretically minimum heat consumption for the drying of an inert material—at least the heat consumption which it is necessary to furnish in the form of fuel—is a quantity both infinitesimal and in-

definite. It will be agreed that some definite, tangible method of reporting the performance of such dryers should be adopted and made uniform, so that the comparison of the performance of different dryers of this type will be rendered easy and intelligible. This is exactly the line which the mechanical engineering profession has followed in adopting the steam consumption per horse-power-hour as the unit for the expression of the performance of the steam engine. The writer suggests the adoption by the chemical engineering profession of the actual heat consumption, expressed in B. t. u. per pound of water evaporated, as the unit for stating the performance of all drying and evaporating systems. If the dryer uses steam as its source of heat the dryer should be charged with the heat content of the steam supplied less the heat content of the condensed steam which is available for return to the boiler. In the case of a dryer fired directly with fuel, the dryer should be charged with the total heat of combustion of the fuel without credits, unless at some point in the apparatus or process heat is recovered for utilization in other processes than that of drying alone, this other apparatus or process being considered as essentially a part of the drying unit.

It is evident that this point regarding the theoretically minimum heat consumption for the evaporation of water from inert materials applies also to the evaporation of water itself. In other words if water is merely to be redistilled it is theoretically possible to use an indefinite number of multiple-effect evaporators for this distillation, and the theoretical heat consumption necessary for the evaporation of a pound of water can be reduced to any desired extent. Therefore, the performance of any evaporative system should as before be expressed as the heat consumption per pound of water evaporated.

Personally, the writer feels that this method of stating performance should apply to the evaporation of solutions as well as to evaporation of water, whether or not mixed with inert materials. On the other hand, the energy consumption in the evaporation of solutions cannot be reduced indefinitely, and furthermore is capable of exact formulation, so that the efficiency of any given evaporative system can be expressed as a per cent, if so desired. The reason for this lies in the fact that the heat consumed in evaporating a solvent from a solution is not again available at the temperature of the boiling solution, because the vapor evolved from that solution is superheated to the extent of the boiling point raising of the solution, and will not give out its latent heat of vaporization until it is cooled to the extent of that superheat. There is, therefore, necessarily a finite drop in temperature between adjacent effects of a multiple-effect evaporating system, and this drop in temperature will be very large for strong solutions. This drop could be made the basis of a calculation of the theoretically minimum heat consumption of an evaporator, but this calculation can be carried out somewhat more simply as follows:

Assume a solution boiling under definite pressure: this pressure,  $p$ , is less than the pressure,  $p_0$ , of the pure solvent at the same temperature. Assume a certain amount of solvent removed from this solution by evaporation. The heat content of the vapor can be recovered without loss in temperature by first compressing it at constant temperature until its pressure is equal to  $p_0$ , that of the pure solvent. The vapor thus obtained can now be introduced into the heating coils of the effect from which the vapor itself came and there condensed at a temperature differentially higher than that of the solution on the other side of the heating surface. The heat of condensation will thus be available for the evaporation of more water from the original solution. The work necessary for the isothermal compression of the vapor from the pressure  $p$  to the pressure  $p_0$  is the necessary energy consumption for the separation of water from the solution in question. If we assume that the vapor obeys the gas laws this work is equal to the expression  $RT \log p_0/p$ . If



this assumption that the vapor follows the gas laws be not allowable, the work can be calculated from the characteristic equation of the vapor. The heat available for evaporation will be not only the heat of condensation of the saturated steam, but also the heat produced by isothermal compression of the vapor between the pressure limits indicated. This heat supply will in general be nearly though not exactly equal to the heat of vaporization of the solution in question. The difference must be supplied or disposed of as the case may be.

It is evident from the above that the thing required for the separation of solvent from a solution is not primarily heat, but energy in the form of work. It is possible to furnish this energy through the mechanism of a drop in temperature, so that heat falls from a higher temperature to a lower one. This furnishes the work through a mechanism which is essentially equivalent to a Carnot heat engine. This is the explanation of the necessity of a drop in temperature between succeeding effects of a multiple-effect evaporating system concentrating solutions, even though that system be ideal in all respects.

The possibility of operating a commercial evaporating unit upon the principles outlined above was first suggested to the writer by P. H. Sadtler, of the Swenson Evaporating Company, in 1910, and we understand that such a unit is now in actual industrial operation on an experimental scale in this country.

While it is theoretically possible thus to calculate the minimum consumption of both heat and energy for the removal of solvent from any solution, the determination of the necessary data and agreement as to the necessary conditions of operation would be so difficult that the method is inadvisable, at present at least, for reporting commercial tests.

The writer therefore recommends that the heat consumption of all types of apparatus for the evaporation of volatile substances be reported as B. t. u. per pound of substance evaporated and that this method of reporting experimental results be made mandatory by the American Chemical Society upon its members.

RESEARCH LABORATORY OF APPLIED SCIENCE  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
BOSTON, May 2, 1916

W. K. LEWIS

## IMMEDIATE AND CONTINUED LIME REQUIREMENT vs. ACTIVE AND LATENT SOIL ACIDITY

*Editor of the Journal of Industrial and Engineering Chemistry:*

IN THIS JOURNAL, 8 (1916), 341, there appeared an article entitled "A New Apparatus for the Determination of Soil Carbonates and New Methods for the Determination of Soil Acidity," by Prof. E. Truog, of the University of Wisconsin. This article contained reference to an article entitled "A Method for the Determination of the Immediate Lime Requirements of Soils," by the undersigned, which appeared in THIS JOURNAL, 7 (1915), 864. From comment in the same paragraph containing reference to the work of the undersigned one might easily infer that no previous lime requirement method had taken in consideration this difference between *immediate* and *continued* lime requirement or "soil acidity." To quote Prof. Truog, "All of the methods just described have been of value in that the results indicate in a comparative way the degree of acidity. None of them, however, indicate the absolute amount of acidity as has sometimes been assumed. Lately, Hutchinson and MacLennan and also MacIntire have described methods in which a solution of  $\text{CaCO}_3$  in carbonated water is used." Again to quote from the preface to the description of the method devised by the undersigned and cited above—"The studies further led to the conclusion that there is a considerable difference between a soil's immediate ability to decompose  $\text{CaCO}_3$  and its propensity to continue the decomposition when soil and an excess of  $\text{CaCO}_3$  continue in moist contact. That this observation is to be found in practice is shown by the analysis of the lime-treated plats of the Pennsylvania Station. Thirty-five per cent of the lime accumulated on these plats after 32 years of treatment is to be found as silicates. In offering the method, the differentiation is, therefore, made between *immediate* and *continuous* lime requirements of soils."

It is thus plain that this difference was recognized and emphasized by italicized type in the method of the writer for lime requirement, which was quoted by Prof. Truog. However, Prof. Truog's article did not state that this prior differentiation in lime absorption by soils had been made. Therefore, one might readily conclude that no mention of the distinction had appeared in print, prior to the appearance of the findings and conclusions of Prof. Truog. Instead of the terms *immediate* and *continued* lime requirements as advanced by the writer, Prof. Truog used the terms *active* and *latent* acidity. This distinction of terms is in harmony with the attributed differences as to the causes of the lime absorption; the writer attributing the decomposition primarily to the absorption of calcium by acid-silicates, while Prof. Truog states in his conclusions: IV—"Data are given indicating as follows: Soil acidity is due to true acids and not selective ion adsorption by colloids." After careful and repeated readings of the article by Prof. Truog, the undersigned has failed to find these data, above mentioned.

In *Bulletin 107* of the Tennessee Station, 1914, the writer, together with Messrs. Willis and Hardy, offered data to demonstrate the continued evolution of  $\text{CO}_2$  from excessive treatment of  $\text{CaCO}_3$  upon soils (where questions of biological influences and organic matter were eliminated) for a period of over two years, while the longest period of observation given in the article by Prof. Truog was 17 hrs. This phenomenon also continued in lesser degree after igniting a soil at white heat for a period of 16 hrs., even where the soils heated contained a large excess of  $\text{CaCO}_3$ . Such an acid as would resist this treatment and still remain, even as "latent acidity," would indeed be an unusual "true acid." The same might be said of acid silicates and colloids in general. Apparently, however,  $\text{SiO}_2$  and  $\text{TiO}_2$  are possessed of such unusual properties that upon moistening after ignition they will continue to evolve  $\text{CO}_2$  from  $\text{CaCO}_3$ , but more particularly from  $\text{MgCO}_3$ .

After describing his procedure and giving his method for quantitatively distinguishing between the two forms of lime requirement or soil acidity, Prof. Truog stated in the concluding paragraph of his article:

"The enormous supply of latent acid substances in many soils of the humid region as indicated by these methods is of the greatest importance in preventing excessive losses of bases by leaching. It also offers a further explanation why MacIntire, Hardy and Willis were able to secure large decompositions of  $\text{MgCO}_3$ , when this material was left in contact with soil that supposedly had been completely neutralized."

One might infer from this statement that Prof. Truog was doubtful whether the full absorption coefficient of the particular soils had really been fully met by the materials applied, *i. e.*, that the "active acidity" had been neutralized while the "latent acidity" had not. If such an explanation alone were capable of accounting for the heavy decomposition of precipitated  $\text{MgCO}_3$  there would needs be attributed to the "latent acidity" a wonderful power of selective absorption of bases; for although the  $\text{MgCO}_3$  treatment equivalent to 16 tons of ground limestone per acre 6 in. had entirely decomposed at the end of 8 weeks, there remained at the end of 9 months approximately 22,000 lbs., of  $\text{CaCO}_3$  where this equivalent treatment was given as ground limestone. Furthermore, at the end of 8 weeks approximately 20,000 lbs. of  $\text{CaCO}_3$  remained where equivalent treatment of precipitated  $\text{CaCO}_3$  had been applied.

Many data reported in *Bulletin 107* of the Tennessee Station and many additional subsequent findings have seemed to justify the conclusion that the extensive decomposition of  $\text{MgCO}_3$  must be attributed to absorption by acid silicates and reaction with hydrated  $\text{SiO}_2$  and  $\text{TiO}_2$ .

ITHACA, NEW YORK  
April 13, 1916

W. H. MACINTIRE

## ANILINE OIL POISONING

*Editor of the Journal of Industrial and Engineering Chemistry:*

At the present time many chemists in this country are beginning the manufacture of aniline oil and it seems a good opportunity now to say a word of warning in regard to the danger to people engaged in this industry and to call attention to the precautions which should be taken to guard the health of the workmen.

The poisoning affects the victim first by an extreme languor which is followed by dizziness and then by unconsciousness, which comes on gradually. If an attack is light, a severe headache the next day is the only bad effect; a more severe case will have blue lips; and in a very severe case even the entire skin becomes blue and death may result.

The poison may be acquired in two ways: through the mucous membranes of the lungs and nose, or directly through the skin. In manufacturing aniline on a large scale the packing around the shaft and other joints of the aniline reducer are liable to leakage of steam and aniline water. Open tanks of aniline water, or of aniline itself, the evaporation of aniline and aniline water, which has been spilled on the floor, apparatus, receptacles and clothes of the workmen, all contribute aniline vapor to the air which must be breathed. Aniline vapor is heavy and accumulates near the floor, and it is, therefore, dangerous to work with the head near the floor. One of the writers had an experience illustrating this last statement while working for a few minutes kneeling down near an aniline reducer, which resulted in a severe headache and indigo-blue lips the next day. The accumulation of these aniline vapors in the building should not be permitted, and very thorough ventilation, especially near the floor, should be rigidly enforced.

The second method of acquiring aniline poisoning is through the skin, and judging from our experience, it would seem as if this source of poisoning, although apparently more gradual, is nevertheless very serious. The spilling of aniline oil and aniline water on the clothes, hands, and floor, where it wets the shoes, thus allowing the aniline water to come in contact with the skin, may result in a severe case of aniline poisoning. One of the writers was poisoned by having his hands wet with aniline water for one or two hours. Another case of aniline poisoning from having the feet of the workman moistened with the residual sludge from the aniline producer has also come to our attention.

The following precautions should be very carefully taken:

1—There should be an adequate, thorough system of ventilation, both near the floor and near the ceiling. It is advisable to make the building in the form of a shed, with removable sides.

2—The floor should be made of some waterproof, impervious material with suitable drains so that the entire premises can be thoroughly flushed out. This flushing should be done often enough to prevent the accumulation of aniline residues.

3—Great care should be taken to keep tight glands and joints wherever aniline water is likely to escape. All tanks containing aniline water should be tightly covered.

4—Employees should be cautioned not to spill liquids containing aniline on their clothes and not to allow them to come in contact with their skin. Scrupulous cleanliness is an important factor for the preservation of the health of the employees.

There is one other precaution which it is advisable to take: *never leave a man in your plant absolutely alone.* Should he be overcome by aniline fumes, he may drop on the spot and be killed by the continued presence of the poisonous vapors. There should always be another man within call, who can come to the assistance of any one in distress and take him out into the fresh air for further treatment.

531 GROSVENOR BUILDING  
PROVIDENCE, RHODE ISLAND  
April 10, 1916

AUGUSTUS H. FISKE  
ERIK H. GREEN

## REDUCTION OF CUPROUS OXIDE IN INVERT SUGAR DETERMINATION

*Editor of the Journal of Industrial and Engineering Chemistry:*

Aug. Wedderburn recently described a method of reduction of copper oxide in vapor of alcohol for use in sugar analysis.<sup>1</sup> Dr. Charles A. Browne, N. Y. Sugar Trade Laboratory, advises the writer by letter that E. Votocek and O. Lexa<sup>2</sup> proposed a similar method and that Vladimir Stanek, Prague Expt. Station,<sup>3</sup> described an almost identical method. Abstracts of these methods have just reached me from the Chemists' Club Library.

Neither Mr. Wedderburn nor the writer could find references to this method in the available sugar works, hence we believed it original with Wedderburn. The foot-note in my Handbook<sup>4</sup> was designed as evidence of the reliability of the method.

It is strange that this exceedingly simple, rapid and accurate method has not been published, so far as the writer can ascertain, in some of the numerous works on sugar that have appeared since Votocek's paper of 20 years ago.

THE CUBAN-AMERICAN SUGAR COMPANY  
NEW YORK AND CUBA, May 8, 1916

G. L. SPENCER

## BUREAU OF STANDARDS' ANALYZED SAMPLES

The Bureau of Standards, Washington, D. C., now has ready for distribution a new sample of its Iron D, No. 6-b, replacing No. 6-a, which has been long out of stock. The composition of the new sample is: Carbon, 2.39; Graphite, 1.79; Silicon, 2.59; Titanium, 0.077; Phosphorus, 0.531; Sulfur (grav.), 0.046; Manganese, 1.54; Copper, 0.044; Chromium, 0.014; Vanadium, 0.025; Nickel, 0.026. Until printed certificates can be had, a provisional certificate of analysis, without details, will be furnished with each sample issued.

NEW YORK CITY  
May 16, 1916

S. W. STRATTON, *Director*

## CEANOTHUS VELUTINUS (SNOW BRUSH) AS A SOURCE OF WAX AND TANNIN—CORRECTION

In the paper by Mr. Blakemore and myself as printed in *THIS JOURNAL*, 8 (1916), 411, the reading "creotic acid" throughout the article is incorrect and should be changed to "cerotic acid." Also, the first sentence in the summary should read as follows: *Ceanothus velutinus*, a widely distributed plant, has been found to contain 7.3 per cent wax and 17.3 per cent tannin.

BERKELEY, CALIFORNIA  
April 25, 1916

CHARLES C. SCALIONE

## GENERAL APPLICABILITY OF THE PAPER PULP FILTER, ETC.—CORRECTION

In the article under the above title, *THIS JOURNAL*, 8 (1916), 317, foot-note 4 should read: *Biochem. Bull.* 5 (1916), 87-94, instead of 4 (1915), 87-94.

WASHINGTON, D. C.  
March 29, 1916

S. L. JODIDI  
E. H. KELLOGG

## ORGANIZATION FOR INDUSTRIAL PREPAREDNESS—CORRECTION

In the article under above title printed in *THIS JOURNAL*, 8 (1916), 462, the name R. H. McKee, Orono, Me., should be changed to M. L. Griffin, Rumford, Me.

CHAPEL HILL, N. C.  
April 29, 1916

CHARLES H. HERTY

<sup>1</sup> *THIS JOURNAL*, 7 (1915), 610; Spencer, "Handbook for Cane Sugar Manufacturers," 5th Ed., 240.

<sup>2</sup> *Chem.-Ztg. Repertorium*, 21, 324.

<sup>3</sup> *Zuckerind. Böhmen*, 32, 497; *Chem. Abs.*, 2, 2315.

<sup>4</sup> *Loc. cit.*



# PERSONAL NOTES

Prof. Arthur B. Lamb, of Harvard University, lectured on "Induced Reactions," in the Havemeyer Chemical Laboratory, New York University, University Heights, on Friday, May 12th.

The New York Sections of the American Institute of Mining Engineers and the American Electrochemical Society held a joint meeting on May 12th. The topic of the evening was "Flotation." George D. Van Arsdale spoke on "The Mechanism of Flotation," and Wilder D. Bancroft on "The Theory of Flotation."

Prof. Ralph H. McKee has resigned his position as head of the department of chemistry, University of Maine, to become head of the research department of the Tennessee Copper Company, with headquarters at Ridgefield Park, N. J.

Dr. Erwin F. Smith, of the Bureau of Plant Industry, delivered an illustrated address on "Resemblances between Crown Gall in Plants and Human Cancer," at the meeting of the Washington Academy of Sciences on May 11th.

Mr. C. C. Creighton, of the Galena-Signal Oil Co., delivered an illustrated lecture entitled "History and Development of the Oil Industry," at the special meeting of the Engineers' Club of Trenton, on April 27th.

Prof. M. T. Bogert, of Columbia University, was elected a member of the National Academy of Sciences at its annual meeting held in Washington, D. C., April 17th to 19th, 1916.

The Potash Aluminum Company of America has been incorporated at Dover, Del., with a capital stock of \$3,000,000, to deal in potash alumina and alkalines, earths, chemicals, etc. The incorporators are H. E. Latter, N. P. Coffin and Clement M. Egner, all of Wilmington, Delaware.

H. S. Kimball has been elected president of the Aetna Explosives Company, Inc., to succeed A. J. Moxham, who has been elected chairman of the board. Mr. Kimball will continue as the president of the American Zinc Lead Smelting Company.

Mr. Floyd W. Robinson spoke on "Modern Facts on Cider Vinegar" at the eighty-first regular meeting of the Detroit Section of the A. C. S., May 18th.

Lucius E. Allen, consulting and constructing engineer, of Belleville, Ontario, Canada, announces the removal of his offices from the Canadian Bank of Commerce Building to the New Bank of Commerce Building.

The Southern Cotton Oil Company announce the removal of their New York offices on May 1, 1916, to the Equitable Building, 126 Broadway.

The United States Civil Service Commission announces the following open competitive examinations: *Junior chemist in radioactivity*, for men only, salary \$1200 to \$1500 per annum, on June 7, 1916; *technical assistant*, for men only, salary \$1200 a year, on June 7, 1916; *physical metallurgist*, for men only, salary \$6 to \$8 per diem, on June 7, 1916.

Mr. C. W. Brown, of the H. K. Mulford Company, Glenolden, Pa., spoke on "The Manufacture of Vaccines and Serums" (lantern slide illustrations), before the Philadelphia Section on May 18th.

A leave of absence for the second half of the academic year 1916-17 has been granted by Harvard University to Professor Theodore W. Richards, director of the Wolcott Gibbs Memorial Laboratory.

The Franklin Institute has awarded its Elliott Cresson Gold Medal to Dr. Robert Gans, of Pankow, near Berlin, Germany. The award is made in recognition of his invention of, and research in connection with, permutit, the sodium-alumino-silicate used for softening the water.

The Washington Section of the A. C. S. and the Washington Society of Engineers held a joint meeting on May 24th. Mr. Joseph Steinmetz, president of the Aero Club of Pennsylvania, gave an illustrated lecture on "The Machine Shop and the Chemical Laboratory as Related to National Preparedness for Defense."

The eleventh annual meeting of the Southern Fertilizer Association will be held in Hot Springs, Virginia, July 11, 1916, headquarters at The Homestead. The twenty-third annual convention of the National Fertilizer Association will follow on July 12th and 13th.

At the annual meeting of the Iron and Steel Institute, on May 4th, the Bessemer gold medal for 1916 was presented to Mr. F. W. Harbord.

The explosion of a tank containing 2,000 gallons of nitric acid partially wrecked the Industrial Chemical Company's plant at Providence, R. I., on May 3rd.

At the Puget Sound Section of the A. C. S., held on May 27th, Dr. H. K. Benson presented a paper on "By-Products of the Lumber Industry," based upon his work with the Federal Bureau.

The New York Section of the A. C. S. will hold its regular meeting at the Chemists' Club on June 9th. The program will be as follows: "Report by the Committee on University and Industry," Charles Baskerville, chairman; "An Account of Some Experiments Relating to Vapor Pressures, Fractional Distillation, Critical Data and Compressibility of Gases," G. A. Burrell, U. S. Bureau of Mines; "The Petrographic Microscope in Analysis," F. E. Wright, Carnegie Institution of Washington.

The Chicago Section of the A. C. S. held a "Preparedness Kommerz" at the University Club on May 20th. It was attended by about 250 members of the Chicago Section with some special guests, among whom were the members of the District Committee for Industrial Preparedness and certain other prominent business men of Chicago. Dr. Henius, the presiding officer, called the meeting to order at eight o'clock. All those present wore shields with their names painted on and rough-rider hats, and there were special song-books, steins and pipes at the place of each member. In connection with the entertainment, several sketches were pulled off, one in which chemical and nonchemical wizards achieved most astonishing results using chemical, mechanical and philological methods to produce the final results. Uncle Sam superintended many of the proceedings. There was a scene between the modern capitalist and the modern chemist suggesting how far apart their points of view are at the present time. Reporters continually wove their way among the crowd and at eleven thirty The Chemical Bully Bullet appeared fresh from the press. The members of the Kommerz "drank their semesters," the "salamander was rubbed" frequently; preparedness cartoons decorated the walls and preparedness songs were sung from time to time.

The Hoskins Manufacturing Company of Detroit announce that they have opened a branch office in Boston, Mass. This branch is in charge of J. E. Hines, and is located at 613 Unity Building, 185 Devonshire Street.

Professor E. C. Franklin, of the Leland Stanford University, has had an unfortunate laboratory accident, through an explosion in his laboratory which caused burns and other injuries. Later news is more reassuring and announces the fact that he is steadily recovering in the hospital and that the accident will not leave serious consequences.

# GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Consular Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Consular Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

## BUREAU OF THE MINT

**Proceedings of Assay Commission, 1916.** Treasury Department Document 2768. 31 pp. Paper, 5 cents. This reports upon the annual test of coinage for the calendar year 1915, gives the laws relating to the annual assay and the rules for organization and government of the Board of Assay Commissioners.

## SMITHSONIAN INSTITUTE

**Smithsonian Physical Tables.** Publication 2269, being a reprint of the 6th revised edition prepared by Frederick E. Fowle. 356 pp. Cloth, \$2.00.

## NATIONAL ACADEMY OF SCIENCES

**Report of the National Academy of Sciences, for calendar year 1915.** 74 pp. Available through the Superintendent of Documents. Paper, 10 cents, or as Senate Document 264.

## ARMY WAR COLLEGE

**Mobilization of Industries and Utilization of the Commercial and Industrial Resources of the Country for War Purposes in Emergency.** War Department Document 517, from the office of the Chief of Staff. This is a report prepared by the War College Division as a supplement to the statement of a proper military policy for the United States including a summary of action taken by other countries, the necessity for action by the United States, and recommendations for legislation.

## PUBLIC HEALTH SERVICE

**United States Public Health Service as a Career.** W. C. RUCKER. Miscellaneous Publication 13. 18 pp. Paper, 5 cents. This pamphlet is of interest to educators who are working with students that may contemplate life work in public health and hygiene.

## HYGIENIC LABORATORY

**Digitalis Standardization, Physiological Evaluation of Fat-Free Digitalis and Commercial Digitalin.** GEORGE B. ROTH. Bulletin 102, Part I. (See next abstract.)

**Preliminary Observation of Metabolism in Pellagra.** ANDREW HUNTER, MAURICE H. GIVENS AND ROBERT C. LEWIS. Part 2 of Bulletin 102, February, 1916. These two articles are published together in a bulletin of 74 pp., available bound in paper at 10 cents.

## UNITED STATES SENATE

**Exploration for and Disposition of Coal, Phosphate, Oil, Gas, Potassium, and Sodium.** Senate Report 319 to accompany bill H. R. 406 issued March 31st. The Senate Committee Report is summarized as follows:

"In conclusion the committee wishes to emphasize the situation that practically all of the known lands of the government containing phosphates, oil, gas, potassium, or sodium are, and for a number of years past have been withdrawn from all forms of location, entry, acquisition, or development; that this situation has continued over such a period of time that it has become almost a calamity to the regions within which

these resources are situated, and the continued tying up of these resources is also of great detriment to the general welfare; that the situation at this time is of special urgency and critical importance; and the committee has, therefore, both as to the substance and detail of the proposed legislation, given many weeks of time and attention to the effort to place the legislation in clear and workable shape before the Senate.

"Therefore, prompt consideration and disposition of this legislation is urged in order that some legal and adequate method may be provided for the development of the national mineral resources, and that, so far as relief contained in this bill is concerned, just and equitable treatment be accorded the citizen, without whose enterprise the Government would not have known the value of its own possessions."

## DEPARTMENT OF THE INTERIOR

**Production, Consumption, and Price of Gasoline.** Senate Document 310. This is a letter from the Secretary of the Interior transmitting certain information in response to a Senate resolution of January 5, 1916, covering questions of the quantity and character of the production of gasoline in the various developed fields and the prospects for further development in other fields, including matters of price over the period of 10 or 15 years past. The general résumé as to price is as follows: "A conclusion justified by a review of the year's record in the oil industry is that the selling price of gasoline is fairly responsive to the supply and demand for gasoline, but is less directly related to the actual supply of crude oil. Attention has also been directed to the possibility of other contributing factors, with the result that the evidence at least suggests that increasing profits to the larger refining corporations have accompanied the upward trend of gasoline prices.

"The obvious fact is that the refining and transporting companies that are strongest in business foresight and financial backing take advantage of both the falling and the rising markets in crude oil to strengthen an already strong position by purchasing both stocks of crude and producing properties. Under these conditions a market shortage of crude may develop which is not wholly warranted by facts of actual production, yet it no less surely leads to higher prices in both crude and refined products. This furnishes the opportunity for the well-supplied refiners to sell at the higher price gasoline which is derived from crude oil purchased in a lower market."

## BUREAU OF MINES

**The Buying and Selling of Ores and Metallurgical Products.** CHARLES H. FULTON. Technical Paper 83. 42 pp. Paper, 5 cents. The general questions of sampling, buying and selling of ores are discussed in order to point out the underlying principles. Particular attention is given to the significance of sampling and analytical methods and there is discussed the question of smelter and mill rates and schedules. Various methods of paying for the metal content of ores and of penalizing for various undesirable constituents are discussed. Numerous examples are given with market quotations to illustrate the points made.

**Methods of Preventing and Limiting Explosions in Coal Mines.** GEORGE S. RICE AND L. M. JONES. Technical Paper 84. 42 pp. Paper, 15 cents.

**Permissible Explosives.** A supplementary list of explosives which have been tested by the Bureau of Mines between March 1st and July 1st of this year and found to be permissible. The list supplements Technical Paper 100.

**Analysis of Natural Gas and Illuminating Gas by Fractional Distillation at Low Temperatures and Pressures.** G. A.



BURKE, F. M. SCHUBERT AND I. W. ROBERTSON. Technical Paper 104. 38 pp. Paper, 5 cents. "This paper describes a method of separating natural gas into its paraffin hydrocarbons. Methane can be removed at the temperature of liquid air and the ethane separated from the propane, butane, etc., at temperatures ranging from  $-150^{\circ}$  to  $-140^{\circ}$  C. The propane is separated from the higher paraffins at temperatures ranging from  $-135^{\circ}$  to  $-120^{\circ}$  C. The method, although somewhat involved, is the only known method applicable to the separation of some hydrocarbons."

The method for illuminating gas considers the separation of the various methane series hydrocarbons and also benzene and the other unsaturated series.

**Production of Explosives in the United States.** Compiled by ALBERT H. FAY. Technical Paper 107. 14 pp. Paper, 5 cents. "The total production of explosives, excluding the amount exported, in the United States during the calendar year 1914, according to figures that the Bureau of Mines has received from manufacturers, was 450,251,489 lbs. (225,126 short tons), as compared with 500,015,845 lbs. (250,008 short tons) in 1913 and 489,393,131 lbs. (244,696 short tons) in 1912.

"The production for 1914 is segregated as follows: Black powder, 206,099,700 lbs.; 'high' explosives other than permissible explosives, 218,453,971 lbs.; and permissible explosives, 25,697,818 lbs. These figures represent a decrease of 23,839,831 lbs. of black powder, 23,932,573 lbs. of high explosives, and 1,987,952 lbs. of permissible explosives as compared with figures for 1913."

The various explosives are classified as follows:

"1—Black blasting powder. All black powder with sodium or potassium nitrate as a constituent is here classified as black blasting powder.

"2—High explosives. Dynamite and all other high explosives of various trade names and compositions, except permissible explosives, are put in this class.

"3—Permissible explosives. In this class are included ammonium nitrate explosives, hydrated explosives, organic nitrate explosives, and certain nitroglycerin explosives containing an excess of free water or carbon. All permissible explosives have passed certain tests of the Bureau of Mines, and are not to be regarded as permissible unless used in the manner specified by the Bureau."

The relation of the use of explosives to fatal accidents is also described and a summary given of the fatalities in coal mines caused by explosives with a classification of causes.

**Composition of the Natural Gas Used in Twenty-Five Cities.** G. A. BURRELL AND G. G. OBERFELL. Technical Paper 109. 20 pp. Paper, 5 cents. This report presents the result of an examination of the natural gas supplied to twenty-five cities indicating analyses, specific gravity, heating value as calculated from analysis and various other properties of minor interest. The following statements taken from the summary of the paper are of particular interest:

"Out of the samples of natural gas from 25 cities in the United States, 5 contain methane only as the combustible gas. The others contain, in addition to methane, higher members of the series of paraffin hydrocarbons.

"Natural gas in two different sands of the same field may vary decidedly in composition.

"Some of the natural gas used in Texas has a heating value of about 740 B. t. u. per cubic foot at  $0^{\circ}$  C., and 760 mm. pressure. The highest heating value determined was 1,312 B. t. u. per cubic foot.

"The natural gas used in Pittsburgh, Columbus, Cleveland, Cincinnati, and many other places in the East is remarkably uniform in composition.

"The ignition temperature of natural gas lies between about  $550^{\circ}$  C. and  $750^{\circ}$  C.

"Oxygen, carbon monoxide, hydrogen, and olefin hydrocarbons are not present in natural gas."

A number of pages are devoted to the discussion of the physiological effects of natural gas. It is concluded as follows: "A large proportion of natural gas in air is required to suffocate men. As far as canaries are concerned, the effect on them of mixtures of natural gas and air is principally due to the lowering of the oxygen content of the air by the diluting action of the gas."

**Monazite, Thorium, and Mesothorium.** KARL L. KITHIL. Technical Paper 110. 29 pp. Paper, 5 cents. Properties, occurrence, history of production, and description of monazite and monazite deposits are given at some length. Mining and milling methods, including flow sheets, are also given. Some methods of chemical analysis and testing the ores, especially the method for the determination of thorium and the separation of mesothorium are presented.

**Inflammability of Mixtures of Gasoline Vapor and Air.** G. A. BURRELL AND H. T. BOYD. Technical Paper 115. 16 pp. Paper, 5 cents. Two methods for determining the gasoline vapor content of air are discussed. The first is a cooling method for the removal of vapor by condensation. The second consists of burning the gasoline with oxygen and calculation from the contraction and the carbon dioxide produced, the percentage of gasoline vapor.

The limits of explosibility and the degree of completeness of combustion with various mixtures are given.

**Exhaustion of the Petroleum Resources of the United States.** M. L. REQUA. Senate Document 363. This is a reprint of the article on exhaustion of the petroleum resources of the United States, showing the present and future supply and demand, also the production of the principal oil fields of the United States, as presented by the author before the American Petroleum Congress at San Francisco last year.

#### FEDERAL TRADE COMMISSION

**Pipe-Line Transportation of Petroleum.** Special unnumbered publication. 27 pp. This pamphlet gives the letter of submittal and the summary and the conclusions of report made by the Federal Trade Commission on this subject to the Senate in response to a resolution of the previous Congress.

#### BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**By-Products of the Lumber Industry.** H. K. BENSON. Special Agents' Series 110. 68 pp. Paper, 10 cents. This bulletin reports on resources available, methods of development now in use, and quantity of material prepared as by-products of the lumber industry. Diagrams and photographs illustrate the various types of apparatus in use and the principal processes are outlined fully. Some of the more important generalizations introducing the report are as follows: "It is obvious, therefore, that wood-using industries will continue for some years as an important financial asset of this country. It is evident also that by the introduction of methods of closer utilization the life of the forests may be greatly conserved and extended.

"In order to ascertain the progress made by the European countries in close utilization of their forests, and especially of their by-products, it was planned to conduct an investigation abroad. This was rendered impracticable on account of the war in Europe. A brief survey of conditions in the United States was thereupon undertaken instead, and this report is intended merely as a preliminary statement covering the manufacture of by-products from wood.

"The term 'by-product' in its unrestricted sense might include every forest product but the lumber itself. . . . For the purposes of this investigation, however, the meaning of the term is restricted to such products as require the use of technical and more or less highly developed manufacturing processes for their production. The scope of the investigation was ac-

cordingly limited to a survey of the industries engaged in the distillation of wood, the manufacture of tannin extract, wood pulp, ethyl alcohol, producer gas, and several minor products.

"Minor processes, such as the manufacture of ethyl alcohol, producer gas, oxalic acid, plastics, and needle oils, are also in limited use."

#### BUREAU OF STANDARDS

**Metric System in Export Trade.** SAMUEL S. STRATTON. Senate Document 241. 80 pp. (Available from the Document Room of the United States Senate only.) This is a report to the International High Commission relative to the use of the metric system in export trade made by the Director of the Bureau of Standards in response to an inquiry through the Secretary of the Treasury on the following questions which are discussed in full in the reply.

"1. What proportion of manufacturers have adopted the metric system in preparing goods for export? Has their experience warranted an expansion of this policy?

"2. What are the chief objections to such action? Are certain lines less adaptable than others?

"3. What will be the effect upon the scale and tool trades of any systematic movement in this direction?

"4. Ought we recommend the compulsory instruction in our schools in the metric system? Or might it be limited to high schools?"

In addition to answering these specific questions a number of practical suggestions as to the adoption of metric units are given. The legal status of the International Metric System in the leading countries of the world and in the United States is summarized. The most interesting portion of the report is, however, the appendix, which contains a large number of extracts from American catalogues showing the uses of the metric system in tables, data, and price lists and describing products made to metric sizes. These examples are taken from a wide variety of industries and afford to the manufacturer interesting suggestions as to the application of this system in various lines of trade.

**Luminosity of a Black Body and Temperature.** PAUL D. FOOTE AND C. O. FAIRCHILD. Scientific Paper 270, issued March 21, 1916. 9 pp. "The relation between luminosity of a black body and temperature has been derived by a new method. The Rasch equation is shown to be unsatisfactory, while the Nutting equation or a slight modification of the Nutting equation holds exceedingly well.

"The luminosity pyrometer appears advantageous for temperature measurements when calibrated in terms of the Nutting equation or the suggested modification of Nutting's equation. Precise measurements on the luminosity-temperature relation of a black body are greatly to be desired."

**Inclusions in the Silver Voltmeter Deposits.** G. W. VINAL AND WILLIAM M. BOVARD. Scientific Paper 271. 27 pp. [See *Journal American Chemical Society*, 38 (1916), 496-515.]

**Correlation of the Magnetic and Mechanical Properties of Steel.** CHARLES W. BURROWS. Scientific Paper 272, issued March 29, 1916. 40 pp. "The experimental evidence, of which only a small portion has been presented in this paper, seems to point to the conclusion that there is one and only one set of mechanical characteristics corresponding to a given set of magnetic characteristics, and conversely there is one and only one set of magnetic characteristics corresponding to a given set of mechanical characteristics.

"It has been shown that magnetic observations taken during the course of a tensile test indicate the time when the true elastic limit, the yield point, the necking-down point, and the ultimate strength are reached. In addition, the magnetic data give some idea of the uniformity of the material.

"If it is once determined what treatment is requisite for a given steel, a magnetic test may be used to determine whether or not the material has been brought into the desired condition.

"It is quite possible that the magnetic data may be used to define a bar of steel. In no other manner than by a magnetic examination is it possible, without doing violence to the specimens, to determine whether two steel bars are identical in properties.

"A determination of the magnetic uniformity of a piece of steel may be used as an index of the mechanical homogeneity.

"A magnetic test indicates the character of the entire cross section of the metal, rather than merely a surface phenomenon, as in the case of certain hardness tests.

"Notwithstanding the possibilities of the magnetic test, it must be remembered that at present they are possibilities only. Before the magnetic characteristics can be of much practical importance a great deal of investigation is necessary and a large number of accurate measurements on specimens of known chemical composition and heat treatment must be made."

**Magnetic Testing.** Circular 17, 3rd Ed., issued March 18, 1916. 50 pp. "This circular deals with the fundamental magnetic quantities, with empirical formulas giving the relations between these quantities, with typical data of magnetic materials, and with the methods of magnetic measurements employed at the Bureau of Standards.

"An effort has been made to include in the circular as much as possible of the general information regarding magnetic subjects which the Bureau from time to time has been called upon to furnish."

**Analyzed Irons and Steels—Methods of Analysis.** Circular 14, 5th Ed., issued March 20, 1916. 17 pp. A revised edition with slight changes.

**Testing of Glass Volumetric Apparatus.** Circular 9, 8th Ed., issued March 31, 1916. 32 pp. A revised edition with slight changes.

**United States Standard Baumé Hydrometer Scales.** Circular 59, 1st Ed., issued April 5, 1916. 13 pp. This circular describes the history of the Baumé scale and discusses the relation between Baumé degrees and specific gravity, giving a table of equivalents for liquids heavier than water and for liquids lighter than water. Particular attention is given to the question of the modulus in the formula for conversion of the degrees Baumé to specific gravity. This is done in order to set forth the facts as to the dispute by the Baumé hydrometer makers as to the value for this modulus. The Bureau concludes as follows: "Having shown that the continued adherence to the modulus 140 is in the interest of uniformity and accuracy and in accordance with established practice, the Bureau of Standards is content to leave the matter in the hands of those who have occasion to make use of the Baumé scale, feeling confident that when the facts are known the American standard Baumé scale represented by the modulus 140 will be employed to the exclusion of all others."

**Some Foreign Specifications for Railway Materials: Rails, Wheels, Axles, Tires.** G. K. BURGESS AND P. D. MERICA. Technologic Paper 61, issued April 20, 1916. 132 pp. "As a part of the Bureau's program relating to the determination of the causes of failure of railway materials, such as wheels, rails, axles, etc., as authorized by Congress, it was considered advisable to find out what is the European practice with respect to specifications for and tests of such types of material, together with any information available concerning the prevalence of accidents abroad caused by failure of railway equipment.

"In pursuance of this idea the Department of State was asked to aid in the securing of the desired information.

"As a result of this inquiry the consuls general of the United States resident in the several countries mentioned took great pains to secure as complete data as possible; and their requests for information were cordially responded to by the several railway administrations, whether under governmental or private control.

"The discussion and comparison of the several types of foreign



specifications and tests of rails, wheels, axles, and tires, treated by subjects, forms the main text of the report, while the detailed specifications and descriptions of tests are given by countries in the appendix.

"It is hoped that the information thus obtained may be of some interest and service to the railways and manufacturers of railway material in the United States, in that it gives an opportunity to compare American and European practice for some of these portions of railway equipment which are most subject to the failures causing accidents."

A brief summary of accident statistics for some of these countries is also included.

**Standardization of the Automobile Tire Fabric Testing.** WALTER S. LEWIS AND CHARLES J. CLEARY. Technologic Paper 68, issued March 17, 1916. 18 pp. This report describes standard methods of testing tire fabrics under conditions which are so closely defined as to give reliable and comparable values.

#### GEOLOGICAL SURVEY

**Publications of the United States Geological Survey.** 163 pp. This list of publications is revised to April, 1916. Available on application to the Survey.

**Publications of the Geological Survey for Sale.** This is a list issued by the Superintendent of Documents as price list 15, 9th Ed., revised to March, 1916. 60 pp. This list gives only those for sale by the Superintendent of Documents; it can be obtained by application to his office.

**Experiments on the Extraction of Potash from Wyomingite.** R. C. WELLS. Professional Paper 98-D, from shorter contributions to General Geology, 1916, pp. 37-40, issued May 13, 1916. "Wyomingite, a lava occurring extensively in the Leucite Hills in Sweetwater County, Wyoming,<sup>1</sup> is composed largely of the mineral leucite, a silicate of alumina and potash. Leucite is far richer in potash than feldspar, which is commonly regarded as one of the most promising prospective sources of potash. Moreover, the potash in leucite, although not soluble in water, seems to be more easily attackable by reagents than that in feldspar, so that if any igneous rock should become a source of potash wyomingite would have advantages over a feldspar-bearing rock. Data on the properties of wyomingite will, therefore, be valuable. While all the experiments to be described here cannot be considered as suggestions of commercial possibilities, a record of them may not only be suggestive to private investigators, but save much repetition of preliminary investigation."

#### COMMERCE REPORTS—APRIL, 1916

An embargo upon asbestos has been put into effect in Canada. (P. 81.)

Three new subsidized companies have been organized in Japan to manufacture **glycerine, formalin and drugs.** (P. 126.)

The **vegetable oil industry** of Hull, England, has undergone great expansion, due largely to increased demand for margarine, in which cottonseed, palm kernel, and copra oils are used. (P. 151.)

**Japanese matches** are now being sold extensively in Great Britain. (P. 159.)

**Turmeric** is found in considerable quantity in Porto Rico, where it is used by the natives as a dye, which is fairly permanent. (P. 212.)

The annual output of **hematite** from Newfoundland is now over \$1,000,000. The output of **pyrites** is decreasing. (P. 216.)

Large amounts of **annato** are available in Porto Rico. Now the plant grows wild but it will probably be cultivated if the demand is increased. (P. 247.)

**Petroleum** as a fuel is being largely substituted for coal in Uruguay. (P. 257.)

Experiments upon **fertilizers** in Bohemia indicate that for winter wheat the use of **potash** alone increased the yield nearly

<sup>1</sup> The quantity of leucite-bearing rock present at this locality is estimated at nearly 2,000,000 tons, containing an average of 10 per cent of potash. See U. S. Geol Survey, *Bull.* 512 (1912), 35.

as much as when **phosphoric acid** or **nitrogen** were employed. (P. 258.)

Scarcity of **paper** in Germany has caused stringent measures in some cities. (P. 279.)

Denmark has nine **beet sugar factories**, and three sugar refineries. (P. 289.)

Investigations are in progress to develop the **natural dyes** of India. Satisfactory, fairly fast shades are obtained from annato. (P. 290.)

A **sugar refinery** has been erected in Ceylon to refine sugar from the sap of the Palmyra palm, making **alcohol** as a by-product. (P. 294.)

Efforts are being made to facilitate the shipment of **logwood** from Yucatan to the United States. (P. 297.)

Experiments of the Austrian Government upon the utilization of **nettle fiber** has shown that the fiber can be separated by water alone; and that from the fiber, thread, etc., very similar to cotton may be prepared. It can readily be dyed and also made water-proof. As a result of these tests, nettles will be planted throughout Austria. (P. 309.)

The output of **antimony** from China shows a marked increase, nearly \$1,000,000 worth being exported to the United States in 1915. Although most of the mining is still done by primitive methods, modern methods are now being introduced. (P. 325.)

#### SPECIAL SUPPLEMENTS ISSUED IN APRIL

Denmark—4a	Brazil—40a
France—5b	Venezuela—48a
Portugal—11a	China—52a
Russia—13a	Japan—55a
Sweden—16a	New Zealand—61a
United Kingdom—19a	Philippines—80a
United Kingdom—19b	

Arrangements have been made by Portugal to divide its output of **tungsten ore** equally between England, France, and the United States. Deposits of **molybdenite** have also been discovered. (Supplement 11a.)

#### STATISTICS OF EXPORTS TO THE UNITED STATES

SHANGHAI—18	HAVRE, FRANCE—Sup. 5b	COPENHAGEN—Sup. 4a
Antimony	Animal Charcoal	Diamonds
Indigo	Antimony	Flint pebbles
Hides	Casem	Fusel oil
Gold	Drugs	Hides
Cottonseed oil	Dyewood extracts	
	Bone fertilizer	LYON, FRANCE—Sup. 5b
	Optical glass	Chemicals
	Glue	Dyes
	Glycerine	Amido-pyrin
	Graphite	Sodium oleate
	Gum benzoin	Argols
	Gutta percha	Copper matte
	Indigo	Hides
	Colza oil	Paper stock
	Peanut oil	Cumin seed
	Flint pebbles	Artificial silk
	Prussiate of potash	
	Rubber	PORTUGAL—Sup. 11a
		Antimony
		Argols
		Crude olive oil
		Rubber
		Pyrite
		Tungsten ore
	VENEZUELA—Sup. 48a	
	Balata	
	Chicle	
	Balsam-copaiba	
	Copper ore	
	Divi-divi	
	Hides	
	Rubber	
	Sugar	
	Gold	
		RUSSIA—Sup. 13a
		Ergot
		Cantharides
		Glycerine
		Lycopodium
		Pine-needle oil
		Santonin
		Birch tar
		Fusel oil
		Hides
		Reclaimed rubber
	JAPAN—Sup. 35a	
	Agar-agar	
	Camphor	
	Coal	
	Copper	
	Vegetable isinglass	
	Menthol crystals	
	Porcelain	
	Sugar	
	Sulfur	
	Glass	
	Gold	
	Graphite	
	Hides	
	Indigo	
	Manganese	
	Matches	
	Vegetable oil	
	Vegetable wax	
		SWEDEN—Sup. 16a
		Aluminum
		Hides
		Iron and steel
		Ferromanganese
		Ferrosilicon
		Matches
		Cresote oil
		Fusel oil
		Paper
		Potash
		Soda
		Wood pulp
		Enamelled ware

A company has been organized in Argentina to produce **dyes**, khaki and fawn color from the **carob** tree. (P. 325.)

**Banana stalks** have been found to yield an ash containing 47 per cent of  $K_2O$ . The material is especially suitable for the preparation of pure **potash**. (P. 334.)

The Bureau of Standards is coöperating in tests upon the possibility of using American clays in **paper making**. (P. 338.)

The **tin industry** of Yuman Province, China, is being put upon a scientific basis by the introduction of modern ore dressing machinery for concentrating the low-grade ore; and by the use of gas-fired reverberatory furnaces for smelting. (P. 340.)

**Indigo** is being extensively planted in China. (P. 341.)

Large supplies of **logwood** in Honduras and the West Indies are held up on account of lack of vessels for shipment. (P. 342.)

Arrangements have been made for supporting research upon the production of **hard porcelain** under the direction of the Pottery School, Stoke-on-Trent, England. (P. 345.)

A British departmental committee has recommended legislation prohibiting the use of any **paint** material containing more than 5 per cent of its dry weight of a soluble lead compound. (P. 353.)

A commission has been appointed in Spain to study the local **iron and steel** situation with special reference to the regulation of exports. (P. 357.)

**Fustic** is now being exported from Honduras to the United States. (P. 359.)

Exports of **cutch** from Burma to the United States have greatly increased. (P. 374.)

A special panel furnace has been constructed at the Bureau of Standards for testing the **fire-resisting** properties of building materials. (P. 382.)

Greece produces about 15 per cent of the world's production of **emery**. (P. 388.)

Arrangements are being made for marketing Mexican **logwood**. (P. 392.)

## BOOK REVIEWS

**Coal and Coke.** By FREDERICK H. WAGNER, Gas by-product lecturer Johns Hopkins University. 418 pp. Illustrated. McGraw-Hill Book Co., Inc., New York and London. Price, \$4.00 net.

The author's purpose in writing this book has been to put before the manufacturer of coal gas and the student of coal-gas production data in a concise form covering the various systems of coal carbonization.

The author has presented the data, but as to presenting it in a concise form we consider that he has failed. The book contains a mass of information, concerning coal, coke and the production of coke, taken from the publications of the United States Bureau of Mines and from the publications of other well known investigators in the subjects of coal, coal gas and coke.

Little space has been given to the subject of coal gas, it being mentioned only in its connection with coal as a by-product of its carbonization.

The book is divided into chapters as follows:

**COAL**—Origin and Classification of Coal, Oxidation and Spontaneous Combustion, Coking and Gas Coals, Analyzing Coal (as the author states, this chapter is taken directly from Technical Paper No. 8 of the U. S. Bureau of Mines), Preparation and Storage of Coal.

**COKE**—Carbonization in Retort Benches, Combustion and Heating of Settings, Flue Gases. Analyses and Their Interpretation, Pyrometry, Euchenic Thermic Reactions, Carbonization in Ovens, Chamber Ovens, Low Temperature Carbonization, Power Production with Waste Heat, Coke.

**APPENDIX**—Heat Units, Chemical Equations for Combustion in Oxygen, Heats of Combustion of Gases in Oxygen, Pressures Exerted on Storage Walls, Angles of Repose and Slide.

**REFERENCES; INDEX.**

There is no doubt as to the great service that a compilation of this kind would render if the information were properly presented. The author, however, has missed the chance of rendering this service by not giving more time and thought to the development of the logical presentation of his subject. The order of the chapters, as well as the order of the various subjects as they are presented in the chapters, is not always logical. The book lacks clearness not only on account of the above fault but also on account of the fact that the author in many instances jumps from one subject to another without indicating the change by other means than that of paragraphing. Long and involved sentences abound, which are never an aid to clearness, and make reading exceedingly laborious.

On account of this lack of logical development and clearness this book is not recommended for the beginner in the field of coal and its by-products. For the more advanced student or practitioner in this field it may be of some use as a book of reference. A good subject catalogue of the works from which this book was compiled would probably be of more use in this latter respect.

JOHN R. SUYDAM, JR.

**Materials of Construction.** By G. B. UFTON, Assistant Professor of Experimental Engineering, Sibley College, Cornell University. 8vo. iv + 327 pp. Illustrated. 1915. John Wiley & Sons, New York. Price, \$2.50.

This book is intended for students in engineering, who are pursuing laboratory work in the testing of materials of construction. It does not cover the work in the testing laboratory such as testing instruments and methods of testing, but rather considers the theoretical side of the properties of engineering materials as disclosed by physical and metallographic tests and control of the properties of materials through heat treatment and processes affecting the internal structure. To these ends the book is divided into two parts, each of which treats the subject under the following chapter headings.

PART I THE DETERMINATION OF THE PROPERTIES OF MATERIALS	
Chapter	Pages covered
I Definition and terms.....	9
II General nature of the internal structure of materials and action under load.....	4
III Tension loading of brittle materials.....	9
IV Tension loading of ductile materials.....	20
V Torsion loading.....	19
VI Transverse loading.....	18
VII Compression loading.....	18
VIII Cross-relationship of loadings and combined loadings.....	7
IX Special tests: Impact and minor tests; hardness fatigue.....	14
X Aging of materials; corrosion, rust, weathering, rot and protection against their effects.....	4
XI Choice of materials, working stresses, factors of safety; selection of test, specifications.....	7
PART II—THE NATURE OF MATERIALS AND CONTROL OF THEIR PROPERTIES	
XII The nature and origin of the structure of alloys.....	13
XIII The shaping of steel and the control of final properties during the shaping process.....	19
XIV Engineering properties of normal carbon steel as functions of the carbon content. Effects of elements other than carbon.....	9
XV General theory of heat treatment.....	44
XVI Engineering heat treatments of carbon steels and properties obtained.....	20
XVII Cast irons.....	19
XVIII Alloy steels.....	19
XIX Non-ferrous metals and alloys.....	22
XX Cement and cement testing.....	19

Practically 87 per cent of the book deals with ferrous metals, 7 per cent with non-ferrous metals and 6 per cent with cement.



The general scheme of the book is admirable in its attempt to associate metallurgy, metallography and stress analysis in a study of materials specifications for engineering service and is a valuable contribution to this end. It is believed that this work in the hands of a student will be of valuable assistance in a comprehensive study of materials in relation to their internal structure and stress characteristics and will serve to steer him from a one-sided appreciation of the subject. The latest experimental researches in the structural and stress characteristics of materials are drawn from in the discussions in each chapter, and in this respect the book is thoroughly up-to-date. In a work of this size it can hardly be expected that all details of the subject will be treated with fullness, nor does this seem desirable in a textbook for students beginning the subject. It is believed, however, that the book could be much improved by a fuller treatment of certain phases of the subject. For example, Chapter XI, which treats of the choice of materials, is very condensed and quite general in its treatment. It is believed that a fuller and more specific treatment of this topic would be of value, particularly since the whole study is to apply the principles disclosed to the selection of materials for engineering service. The designer or student of designing will be disappointed in this chapter. A selected range of problems, illustrating typical procedure in materials selection for varying service conditions, would be most helpful to the student. An extended treatment of the subject at this point could serve to focus all phases of the problem and define principles of procedure, which are now lacking.

Again, there appears to be an entire lack of data on working stresses used in engineering practice in different machine parts, subjected to various service requirements, together with justification for the use of such stresses. Typical specifications are also lacking, which, if provided, may serve as a basis for analysis to disclose the significance of each item and its relation to the service requirements. The book is somewhat academic in its omission of these practical and specific phases of the problem. There is also a tendency to the use of broad statements which may mislead the student. For example, on page 90, the broad statement is made that "Engineering loads in practice are commonly gravity loads." It is at once apparent that this is not true for machine members. The language of this paragraph is also obscure in the use of "maximum load" and "breaking load" since it is stated that "A load as large as the maximum will ..... finish the piece." On page 26 appears a lack of clearness in the statement that "Primary stresses are the *obvious* stresses set up by *their* loadings." It seems that the student might be confused in the meanings of "obvious" and "their." A number of failures to use clear English occur throughout the book and these, together with a tendency to indulge in short, dogmatic statements, constitute a style of presentation of subject matter which is unfortunate. Nevertheless the book will be found to be very useful in the classroom to interpret the phenomena presented in the laboratory. The printing and illustrations are clear and the book maintains the high standard of the publishers.

WALTER RAUTENSTRAUCH

**The Industrial Arts Index.** Published by The H. W. Wilson Company, of White Plains, N. Y. Subscription price supplied on request.

This work is a cumulative index to engineering and trade periodicals. It is published in February, April, June, October and December by the Wilson Company. The list of periodicals indexed in these pages makes the index well worth while, as it covers almost everything in the arts and sciences. The Index will prove a valuable addition to the book shelves of practical literature.

## Technology of Cellulose Esters. Vol. VIII. Cellulose Acetate.

By E. C. WORDEN. In 10 volumes. 8vo. xxxvi + 577 pp. D. Van Nostrand Co. Price, \$5.00 net.

The success of Worden's "Nitrocellulose Industry," published in 1911 has encouraged the author so to amplify and bring to date the subject of this work that it covers ten volumes instead of two. In these ten volumes he has undertaken to present the combinations of cellulose with acid radicals in such completeness that inability to find the information sought will be evidence that it is nonexistent or of no value.

Volume VIII devoted to Cellulose Acetate is the first of the new work to appear and the other volumes are promised at short intervals. These volumes should fulfill the author's claims for completeness if the one which has appeared is any criterion, for nearly 600 pages are given to what was covered in some 70 pages devoted to cellulose acetates in the "Nitrocellulose Industry."

In this volume the raw materials used in the manufacture of cellulose acetate and formate are described; then follow chapters on the manufacture of cellulose esters, the solvents for cellulose acetate, commercial application of the unflammable cellulose esters, analysis and appendix including index of patents, names and subjects. The study of these chapters is facilitated by putting the important matter in the text and the more abstruse parts in foot-notes. This arrangement of the type makes it possible to read rapidly through and where a subject of particular interest is found to get more complete information in the foot-notes with references to the original sources. It has the further advantage of making it possible to cover the subject thoroughly without making the book unduly bulky.

Other efforts to save space do not work out so well, such names as W. Walker, C. Cross and A. Little being scarcely recognizable with the middle initial omitted. On the other hand the name of the Newark parson who delved into science is printed with a prominence which probably will not be appreciated by certain readers.

The criticism made of the "Nitrocellulose Industry" of not making it possible to judge of the relative importance of processes from the arrangement of the text holds good in the present work although to a less extent, such a process as the coating of celluloid collars and cuffs with acetyl cellulose lacquers being given in full-sized type. The subject matter of paragraphs is indicated in some cases by heavy-faced type but this is not done systematically with the result that one might miss important data or read much that is irrelevant; for example, under Kinematograph Picture Films there appear four other distinct subjects.

A similar criticism would apply to a general lack of logical sequence in presenting facts. In the appendix the process of acetylation is compared with nitration with a view to obtaining a better knowledge of the cellulose molecule. This discussion goes into the presence of sulfuric esters, maximum limit of nitration, effect of different catalysts, and ends with the determination of acetyl in starch acetate, all interesting facts bearing on the constitution of cellulose but with no central thought or conclusion.

Lack of coherence is again evident where the method of taking moving pictures is inserted in the midst of commercial applications of acetyl cellulose; an interesting subject intrinsically but giving the reader occasion to wonder why it was introduced at that particular place.

This and other applications of acetyl cellulose, described such as the Paschke process for flexible glass, are more commonly applications of nitrocellulose. They are probably given undue emphasis by the author's enthusiasm for unflammable products.

The above comments are given more in the spirit of suggestion than criticism, for the book as a whole gives a complete, accurate and at the same time readable presentation of the subject. The volumes which are to follow will be looked forward to with great interest.

C. M. JOYCE

# NEW PUBLICATIONS

By IRENE DeMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

- Benzol:** Die Leitfähigkeit und elektrische Erregbarkeit von Benzin, Benzol und ähnliche feuergefährliche Flüssigkeiten. D. HOLDE. 8vo. 5 pp. Price, \$0.25. Verlag fuer Fachliteratur, Berlin.
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## RECENT JOURNAL ARTICLES

- Acetylene:** Wirkt Acetylen auf Metalle ein? H. RECKLEBEN AND JOHANN SCHREIBER. *Chemiker-Zeitung*, Vol. 40 (1916), No. 45, p. 325.
- Aluminum:** Estimating Metallic Aluminum in Aluminum Dust. J. E. CLENELL. *Engineering and Mining Journal*, Vol. 101 (1916), No. 19, pp. 813–815.
- Ammonia:** Troubles and Care of Ammonia Compressor Valves. A. G. SOLOMON. *Power*, Vol. 43 (1916), No. 19, pp. 643–645.



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Acetate of Lime, pure.....	100 Lbs.	7.00	@	7.05
Alum, lump.....	100 Lbs.	4.25	@	4.75
Aluminum sulfate, high grade.....	100 Lbs.	5.00	@	6.00
Ammonium carbonate, domestic.....	Lb.	72 1/2	@	10
Ammonium Chloride, gray.....	Lb.	8	@	9
Ammonium Phosphate, commercial, 98-100%.....	Lb.	6	@	—
Aqua Ammonia, 16% drums.....	Lb.	2 1/4	@	2 1/2
Arsenic, white.....	Lb.	6 1/2	@	—
Barium Chloride.....	Ton	100.00	@	125.00
Barium Nitrate.....	Lb.	15	@	16
Barytes, prime white, foreign.....	Ton	30.00	@	—
Bleaching Powder, 35 per cent.....	100 Lbs.	6.00	@	6.25
Blue Vitriol, bulk.....	Lb.	19	@	—
Borax, crystals, in bags.....	Lb.	6 1/2	@	7
Boric Acid, powdered crystals.....	Lb.	11 1/4	@	15
Brimstone, crude, domestic.....	Long Ton	35.00	@	—
Bromine, technical, bulk.....	Lb.	3.50	@	—
Calcium Chloride, lump.....	Ton	11.75	@	12.00
Calcium Chloride, granulated.....	Ton	14.78	@	15.00
Caustic Soda, 74 per cent.....	Lb.	5	@	5 1/4
Chalk, light precipitated.....	Lb.	4 1/4	@	5 1/4
China Clay, imported.....	Ton	15.00	@	18.00
Feldspar.....	Ton	8.00	@	12.00
Fuller's Earth, foreign, powdered.....	100 Lbs.	80	@	1.05
Glauber's Salt, in bbls.....	100 Lbs.	60	@	70
Green Vitriol, bulk.....	100 Lbs.	1.25	@	1.50
Hydrochloric Acid, commercial, 18%.....	100 Lbs.	2.50	@	3.00
Hydrochloric Acid, C. P., conc., 22%.....	100 Lbs.	3.00	@	3.50
Iodine, resublimed.....	Lb.	4.25	@	4.50
Lead Acetate, white crystals.....	Lb.	15 1/2	@	15 1/4
Lead Nitrate.....	Lb.	16	@	17
Litharge, American.....	Lb.	9 1/4	@	—
Lithium Carbonate.....	Lb.	90	@	1.00
Magnesium Carbonate.....	Lb.	9	@	10
Magnesite, "Calcined".....	Ton	—	@	—
Nitric Acid, 36%.....	Lb.	6 1/4	@	7
Nitric Acid 42%.....	Lb.	8 1/4	@	9 1/4
Phosphoric Acid, sp. gr. 1.750.....	Lb.	30	@	31
Phosphorus.....	Lb.	—	@	—
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, casks.....	Lb.	58	@	60
Potassium Bromide.....	Lb.	4 1/2	@	—
Potassium Carbonate, calcined, 80 @ 85%.....	Lb.	80	@	85
Potassium Chlorate, crystals, spot.....	Lb.	70	@	—
Potassium Cyanide, bulk, 98-99 per cent.....	Lb.	—	@	40
Potassium Hydroxide.....	Lb.	85	@	95
Potassium Iodide, bulk.....	Lb.	4.30	@	4.35
Potassium Nitrate.....	Lb.	—	@	—
Potassium Permanganate, bulk.....	Lb.	1.80	@	1.90
Quicksilver, flask, 75 lbs.....	Lb.	86.00	@	—
Red Lead, American, dry.....	Lb.	9 3/4	@	—
Salt Cake, glass makers'.....	Ton	8.00	@	10.00
Silver Nitrate.....	Oz.	45 1/4	@	—
Soapstone in bags.....	Ton	12.00	@	—
Soda Ash, 48 per cent.....	100 Lbs.	3.00	@	4.00
Sodium Acetate.....	Lb.	14	@	17
Sodium Bicarbonate, domestic.....	100 Lbs.	1.75	@	2.00
Sodium Bicarbonate, English.....	Lb.	3 1/2	@	3 3/4
Sodium Bichromate.....	Lb.	45	@	47
Sodium Carbonate, dry.....	100 Lbs.	3 1/2	@	—
Sodium Chloride.....	Lb.	35	@	—
Sodium Fluoride, commercial.....	Lb.	18	@	20
Sodium Hyposulfite.....	100 Lbs.	2.00	@	—
Sodium Nitrate, 95 per cent, spot.....	100 Lbs.	3.15	@	—
Sodium Silicate, liquid.....	100 Lbs.	1.25	@	1.75
Sodium Sulfide, 30%, crystals, in bbls.....	Lb.	2	@	2 1/2
Sodium Bisulfide, powdered.....	Lb.	6	@	7
Strontium Nitrate.....	Lb.	40	@	50
Sulfur, flowers, sublimed.....	100 Lbs.	2.30	@	2.70
Sulfur, roll.....	100 Lbs.	1.95	@	2.25
Sulfuric Acid, chamber, 60%.....	Ton	30.00	@	—
Sulfuric Acid, conc., sp. gr. 1.842.....	100 Lbs.	2.50	@	3.00
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Terra Alba, American, No. 1.....	100 Lbs.	75	@	80
Tin Bichloride, 50%.....	Lb.	16 1/2	@	17
Tin Oxide.....	Lb.	58	@	62
White Lead, American, dry.....	Lb.	9 3/4	@	—
Zinc Carbonate.....	Lb.	30	@	40
Zinc Chloride, commercial.....	Lb.	13	@	15
Zinc Oxide, American process.....	Lb.	8 1/4	@	8 3/4
Zinc Sulfate.....	Lb.	6 1/2	@	7 1/4

## ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.....	Lb.	1.00	@	1.25
Acetic Acid, 28 per cent, in bbls.....	Lb.	5 1/4	@	6
Acetic Acid, glacial, 99 1/2%, in carboys.....	Lb.	45	@	50
Acetone, drums.....	Lb.	40	@	50
Alcohol, denatured, 180 proof.....	Gal.	59	@	61

Alcohol, grain, 188 proof.....	Gal.	2.64	@	2.70
Alcohol, wood, 98 per cent, refined.....	Gal.	65	@	68
Amyl Acetate.....	Gal.	5.25	@	—
Aniline Oil.....	Lb.	60	@	65
Benzene Acid, ex toluol.....	Lb.	6.50	@	7.00
Benzol, 90 per cent.....	Gal.	72 1/2	@	—
Camphor, refined in bulk, bbls.....	Lb.	52	@	—
Carbolic Acid, U. S. P., crystals, drums.....	Lb.	80	@	85
Carbon Bisulfide.....	Lb.	8	@	—
Carbon Tetrachloride, drums, 100 gals.....	Lb.	18	@	—
Chloroform.....	Lb.	50	@	80
Citric Acid, domestic, crystals.....	Lb.	65	@	70
Cresol, U. S. P.....	Gal.	1.35	@	1.40
Dextrine, corn (carloads, bags).....	100 Lbs.	3.30	@	3.40
Dextrine, imported potato.....	Lb.	—	@	—
Ether, U. S. P., 1900.....	Lb.	15	@	20
Formaldehyde, 40 per cent.....	Lb.	13 1/2	@	14
Glycerine, dynamite, drums included.....	Lb.	55	@	60
Oxalic Acid, in casks.....	Lb.	73	@	—
Pyrogallie Acid, resublimed bulk.....	Lb.	2.75	@	—
Salicylic Acid.....	Lb.	3.10	@	—
Starch, cassava.....	Lb.	3 3/4	@	4 1/2
Starch, corn (carloads, bags).....	100 Lbs.	2.35	@	—
Starch, potato.....	Lb.	12	@	—
Starch, rice.....	Lb.	8	@	10
Starch, sago.....	Lb.	3 1/2	@	4
Starch, wheat.....	Lb.	5	@	6
Tannic Acid, commercial.....	Lb.	60	@	64
Tartaric Acid, crystals.....	Lb.	66	@	68

## OILS, WAXES, ETC.

Beeswax, pure, white.....	Lb.	47	@	55
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2	@	—
Castor Oil, No. 3.....	Lb.	20	@	28
Ceresin, yellow.....	Lb.	10	@	14
Corn Oil, crude.....	100 Lbs.	9.50	@	—
Cottonseed Oil, crude, f. o. b. mill.....	Gal.	72 1/2	@	75
Cottonseed Oil, p. s. y.....	Lb.	11	@	—
Cresote, beechwood.....	Lb.	6.75	@	—
Cylinder Oil, light, filtered.....	Gal.	21	@	—
Fusel Oil, crude.....	Lb.	4.50	@	—
Japan Wax.....	Lb.	17	@	20
Lard Oil, prime winter.....	Gal.	1.08	@	1.12
Linsed Oil, raw (car lots).....	Gal.	71	@	—
Menhaden Oil, crude (southern).....	Gal.	—	@	—
Naphtha, 68 @ 72%.....	Gal.	33	@	—
Neat's-foot Oil, 20%.....	Gal.	1.10	@	1.20
Paraffine, crude, 118 & 120 m. p.....	Lb.	5	@	—
Paraffine Oil, high viscosity.....	Gal.	29 1/2	@	—
Rosin, "F" Grade, 280 lbs.....	Bbl.	5.40	@	—
Rosin Oil, first run.....	Gal.	32	@	—
Shellac, T. N.....	Lb.	24	@	25
Spermaceti, cake.....	Lb.	25	@	26
Sperm Oil, bleached winter, 38%.....	Gal.	80	@	82
Spindle Oil, No. 200.....	Gal.	24	@	25
Stearic Acid, double-pressed.....	Lb.	13	@	13 1/4
Tallow, acidless.....	Gal.	88	@	92
Tar Oil, distilled.....	Gal.	30	@	31
Turpentine, spirits of.....	Gal.	44	@	—

## METALS

Aluminum, No. 1, ingots.....	Lb.	58	@	60
Antimony, ordinary.....	Lb.	29	@	30
Bismuth, N. Y.....	Lb.	3.15	@	3.25
Copper, electrolytic.....	Lb.	29 1/2	@	—
Copper, lake.....	Lb.	29 1/4	@	—
Lead, N. Y.....	100 Lbs.	7.50	@	—
Nickel, electrolytic.....	Lb.	50	@	—
Nickel, shot and ingots.....	Lb.	45	@	—
Platinum, refined.....	Oz.	80.00	@	—
Silver.....	Oz.	75 1/4	@	—
Tin.....	100 Lbs.	49.50	@	—
Zinc, N. Y.....	Lb.	15 1/4	@	—

## FERTILIZER MATERIALS

Ammonium Sulfate.....	100 Lbs.	3.55	@	—
Blood, dried.....	Unit	2.50	@	—
Bone, 4 1/2 and 50, ground, raw.....	Ton	—	@	—
Calcium Cyanamid.....	Unit of Ammonia	2.55	@	—
Calcium Nitrate, Norwegian.....	100 Lbs.	—	@	—
Castor Meal.....	Unit	—	@	—
Fish Scrap, domestic, dried, f. o. b. works.....	Unit	—	@	—
Phosphate, acid.....	Unit	80	@	85
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	2.75	@	3.00
Tennessee, 78-80 per cent.....	Ton	5.00	@	5.50
Potassium "muriate," basis 80 per cent.....	Ton	425.00	@	—
Pyrites, furnace size, imported.....	Unit	15	@	15 1/2
Tankage, high-grade; f. o. b. Chicago.....	Unit	2.85	@	10

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## EDITORIALS

### AMMONIUM SULFATE AS A SOURCE OF COMBINED NITROGEN

After reading the interesting article entitled "Fixation of Atmospheric Nitrogen before Congress," printed in a recent issue of *Metallurgical and Chemical Engineering*, one has the feeling that the case of ammonium sulfate as a great additional source of fixed nitrogen for fertilizer and munition purposes has not received just consideration. It is scarcely fair to dismiss the subject with such finality, without bringing to bear at least one valid argument against it. This subject often has been dismissed with the bare statement that coal will never be distilled solely for the ammonia which its distillation yields, a statement that sounds entirely reasonable and probably is true. The proposal, it appears, has never been to distill coal for that purpose alone, but is merely to increase the ammonia output by recovering a larger portion of that ammonia now being allowed to go to waste. The proposition, in its simplest form, is not to coke more coal but to coke more of the coal now coked by methods admitting of ammonia recovery.

It is idle to take the position that this cannot be done, for not only is there no important reason why it should not be done, but also, at the outset, one is confronted by the fact that it is being done, at such a rate of increment as to leave no doubt of its entire feasibility. In 1915, the production of ammonia in the United States, reckoned as ammonium sulfate, was 220,000 tons. From the by-product ovens now in operation, under construction and contracted for, the production for 1917 will be no less than 376,000 tons.

In 1914 only 32 per cent of the coal coked in this country was treated in by-product recovery ovens; that is to say, only 32 per cent of the ammonia produced in the coking industry was saved. The 68 per cent lost in that year from coking 35,000,000 tons of coal in bee-hive ovens, reckoning a production of 20 pounds ammonium sulfate per ton of coal (the average production), was equal to 700,000,000 pounds, or 350,000 tons, which, at wholesale market prices obtaining on March 20, 1916 (\$3.75 per hundred weight), would have an annual value of \$26,000,000. There is to be observed yearly a decided increase in the production of by-product ammonia due to the transition from the bee-hive to the by-products oven; at the same time there will be an ultimate, though possibly a fluctuating increase in the total production of coke, due to the further introduction of its use and the growth of the industries now using it. The prosperity of the latter industries, especially of the steel industry, will induce fluctuations in output; but we may look forward with confidence to the ultimate abandonment of the bee-hive oven.

To what extent would this quantity of ammonia meet the nation's needs for nitric acid? By the processes whereby ammonia is converted into nitric acid, a yield of 85 to 95 per cent of the theoretical is claimed. On the basis of 90 per cent yield, from 350,000 tons

of ammonium sulfate could be produced 300,000 tons anhydrous nitric acid, equivalent to 400,000 tons sodium nitrate or 190,000 tons calcium cyanamide. Such a quantity of ammonia could not find place in the fertilizer trade of the country as it now exists without displacing all other ammoniates, for it, together with that now used in that way, would be adequate to supply all the nitrogen now consumed in that industry. Obviously, at present prices, it would have to find application in some other industries, probably the explosives industry, in which, in normal times, it is estimated approximately 275,000 tons sodium nitrate are employed annually. The extent to which this displacement would take place would be determined by the cost of nitric acid from ammonia as compared with that from Chilean nitrate. Successful competition with the latter commodity would afford it a very large domestic market and keep at home a proportionately large sum now paid annually for Chilean nitrates. Thus, by the normal development within the coking industry, is being supplied, as demanded, a quantity of combined nitrogen capable of withstanding competition from foreign sources and adequate for normal conditions.

What are the possibilities in by-product ammonia for abnormal, or emergency, conditions? The by-product oven likewise renders available the surplus gas not needed in the coking process itself which, under emergency conditions, could be applied to the generation of electrical energy for the fixation of a further quantity of nitrogen. From 35,000,000 tons of coal thus coked could be generated over 800,000 continuous horse power, from which it would be possible to produce fixed nitrogen equivalent to an additional 1,400,000 tons of ammonium sulfate. To this, in time of emergency, could be added also the not inconsiderable quantity of ammonium sulfate now entering fertilizers; for that part of agriculture which furnishes the great basic food and forage crops is not the part that at present uses the bulk of the fertilizer now employed in this country. If conditions came about such that imports were shut off, that is, conditions under which we should be thrown upon domestic sources of fixed nitrogen for munition purposes, exports likewise would be prohibited; in such case we should have available for home consumption the large surplus of food and other agricultural products which normally we export. So instead of a stimulated agriculture, requiring fertilizers, as is now the case in certain European countries whose imports are restricted by blockade, conditions almost inevitably would lead to a restricted agricultural production. There would be, then, no stimulated demand for fertilizer materials.

The investment which is making available this large volume of ammonia is large. The cost of installation of by-product retort ovens is approximately \$1,500 per ton of daily coal capacity. However, it must not be forgotten that ammonia is only a by-product of

the coking industry and does not alone have to pay interest on the investment. This is borne also by the coke (the main product), gas, tar, and benzol, the last two of rapidly increasing importance due to the stimulated demand for domestic coal-tar products and the enhanced price of gasoline. So the capital requirement really does not enter into the present discussion so long as there is some product to pay the interest demanded. The rapid installation of the by-product oven is proof enough that the interest on investment is forthcoming. By-product ammonia, therefore, fortified by the other products produced simultaneously, is in a position to withstand the rigors of market. It yet remains to be demonstrated that ammonia from any other artificial source can be made to pay interest on investment under American conditions.

By-product ammonia may lack the further characteristic, elasticity, desirable in a source of fixed nitrogen for emergency purposes, may not be susceptible of an immediate, enormously increased production. But this quality is lacking to any proposal which does not involve the erection of industrial plants to lie idle during those periods when there is no emergency; or if not lying idle, to operate under artificial conditions, affording no profit and therefore requiring public subsidy. That it is susceptible of enormous increase, should the people demand such an increase, becomes evident when it is recalled that there are enormous quantities of low-grade coal produced as a by-product in coal mining, other quantities available for mining, and immense beds of lignites and peat, practically untouched, all of which, on distillation, yield ammonia and other by-products; the residual carbon, valuable for fuel or gas production, and large volumes of gas for fuel or power production, is available for the manufacture of additional great sources of ammonia by fixation methods. In this connection it should be added that by-product gas as a source of power for the electrical fixation of nitrogen has the advantage over water power that by-product ovens can be erected and put into operation in a much shorter time than can the usual stream be dammed and its water power developed.

Likewise, coal as a power producer is much more efficiently used when it is first converted into gas and the gas used in gas engines, effecting a great saving over the steam engine—a practice which, if instituted, would make available the ammonia and other by-products of the coal now used for power production. Finally, as an extreme though visionary measure, at the same time one of enormous value to the public and one that should be looked forward

to by the public as an end to be striven for, the unrestricted use of bituminous coal as a fuel could be prohibited by public enactment and the universal use of coke or gas encouraged, thus conserving to the public the enormous aggregate wastage now existing in present methods of using coal. Such an enactment, it is reported, has been in effect in Germany since 1914. It is needless to compute the quantity of ammonia which thus would be made available for all uses or to speculate on the effect on American agriculture which such a supply of cheap and valuable fertilizer would have.

As preparedness measures let us advocate those things which will work for the good of the people as a whole. The salient feature of the foregoing is that it is a conservation measure affording profits under normal conditions and therefore not requiring a public subsidy to guarantee profits. Difficulties which appear in connection with it should not be permitted to prevail against the considerations which commend it. There is no conflict between true preparedness and true conservation since there can be no true preparedness with which conservation does not go hand in hand; and both are only applied common sense. That nation is best prepared for any emergency whose people are united and are working together to obtain the best possible returns from their common natural resources and labors. Any preparedness measure which does not have first consideration for conservation, for the welfare of the people as a whole, should be regarded with suspicion.

It is apparent from the above that we have at hand a source of fixed nitrogen adequate for normal times and capable of immense expansion in case of emergency. Let us then not hurry into the adoption of measures which later may come to be a source of humiliation. Let us rather with diligence and with the welfare of the nation in mind, investigate in the scientific way, in our laboratories and mills, these questions about which there is doubt and which demand no instantaneous decision. The atmosphere doubtless must be looked to ultimately to supply combined nitrogen for human needs. Progress to the present in that field, marked as it is, should only inspire investigation, and not acceptance of the position that the problem of combining nitrogen is solved. It is not solved. From our point of view it can be regarded as solved only when the fixation of atmospheric nitrogen becomes commercially feasible under the conditions that normally exist in this country.

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U. S. BUREAU OF SOILS  
WASHINGTON, D. C.

## ORIGINAL PAPERS

### THE OCCURRENCE OF GERMANIUM IN ZINC MATERIALS

By G. H. BUCHANAN

Received May 29, 1916

In a recent issue of *THIS JOURNAL*,<sup>1</sup> W. F. Hillebrand and J. A. Scherrer contribute a short article

<sup>1</sup> *THIS JOURNAL*, 8 (1916), 225.

on "The Recovery of Gallium from Spelter in the United States." In addition to the observations on gallium, mention is made of the fact that Dr. K. Burns, of the Bureau of Standards, has examined spectroscopically several samples of zinc ore from various sources, and has identified in several of them,



notably in a Missouri sulfide, the very rare element germanium. These observations concerning germanium are of particular interest to us since in recent work we also have encountered this element in a by-product derived from Wisconsin blende. The exact nature of this by-product it is not possible to disclose at present.

The occurrence of germanium in blendes has been noted by Urbain.<sup>1</sup> By spectroscopic methods this investigator detected germanium in thirty-eight out of eighty-four blendes from various localities. From five hundred and fifty kilos of one of the richest of these, a Mexican blende, he obtained five grams of pure germanium. The amounts of the element found have always been small, the aid of the spectroscope being usually required to establish the identification. In the material at our disposal, however, germanium was found in sufficient quantity to be readily detected by the ordinary chemical reagents.

The presence of an unusual element had been indicated in the course of analysis and further investigation showed that this was some member of the tin sub-group of the hydrogen sulfide group. The materials were therefore examined for the less common elements of this group. By the experiments briefly outlined in the succeeding paragraphs we convinced ourselves that we were dealing with an altogether unsuspected constituent, the element germanium, and that it was present in considerable amount.

Several one hundred-gram portions of the substance were treated with concentrated hydrochloric acid and the resulting solutions were distilled to about one-half volume, a current of chlorine being passed through the boiling mixture to maintain the arsenic in the pentavalent form. The distillate contained the unknown element.

On dilution of the distillate with a small amount of water and treatment with hydrogen sulfide a white flocculent precipitate was formed. If, however, the distillate was greatly diluted with water such precipitation took place but slowly and incompletely; the addition of strong hydrochloric acid to such solutions caused immediate precipitation. A considerable excess of strong acid was always found necessary for rapid precipitation of the sulfide.

The white sulfide, precipitated from strongly acid solutions, was somewhat soluble in water. It was readily soluble in ammonia and in alkaline sulfide solution. The sulfide yielded on ignition a white residue, soluble in water and in ammonia.

To an aqueous solution of the sulfide a little hydrofluoric acid was added and the solution saturated with solid potassium chloride. A heavy grayish white gelatinous precipitate resulted.

These reactions agree throughout with the properties ascribed to germanium by Winkler. The boiling point of the tetrachloride of germanium is 86°. The sulfide of germanium is white. It is soluble in water and in alkali and is precipitated only from strongly acid solutions. The formation of a double potassium fluoride is particularly characteristic.

From two portions of a solution of germanium sulfide in water the sulfide was precipitated with strong acid and hydrogen sulfide. The sulfide was filtered on a Gooch, dried at 110° and weighed. It was then dissolved in ammonia and the crucibles reweighed. The ammoniacal solutions were evaporated to dryness in platinum and the residues transformed to oxides by the method recommended by Winkler. The results follow.

Determination No.	1	2
Weight of sulfide.....	0.0820	0.0812
Weight of oxide.....	0.0614	0.0604
Ratio oxide/sulfide.....	0.749	0.744

The theoretical ratio  $\frac{\text{GeO}_2}{\text{GeS}_2}$  is 0.766, assuming

the value 72.5 for the atomic weight of germanium.

A roughly quantitative determination of the amount of germanium present in the material was carried out as follows: After distillation with hydrochloric acid and chlorine the sulfide was precipitated from the distillate with hydrogen sulfide. In some experiments the sulfide was weighed directly; in others it was transformed into oxide with nitric acid and weighed as  $\text{GeO}_2$ . The mean of several closely agreeing determinations gave the value  $\text{GeO}_2 = 0.25$  per cent.

To show whether or not germanium could be found in other zinc ores, samples of similar by-products from different ores were distilled with hydrochloric acid and chlorine. The distillates, after dilution, were treated with hydrogen sulfide. If no precipitate was obtained the test was considered negative. If a precipitate was obtained (other than the turbidity of sulfur) it was filtered off and transformed to oxide with nitric acid. The final test consisted in the formation from the residue of the double potassium fluoride with hydrofluoric acid and potassium chloride.

From several of the materials very definite confirmatory tests were obtained; others gave satisfactory blanks, while in only a few instances were the results uncertain. In none of the cases where positive results were secured was there found an amount of germanium at all comparable to that found in the material first examined, probably not one-tenth as much. A positive test was secured from Joplin ore and also from some Mexican ores. The Franklin ores gave negative results.

The germanium oxide prepared as described above has been examined spectroscopically by Dr. Burns, of the Bureau of Standards, who reports as follows: "It shows: zinc, *absent*; lead, *weak*; silicon, *present*; tin, *fairly strong*; copper, *present* (possibly the last three were introduced accidentally by us); cadmium, *trace*; germanium, *principal constituent*; gallium, *present*; indium, *trace*."

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#### SODIUM SULFATE AS A SUBSTITUTE FOR POTASSIUM SULFATE IN THE GUNNING MODIFICATIONS FOR DETERMINING NITROGEN

By W. L. LATSHAW  
Received June 9, 1916

Owing to the extremely high price of potassium sulfate, chemists who favor the Gunning modification

<sup>1</sup> *Compt. rend.*, **149**, 602; **150**, 1758.

of the Kjeldahl method for determining nitrogen are looking for a cheaper substitute to take the place of the more expensive potassium sulfate. Quotations recently received at this laboratory from several firms range in price from \$1.25 to \$2.25 per lb. for the powdered chemical suitable for use in nitrogen work, while quotations on suitable sodium sulfate were only 15 c. per lb. Because of the similarity in chemical characteristics between potassium sulfate and sodium sulfate, a series of determinations was made to compare the use of these two salts in making nitrogen determinations.

In the first trials, where 10 g. of the water-free salts were used in comparison, both worked very nicely during digestion, but on cooling, the digest in which sodium sulfate was used caked into a solid mass, and as this was objectionable 7 to 8 g. of sodium sulfate were used with the results shown in Table I.

As nitrogen determinations must be made on materials differing widely in nitrogen content, it was thought well to use such a variety as one might ordinarily be called upon to analyze in every-day work. For this reason the ten different samples listed in the table were used in these determinations.

TABLE I

(RESULTS IN PERCENTAGES)

SUBSTANCES	THE GUNNING COPPER METHOD SUBSTITUTING SODIUM SULFATE			THE OFFICIAL GUNNING COPPER METHOD		
	No. of Dets.	Max.	Min.	No. of Dets.	Max.	Min.
Dried blood...	3	14.97	14.93	3	14.96	14.92
Casein.....	3	12.72	12.68	3	12.71	12.67
Milk albumin...	6	9.07	8.89	3	9.00	8.96
Fertilizer.....	3	3.51	3.46	3	3.51	3.49
Alfalfa leaves...	5	3.78	3.61	3	3.80	3.73
Alfalfa stems...	3	1.63	1.55	3	1.63	1.59
Cob chop.....	3	1.36	1.32	3	1.38	1.35
Bone meal.....	3	0.96	0.92	3	0.94	0.90
Skim milk.....	3	0.53	0.50	3	0.53	0.51
Soil.....	4	0.043	0.038	3	0.041	0.037

The figures in the table explain themselves, and as these ten samples include compounds of the highest to the lowest nitrogen content, the writer feels confident in saying that he believes sodium sulfate can be used instead of potassium sulfate when determining nitrogen in any kind of material. The analyses were carried out under exactly duplicate conditions. The period of digestion was 2 hrs. after the solution cleared.

Sodium sulfate, when used in the amounts mentioned, did not in any way prove objectionable in this work. It proved itself just as good an oxidizing agent as potassium sulfate and as it has a higher boiling point, it would be expected to be even better than potassium sulfate. The writer does not maintain that sodium sulfate is preferable to potassium sulfate in nitrogen determinations. There are cases where caking will take place, although this can readily be avoided by diluting as soon as cool. As far as chemical efficiency is concerned, the two chemicals compare very favorably. Where a large number of nitrogen determinations are being made and potassium sulfate is ordered in 50 and 100 lb. lots, a great saving will be realized by using sodium sulfate; as much as \$60 can be saved on one order of 50 lbs.

It should be mentioned here that we have found it more convenient and inexpensive to use copper wire instead of copper sulfate. As is known,<sup>1</sup> the use of

copper sulfate has been adopted officially for use in nitrogen determinations. Its good points have previously been discussed<sup>1</sup> and need no further elaboration. Pieces of copper wire approximating 0.1 g. can readily be cut with a wire cutter.

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## SOME DATA ON THE OXIDATION OF AUTOMOBILE CYLINDER OILS

By C. E. WATERS<sup>2</sup>

Received April 1, 1916

### INTRODUCTION

It has long been known that mineral oils become oxidized when subjected to the combined action of sunlight and air. The literature of the subject was rather fully reviewed in a paper published some time ago.<sup>3</sup>

The so-called "carbonization" of automobile cylinder oils is due, to only a very limited extent if at all, to cracking, but is caused by oxidation<sup>4</sup> and subsequent polymerization. In order to learn whether there is any close connection between the rate of oxidation of different oils on exposure to light and air, and their carbonization values at elevated temperatures, both before and after oxidation in the light, an extended series of tests was made with three automobile cylinder oils of well known brands. Certain other constants were also determined. As supplemental to the above, the influence of the time and temperature of heating upon the carbonization value was also studied.

A sufficient supply of each of the oils was purchased in the open market. In order to remove adventitious particles of iron rust or other material that might affect the carbonization values and possibly other determinations,<sup>5</sup> the samples were filtered directly into clean cans. One-liter portions were kept for convenience in dark brown bottles.

The flash and fire points were as follows, the determinations being made in the Pensky-Martens closed cup apparatus:

Oil No.	1	2	3
Flash point.....	215°	210°	205°
Fire point.....	270°	260°	250°

### OXIDATION IN SUNLIGHT

In the earlier paper on this subject<sup>6</sup> it was shown that when an oil is oxidized in the sunlight some water and carbon dioxide are given off. The oil becomes highly acid and an insoluble oxidation product is thrown down, sometimes after only a few hours' insolation. In order to follow the changes in weight of the oils under investigation, seven 10-g. portions of each were placed in 150-cc. Erlenmeyer flasks, the mouths of which were covered with filter paper

<sup>1</sup> A. J. Patten, *Journal A. O. A. C.*, **1**, No. 3, pp. 394-395; O. F. Jensen, *This Journal*, **7** (1915), 38-39.

<sup>2</sup> Published by permission of the Director of the Bureau of Standards. The complete paper has just appeared as *Technologic Paper 73* of the Bureau of Standards.

<sup>3</sup> Bureau of Standards, *Bull.* **7** (1910), 227-234; *This Journal*, **2** (1910), 451-4.

<sup>4</sup> Bureau of Standards, *Bull.* **7** (1910), 372, 375; Bureau of Standards, *Technologic Paper 4* (1911), 11; *This Journal*, **3** (1911), 236, 237, 815.

<sup>5</sup> Bureau of Standards, *Technologic Paper 4* (1911), 10, 13; *This Journal*, **3** (1911), 815.

<sup>6</sup> Bureau of Standards, *Bull.* **7** (1910), 232; *This Journal*, **2** (1910), 453.

<sup>1</sup> *Journal A. O. A. C.*, **1**, No. 4, Part II, 18-21-23.

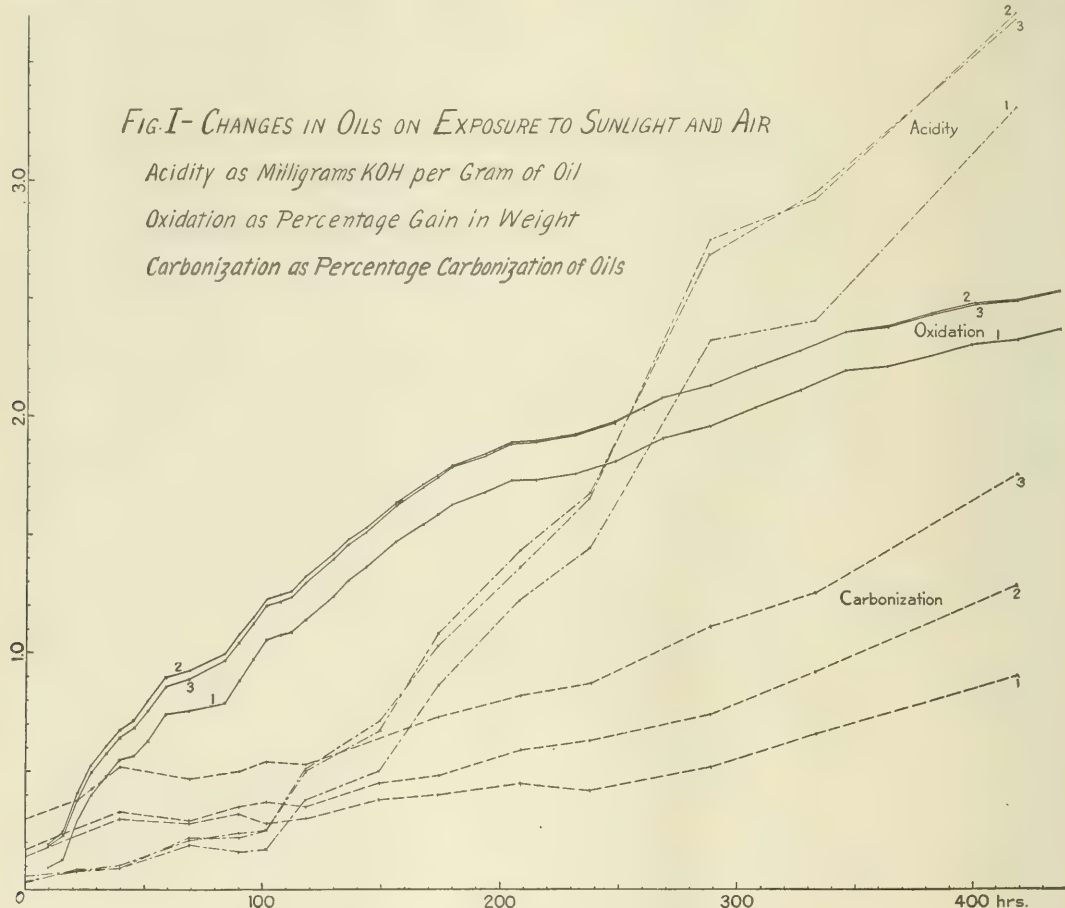


to exclude dust. The flasks were held in racks, the tops of which were covered with white paper. On every bright day, for a total of 438 hrs., they were placed outside a window facing south. At first the flasks were weighed every day, but later on, as the rate of oxidation became less rapid, this was done only every 3 or 4 days. All weighings were made against a balance.

Twenty-one flasks was all that could be placed, without shading one another, upon the window-sill. Great care was taken to keep the racks level, and to avoid getting the oil on the sides of the flasks, thus increasing the area of oil surface exposed. Only three

Exposure Hrs.	GAIN IN WEIGHT Milligrams			Exposure Hrs.	Acidity Milligrams KOH			CARBONIZATION Percentages		
	No. 1	No. 2	No. 3		No. 1	No. 2	No. 3	No. 1	No. 2	No. 3
0	9.1	19.3	18.2	None	0.06	0.04	0.03	0.14	0.17	0.30
81.5	6.9	6.7	7.5	22	0.08	0.08	0.08	0.23	0.26	0.38
90	8.8	10.2	104.0	40	0.09	0.10	0.09	0.30	0.33	0.52
140	13.8	141.7	139.2	69	0.19	0.21	0.22	0.28	0.29	0.47
167.5	13.1	130.9	169.6	90	0.16	0.24	0.22	0.32	0.35	0.50
205	17.2	6.188.8	188.2	101.5	0.17	0.25	0.25	0.28	0.37	0.54
249	180.7	197.1	197.0	118	0.38	0.51	0.50	0.30	0.35	0.53
289	195.4	212.7	212.6	149	0.50	0.71	0.67	0.38	0.44	0.64
327	210.8	237.2	227.2	174	0.86	1.03	1.08	0.40	0.48	0.73
364	220.4	237.8	237.4	208.5	1.22	1.36	1.43	0.45	0.59	0.82
402	229.9	247.4	246.7	238	1.44	1.65	1.67	0.42	0.63	0.87
438	236.2	252.9	252.1	289	2.32	2.74	2.68	0.52	0.74	1.11
				333	2.40	2.91	2.94	0.66	0.92	1.25
				419	3.40	3.70	3.67	0.90	1.38	1.75

The curves shown in Fig. I are plotted from the average gains for each set of flasks and the number



flasks of each set were exposed for the entire 438 hrs., because on two occasions two flasks of each oil were used for special tests. Although the remaining flasks were those showing gains furthest from the respective averages, yet at the end of the experiment the differences between the highest and the lowest gain for each oil were only 7.5, 4.5 and 6.9 mg., respectively. These are the maximum differences found during the test.

In Table I are given the average gains in weight for the three oils at approximately equal intervals.

of hours they were exposed to light. It will be seen that, except for breaks caused by unfavorable weather, the curves apparently show that the oxidation proceeds at a slowly decreasing rate. But it must be remembered that the gain is the algebraic sum of the oxygen absorbed and the carbon dioxide and water lost.<sup>1</sup> Hence curves showing the actual rate of oxidation would lie somewhat above those drawn.

To follow the changes in weight, carbonization, and acidity, not to mention a few special tests, more

<sup>1</sup> Low et al.

than 200 ten-gram portions of oil were used. T have had these in separate flasks would have been impracticable, so that about a liter and a half of each oil was oxidized in crystallizing dishes 24 cm. in diameter. The dishes were covered with watch glasses which excluded dust but did not prevent access of air. At certain intervals, enough to make the desired tests was removed, after thoroughly stirring the contents of the dishes. Satisfactory sampling was not difficult even after the insoluble oxidation product<sup>1</sup> began to form, because the particles settled very slowly through the oil.

It was foreseen that the oil in the dishes could not be oxidized as rapidly as that in the flasks, on account of its being in a much deeper layer. For this reason the curves showing the increase in acidity and carbonization are not strictly comparable with those showing the gain in weight. This does not, however, affect the general results. The more important determinations were made on samples that had received the same treatment.

#### INCREASE IN ACIDITY BY OXIDATION

From time to time representative samples were removed from the dishes. Ten-gram portions were warmed with measured volumes of alcohol and gasoline and titrated with 0.1 *N* alkali, using phenolphthalein as indicator. At first there was no difficulty about this, but as the oils became more strongly acid the end-point was increasingly difficult to detect, owing to their great tendency to emulsify. This is not surprising when it is remembered that soap is formed by the action with the alkali.<sup>2</sup>

The results appear in Table I and are also plotted in Fig. I. The ordinates show the number of milligrams of potassium hydroxide required to neutralize 1 g. of oil. It will be seen that the curves for Oils 2 and 3 lie very close to one another throughout the greater part of their extent, the maximum deviation being equivalent to only 0.07 mg. of caustic potash. In this respect they resemble the curves showing the increase in weight. In both cases also, Oil 1 lies below these two. The general trend of the curves indicates that the rate of formation of acids gradually increases. A maximum acidity must eventually be reached, but the curves give merely an uncertain indication of this by their slightly decreased slope. The two abrupt breaks in the curves between 69 and 149 hrs. are the results of unfavorable weather.

It was found that the percentage of the insoluble oxidation product thrown down by petroleum ether is not proportional to the gain in acidity. The percentages found at the end of the exposure test were 0.38, 0.51 and 0.60, respectively.

#### THE CARBONIZATION OF OILS OXIDIZED IN SUNLIGHT

The carbonization values of the oxidized oils were determined on samples taken at the same times as those used for the determination of acidity. The procedure followed was the same as described in earlier

papers,<sup>1</sup> but an electrically heated and controlled air bath was used instead of one heated by gas. Ten-gram portions of oil, contained in 150-cc. Erlenmeyer flasks, were heated to 250° for 3 hrs., allowed to cool and diluted with 50 cc. of petroleum ether. The flasks were then tightly corked and set aside for about 24 hrs. The precipitate was filtered off in a Gooch crucible prepared with a disk of filter paper (S. & S. No. 589 blue ribbon) covered with a thin layer of asbestos to keep it in place. It was washed with petroleum ether, dried at 95–100°, and weighed. The results obtained are included in Table I and are shown in Fig. I.

The curves showing the percentages of carbonization of the oxidized oils are strikingly different from those showing the gains in weight and in acidity. Oils 2 and 3 no longer give nearly the same values, but quite different ones. After 419 hours' exposure to sunlight, Oil 2 has a carbonization value that is slightly greater than the mean of the values for the other two oils. A similar relationship held for the amounts of insoluble oxidation product formed, at ordinary temperatures, in sunlight.

#### MISCELLANEOUS DETERMINATIONS

In order to learn whether or not there is any connection between the tendency of an oil to oxidize and certain other of its properties, the power to form emulsions with water and the Maumené and iodine numbers were determined.

**DEMULSIBILITY**—When oils are vigorously stirred or shaken with water, more or less permanent emulsions are produced. The rates at which the two liquids separate differ widely, some emulsions lasting for days, while with others the two original layers reappear in a few minutes. The "demulsibility,"<sup>2</sup> or rate of separation of an emulsion into layers, is an indication of the quality of an oil. A high demulsibility, measured in cubic centimeters per hour, for instance, indicates an oil of good quality.

W. H. Herschel, of this Bureau, using an apparatus devised by him,<sup>3</sup> determined the demulsibilities of the original oils or the oils after 238 hrs.' insolation and of the latter after they had been filtered through bone-black. The carbonization values of two of the filtered oils were also determined. The results are given in Table II.

It is plain that oxidation caused a decided deterioration of the oils, and that a distinct improvement was effected by shaking with bone-black and filtering soon thereafter. This is in agreement with the work of Schwarz and Marcusson,<sup>4</sup> who were able to extract from oils certain resinous substances which, when heated to 120° in the air, blackened and were trans-

<sup>1</sup> Bureau of Standards, *Bull.* 7 (1910), 370; Bureau of Standards, *Technologic Paper* 4 (1911), 4; *THIS JOURNAL*, 3 (1911), 235, 813.

<sup>2</sup> The expression "demulsification value" has been used by Arnold Philip (*J. Soc. Chem. Ind.*, 34 (1915), 700) to denote the percentage of oil which separates in 24 hours. The word selected by Mr. Herschel is not only a shorter expression but refers to a different unit.

<sup>3</sup> There is in course of preparation a paper describing the apparatus and procedure for making this determination.

<sup>4</sup> *Z. angew. Chem.*, 26 A (1913), 385.

<sup>1</sup> Bureau of Standards, *Bull.* 7 (1910), 230; *THIS JOURNAL*, 2 (1910), 452.

<sup>2</sup> Cf. Schaal, D. R. Pat. 32,705; *Chem.-Ztg.*, 9 (1885), 1520.



formed into asphalt that was insoluble in benzene.<sup>1</sup>

**MAUMENÉ NUMBERS.** Chiefly as a matter of interest the Maumené numbers of the oils, before and after exposure to sunlight for 438 hours, were determined. Fifty gram samples were mixed with 10 cc. of concentrated sulfuric acid and stirred vigorously until no further rise of temperature was observed. The oil-acid mixture was contained in a 100 cc. tall beaker surrounded with a thick layer of cotton batting in a larger beaker. A simple mechanical stirrer, using the laboratory blast for motive power, was employed. Temperatures were read on an Anschütz thermometer having a range of 50° and graduated to 0.2°. The results obtained appear in Table II.

The Maumené number, like the heat of bromination and the iodine number, is supposed to be a measure of the degree of unsaturation of an oil. The non-drying oils give lower values than the drying oils.<sup>2</sup>

**IODINE NUMBERS.** Kissling long ago pointed out that for different oils the resinification number (carbonization value) may vary much more than the

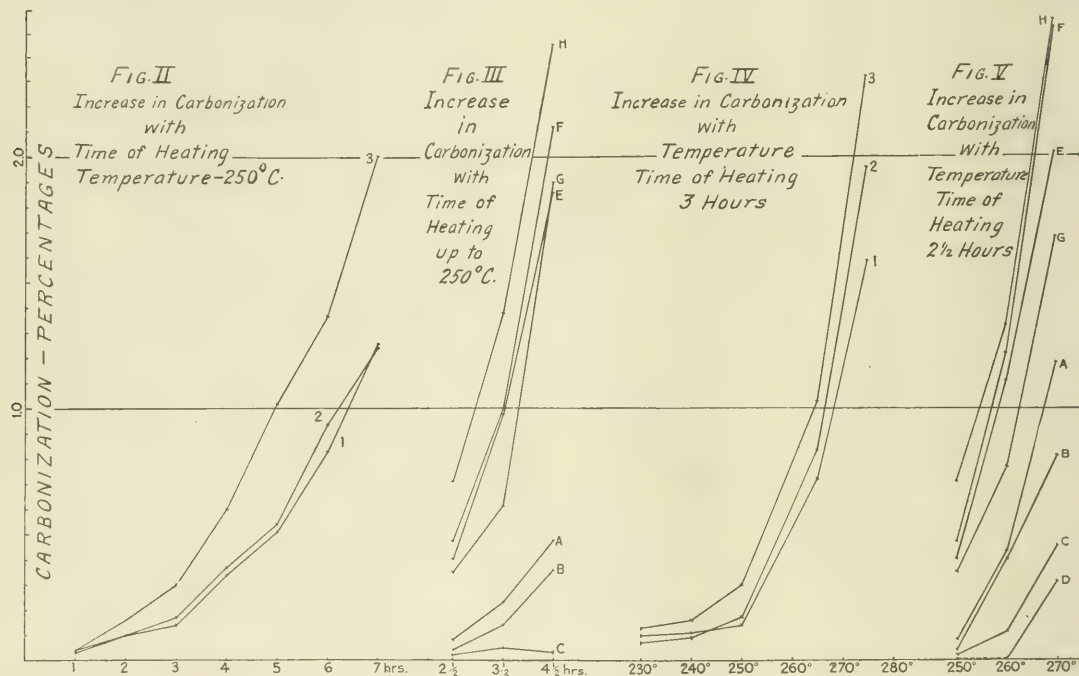
TABLE II DETERMINATIONS ON ORIGINAL AND OXIDIZED OILS

	ORIGINAL OILS			Untreated OXIDIZED OILS			Filtered	
	No. 1	No. 2	No. 3	No. 1	No. 2	No. 3	No. 1	No. 2
Densibility (20°) (sp. gr.)	270	270	360	20	32	45	90	163
Carbonization (Per cent)	0.14	0.17	0.30	0.42	0.63	0.87	0.34	0.55
Maumené No.	8.3°	7.3°	7.1°	20.6°	20.0°	18.8°	.....	.....
Rise in temp.	8.2°	7.2°	7.1°	21.1°	19.7°	18.9°	.....	.....
Iodine No.	81	29.8	30.0	20.4	19.1	20.6	.....	.....
	31.5	29.8	30.3	20.4	19.1	20.6	.....	.....

of this Bureau. His results (Table II) confirm the statement of Kissling. Oils 1 and 2 show a slightly greater drop in the iodine number than does Oil 3, but the difference is perhaps not great enough to be worthy of special comment.

#### EFFECT OF THE TIME OF HEATING UPON THE PERCENTAGE OF CARBONIZATION

In order to learn whether the percentage of carbonization is directly proportional to the time of heating, or whether the reaction is progressively more or less rapid, a series of determinations was made upon the three oils under investigation. Ten-gram samples were heated to 250° for one, two, etc., up to



Maumené and iodine numbers.<sup>3</sup> The iodine numbers of Oils 1, 2 and 3, and of the same oils after 438 hours' insolation, were determined by J. H. Bower,

<sup>1</sup> For other data having a bearing upon this general subject, including the formation of asphalt, see Schwarz and Schlüter, *Chem.-Ztg.*, **35** (1911), 413-5; Holde and Eickmann, *Mitt. kgl. Materialprüfungsamt*, **1907**, 145; cf. *Z. angew. Chem.*, **20** (1907), 1263, 1293; Southcombe, *J. Soc. Chem. Ind.*, **30** (1911), 261-4; Zaloziecki and Zelinski, *8th Internat. Cong. Appl. Chem.*, **10** (1912), 335-341; *Chem.-Ztg.*, **36** (1912), 1305; Gurwitsch, *Z. Kolloide*, **11**, 17; *Petroleum*, **8**, 65-8; *Chem. Zentr.*, **83**, II (1912), 1792.

<sup>2</sup> For interesting data on variations and irregularities in the iodine numbers of certain oils, see Jenkins, *J. Soc. Chem. Ind.*, **16** (1897), 193-4; Archbutt, *Ibid.*, **6** (1886), 312; Ballantyne, *Ibid.*, **10** (1891), 32; Lewkowitsch, "Chem. Techn. and Anal. of Fats, etc.," 5th Ed., Vol. I, pp. 484-5.

<sup>3</sup> *Chem.-Ztg.*, **30** (1906), 932-3.

seven hours, the insoluble precipitate being thrown down and determined in the usual way. The results are shown in Table III and are plotted in Fig. II.

TABLE III VARIATION IN CARBONIZATION (PERCENTAGES) WITH TIME OF HEATING TO 250°

Carbonization (Hrs.)	1	2	3	4	5	6	7
Oil No. 1.....	0.03	0.10	0.14	0.34	0.51	0.83	1.26
Oil No. 2.....	0.04	0.10	0.17	0.37	0.54	0.92	1.25
Oil No. 3.....	0.04	0.16	0.30	0.60	1.02	1.37	2.01

The time was counted from the moment the heating current was turned on. About half an hour was required to heat the bath to 250°, but long before this temperature was reached, oxidation began.

All the oils gave practically the same results on heating for one hour, but by the end of two hours Oil 3 already showed a decided deviation from the other two. This deviation became increasingly greater as the period of heating was lengthened, while Oils 2 and 3 kept close together throughout. The ordinary physical and chemical tests gave no indication that the oils would behave so differently on heating. As Kantorowicz says, "the slight differences in the asphalt content of cylinder oils in contrast with the great differences in practice, would make it appear advisable to test oils quantitatively as to their ability to form new asphalt under definite conditions."<sup>1</sup>

The curves show that the conditions obtaining at elevated temperatures effect a grouping of the oils different from that due to oxidation at ordinary temperatures in sunlight, if we consider only the gains in weight and in acidity. The carbonization values of the oxidized oils will be discussed further on.

It is important, from the standpoint of routine laboratory testing, to learn whether or not two oils that yield nearly the same percentages of carbonized matter when heated for 2 or 3 hrs. remain equally close together if heated for a longer time. Eight oils of well known brands were heated for 2<sup>1</sup>/<sub>2</sub>, 3<sup>1</sup>/<sub>2</sub> and 4<sup>1</sup>/<sub>2</sub> hrs. and the insoluble matter was determined as usual. A and C were light and heavy grades of

TABLE IV—CARBONIZATION OF EIGHT SPECIAL OILS HEATED TO 250° FOR DIFFERENT PERIODS OF TIME

Oil	Flash point	Fire point	Percentage carbonization when heated for		
			2 <sup>1</sup> / <sub>2</sub> hrs.	3 <sup>1</sup> / <sub>2</sub> hrs.	4 <sup>1</sup> / <sub>2</sub> hrs.
A.....	190°	245°	0.08	0.23	0.48
B.....	225°	250°	0.04	0.14	0.36
C.....	235°	280°	0.02	0.05	0.03
D.....	230°	265°	Trace	Trace	1.86
E.....	145°	200°	0.40	0.98	2.12
F.....	165°	200°	0.47	1.00	2.12
G.....	185°	230°	0.35	0.62	1.90
H.....	160°	190°	0.70	1.38	2.45

the same brand. B and D were light and heavy grades of a second brand. E, F and H were from the same company, while G was a fourth brand. The data obtained are given in Table IV and are plotted in Fig. III.

The data confirm the results found for Oils 1 to 3, and do not call for any special comment. In saying this it must be understood that the amount of carbonized matter formed by heating to 250° for only one hour is disregarded.

#### EFFECT OF DIFFERENT TEMPERATURES UPON THE CARBONIZATION VALUE

Just as the carbonization value depends upon the length of time the oil is heated, so also it must vary with the temperature. In order to determine the magnitude of the changes, a series of tests was made at temperatures varying from 230° to 275°. The data are given in Table V and are plotted in Fig. IV.

TABLE V—INFLUENCE OF TEMPERATURE UPON THE CARBONIZATION VALUE

Sample	Carbonization value when heated to			
	230°	240°	250°	265°
No. 1.....	0.10	0.11	0.14	0.72
No. 2.....	0.07	0.09	0.17	0.84
No. 3.....	0.13	0.16	0.30	1.03

The time of heating, in each series, was 3 hrs. The curves are of the same general form as those showing the effect of lengthening the period of heating, although

in this series of determinations no two of them lie close together at the highest temperatures.

The eight oils, A to H, which were tested as a further check upon the influence of the time of heating, were carbonized for 2<sup>1</sup>/<sub>2</sub> hrs. at each of three temperatures. Table VI gives the data obtained. The corresponding curves are shown in Fig. V. It is interesting to see

TABLE VI—CARBONIZATION OF EIGHT SPECIAL OILS HEATED TO DIFFERENT TEMPERATURES

Temp.	A	B	C	D	E	F	G	H
250°.....	0.08	0.04	0.02	Traces	0.40	0.47	0.35	0.70
260°.....	0.43	0.40	0.11	Traces	1.11	1.22	0.77	1.33
270°.....	1.18	0.81	0.45	0.31	2.02	2.51	1.68	2.54

that Oil D, which gave only traces of carbonized matter even when heated for 4<sup>1</sup>/<sub>2</sub> hrs. at 250°, and which in this series of tests did not carbonize to any extent at 260°, shows a sudden increase in insoluble matter at 270°. The curves of the other oils are of the expected form. They are a further justification of the conclusion already drawn, that the greater the carbonization value is at 250°, the more rapidly does it increase when the oil is heated to a higher temperature.

#### GENERAL CONSIDERATIONS

Experience has shown that, while it is easy to obtain concordant results in determining the carbonization values of "good" oils, it is an entirely different matter when the percentage of precipitate is in the neighborhood of one per cent or more. It is believed that this is not due to unequal heating of the flasks in different positions in the bath, and it is certainly not due to differences in the thickness of the flasks. The most reasonable explanation appears to be that occasional particles of foreign matter, such as metal or rust, act catalytically, giving the portion of oil in which they happen to be a start over the others.

An interesting case bearing upon this came to light in testing a sample in which there were numerous black particles. The bottle was left undisturbed for 24 hrs. to allow these to settle and the oil was then tested. The value found was 0.91. A few weeks later, the bottle having been untouched meanwhile, the carbonization value was 0.55, a figure that agreed closely with the value for other samples of the same brand. This experience emphasizes the need of taking every precaution in sampling, as well as in testing the oil. In this connection may be mentioned the work of Schlüter,<sup>1</sup> who found that in most of the cylinder deposits examined by him, the trouble did not lie in the quality of the oil used, but was caused by sand and other foreign matter accidentally introduced or carelessly left in the engine cylinders, etc.

It may be well to repeat, parenthetically, the statement that there is no direct connection between the loss by evaporation when an oil is heated and the percentage of carbonized matter formed at the same time.<sup>2</sup> Because this statement has been questioned, though not in print, it may be well to give the following data showing that this is true not only for the same, but also for different oils.

<sup>1</sup> Chem.-Ztg., **37** (1913), 221-3.

<sup>2</sup> Bureau of Standards, *Technology Papers* **4** (1911, 12), THIS JOURNAL, **3** (1911), 815.

<sup>1</sup> Chem.-Ztg., **37** (1913), 1594-5.



TABLE VII—SHOWING INDEPENDENCE OF CARBONIZATION VALUE AND EVAPORATION LOSS ON HEATING TO 250°

	Oil No. 1		No. 2		No. 3	
Evaporation in 3 hrs., per cent.	12.3	19.4	19.6	23.0	21.0	22.5
Carbonization, carbonization, per cent., . . . .	0.16	0.11	0.17	0.18	0.30	0.40
Evaporation in 5 hrs., per cent.	21.3	24.3	27.2	30.7	26.8	29.5
Carbonization, carbonization, per cent.	0.51	0.51	0.56	0.58	1.09	1.08

It so happens that these oils have carbonization values that increase as the flash and fire points become lower. That this is accidental can be seen from Table VIII, which gives data on a few oils recently tested, and shows that the flash and fire points are also independent of the carbonization value:

TABLE VIII—SHOWING INDEPENDENCE OF CARBONIZATION VALUE AND THE FLASH AND FIRE POINTS

Flash point, ° C. . . . .	125°	165°	190°	195°	195°	200°	200°	205°	225°
Fire point, ° C. . . . .	205°	205°	220°	235°	235°	240°	250°	245°	265°
Carbonization per cent.	0.42	0.41	0.06	0.29	0.16	1.05	0.22	0.39	0.06

## SUMMARY

In order to determine whether there is any close connection between the rate of oxidation of automobile oils when exposed to sunlight and air, and their carbonization values when heated to comparatively high temperatures, a study was made of three brands of oil. The gains in weight and in acidity and the increase in the carbonization value were determined at frequent short intervals. In the first two of these tests, two of the oils showed nearly identical gains, the third differing quite noticeably. In the carbonization test the values for the three oils were quite far apart.

Of minor importance were determinations of the demulsibility, the iodine number and the Maumené number. The effect of oxidation was to increase the tendency to form emulsions with water. The iodine numbers were lower and Maumené numbers higher for the oxidized than for the original oils.

The changes in the carbonization values caused by heating the above three oils and eight others to 250° for different lengths of time were then studied, as well as the changes caused by heating to different temperatures for three hours. It was found that in both cases the greater the carbonization value at first, the more rapidly did it increase as the temperature was raised or the time of heating extended. In other words, an oil which has a low carbonization value if heated to 250° for two or three hours and an oil showing a somewhat higher value under the same conditions will be farther and farther apart as the conditions become more strenuous. The carbonization value of an oil is coming to be recognized as a valuable criterion in routine testing, and methods for its determination are finding their way into text-books, as well as into the journals. Most of these methods prescribe heating the oil for many hours, but it seems, from the work described above, that this is unnecessary. In most cases heating for 2½ hrs. is sufficient and has the advantage of permitting two runs in a working day, with the necessary interval of an hour or more for the bath to cool. Of far greater and, indeed, of vital importance, is the exercise of extreme care in taking and preserving samples, as well as in testing them.

A study of all the data obtained shows that there is no direct proportionality, but only a rough parallelism, between the results of the different tests described above.

In conclusion, it is shown that the carbonization value is independent of the flash and fire points, and of the evaporation loss on heating.

BUREAU OF STANDARDS, WASHINGTON

KJELDAHL MODIFICATION FOR DETERMINATION OF NITROGEN IN NITRO SUBSTITUTION COMPOUNDS<sup>1</sup>

By W. C. COPE

Received March 21, 1916

The Bureau of Mines has received numerous requests for information in regard to the determination of nitrogen in nitro substitution compounds, and as many requests have come from skilled chemists it appears that the information usually at hand lacks details which are necessary to obtain trustworthy results.

The following method has been evolved from the work of Kjeldahl,<sup>2</sup> Gunning,<sup>3</sup> Jodlbauer,<sup>4</sup> and others, and has given good results on a variety of compounds over a period of a year and half, and since several members of the laboratory force have obtained consistent results it is believed that the method is suitable for general analytical work.

## METHOD

Weigh accurately about 0.5000 g. of the nitro substitution compound and place in a 500 cc. long-necked Kjeldahl digestion flask. Then add 30 cc. sulfuric acid (96 per cent), containing 2 g. of salicylic acid, and dissolve the nitro compound by rotating the flask, or by heating over a steam bath if necessary. After cooling, add 2 g. of zinc dust in small portions at a time, continually rotating the flask and cooling to prevent heating above room temperature. After all the zinc has been added, rotate the flask at 10 or 15 min. intervals for about 1½ to 2 hrs. and then let stand over night at room temperature.

Heat the flask very gently over a small flame until evolution of fumes has ceased (requiring usually 1½ to 2 hrs.), then bring to boiling and continue boiling for 1½ to 2 hrs.; cool slightly and add 1 g. of yellow mercuric oxide (HgO) and boil 1 to 1½ hrs. longer. Now add, after cooling, 7.5 g. potassium sulfate (K<sub>2</sub>SO<sub>4</sub>) and 10 cc. more sulfuric acid, and boil 1½ to 2 hrs. longer. If the solution is clear and practically colorless the digestion is complete; if not, add 1 g. more potassium sulfate and boil for ½ to 1 hr. longer.

Cool the liquid in the flask and add 250 cc. distilled water to dissolve cake formed; then add 25 cc. potassium sulfide solution (80 g. per liter of distilled water), 1 g. granulated zinc, and 85 to 90 cc. sodium hydroxide solution (750 g. per liter of distilled water), completing the determination as is usual for all modifications of the method.

<sup>1</sup> Published by permission of the Director, U. S. Bureau of Mines.

<sup>2</sup> J. Kjeldahl, *Z. anal. Chem.*, Bd. 22 (1883), 366.

<sup>3</sup> Gunning, *Ibid.*, Bd. 28 (1889), 188.

<sup>4</sup> M. Jodlbauer, *Chem. Zentr.* (3 F.), Bd. 17, 433.

PERCENTAGE NITROGEN FOUND BY AUTHOR'S METHOD

<b>MONO-NITROTOLUENE</b>				
Sample (a).....	10.06	10.11	10.20	10.06
(b) Redistilled.....	10.16	10.19	10.14	10.20
(c) Crude.....	9.62	9.61	.....	.....
<b>LIQUID DI-NITROTOLUENE</b>				
Sample (a).....	15.01	15.14	15.01	15.13
Sample (b).....	15.39	15.40	15.45	.....
<b>TRI-NITROTOLUENE</b>				
Sample 1859.....	18.36	.....	.....	.....
Sample 1860.....	18.30	18.38	.....	.....
Sample L.....	18.41	18.48	.....	.....
Sample D.....	18.24	18.28	.....	.....
<b>LIQUID TRI-NITROTOLUENE</b> .....	16.18	16.19	16.21	16.18
<b>DI-NITROBENZENE</b>				
.....	16.18	16.23	16.29	.....
(p).....	16.39	16.39	.....	.....
(m).....	16.51	16.58	16.63	.....
<b>NITROPHENOL</b>				
(o).....	9.90	9.84	9.92	10.12
(p).....	9.99	10.08	.....	.....
<b>META-NITROANILINE</b> .....	.....	20.04	19.92	.....
<b>MONO-NITRONAPHTHALENE</b> .....	.....	8.08	8.04	.....
<b>DI-NITRONAPHTHALENE (1 : 3)</b> .....	.....	11.89	12.09	.....
<b>DI-NITROANILINE (1 : 2 : 4)</b> .....	22.63	22.70	22.73	22.78
<b>PICRIC ACID</b> .....	18.36	18.31	18.28	18.24

A blank determination should be used to correct for nitrogen in reagents and it is also advisable to check the method with pure picric acid or some other pure nitro substitution compound.

Cooling during the addition of the zinc for reduction and the long standing before heating the acid solution have been found necessary in order to prevent low results, and for the same reason the heating should be gradual.

The results given in the table indicate that the method is especially applicable for picric acid and the nitrotoluenes but is not good for tetra-nitroaniline, tetra-nitromethylaniline, and di-nitronaphthalene.

BUREAU OF MINES, WASHINGTON

## THE DECOMPOSITION OF HYDROCARBONS AND THE INFLUENCE OF HYDROGEN IN CARBURETED WATER GAS MANUFACTURE<sup>1</sup>

By M. C. WHITAKER AND E. H. LESLIE

Received June 1, 1916

Although numerous studies of hydrocarbon decomposition have been made, no one, nor all combined, comprise a complete investigation. On account of the variety of the materials which have been worked upon, the extreme complexity of the changes which take place in any case, the differences in the types of apparatus used, and the apparent inclination of many writers to allow the reader to do the greater part of the interpretation of the results, which in many cases is well-nigh impossible, the presentation of this material in condensed form is obviously impossible in a brief article, so that only those points will be mentioned that are necessary for the interpretation of the results reported herein. In this connection the work previously done may be classified as follows:

(1)—The primary decomposition of high molecular weight paraffin and naphthene hydrocarbons.

(2)—The various ideas in regard to the mode of reaction of the products of the primary decomposition.

(3)—The thermal reactions of the simpler com-

<sup>1</sup> Authors' abstract of dissertation offered in part fulfillment of the requirements for the Ph.D. degree at Columbia University, 1916. The dissertation itself contains detailed information as to the results of the various researches bearing on the subject and discusses fully their relations to each other.

pounds such as methane, ethane, ethylene, and similar hydrocarbons.

(4)—Aromatic hydrocarbons.

(5)—The influence of hydrogen on the above reactions.

(6)—The transfer of heat in gas machines.

In the work bearing on the primary decomposition of paraffin hydrocarbons of high molecular weight the greater portion of the experimental evidence points to a splitting of the carbon chain with formation of olefin and paraffin. Conditions determine where the rupture takes place—low temperature and high pressure tending to favor the splitting near the middle of the chain while at lower pressures and higher temperatures the breaking off of low molecular weight hydrocarbons, such as methane, ethane, and ethylene, but particularly methane and ethane, becomes the important reaction. The members of the paraffin series down to butane in all probability follow some such mode of reaction as this.

The first problem to be considered in the study of the secondary reactions, then, is the fate of the high molecular weight olefins which arise. It seems that the chief reaction undergone by these high molecular weight olefins is a splitting into lower molecular weight olefins. A decomposition into methane and compounds with two double bonds or one triple bond also takes place. The intramolecular change of olefins into cycloparaffins is possible, but from the evidence available it is difficult to state what proportion of the naphthene formation must be ascribed to this reaction. Hydrogenation of olefins takes place to some extent. Polymerization of olefins to naphthenes occurs, also polymerization of the high molecular weight unsaturated compounds to tarry compounds.

The reactions which form the lower molecular weight hydrocarbons are in general more rapid in their progress than the reactions of decomposition of these lower hydrocarbons. Methane, in particular, is stable under the action of heat at those temperatures which are used in the various apparatus used in the manufacture of gas. Thus those reactions which result in the formation of methane and ethylene reach a condition nearly corresponding to equilibrium proportions on account of the slow decomposition of ethylene and methane; but the system as a whole cannot be regarded as in equilibrium. In considering the discussion of the reactions of the individual hydrocarbons the effect of the presence of the end products of a particular reaction must always be kept in mind. Also the changing concentration conditions as the gas volume increases with the progress of the changes involved must not be forgotten.

**METHANE**—The study of the influence of heat at various temperatures on the hydrocarbon methane has usually been made with the idea in mind of finding the equilibrium proportions of methane and hydrogen in the system carbon-hydrogen-methane. The equilibrium proportions are never even approximated in experiments made after the manner of those discussed in the latter part of this paper, nor under the conditions maintained in the technical production of coal, oil, and water gas. The preservation of methane is desired in all these cases, for its decomposition into carbon and hydrogen means loss of valuable carbon from the gas and the production of gases high in hydrogen which are unsuited for distribution. Hence the studies of the methane equilibrium are of interest only in so far as they indicate the tendency of methane to decompose under certain temperature conditions.

In summing up the work on methane it can be said that the chief reaction is the decomposition into carbon and hydrogen,  $\text{CH}_4 \longrightarrow \text{C} + 2\text{H}_2$ , and that the reaction,  $2\text{CH}_4 \longrightarrow \text{C}_2\text{H}_2 + 3\text{H}_2$ , takes place to a small extent only.



Under the conditions of operation of a carbureted water gas set very little methane is decomposed. Though the temperatures of the retort walls in coal gas manufacture are much higher than those in the interior of the carburetor and superheater of a water gas set it is obvious that the gases do not reach the temperature of the refractory surfaces.

**ETHANE.** The work done on ethane seems to indicate that this gas is an intermediate product, passing to acetylene or ethylene.

**ETHYLENE.**—It appears that at temperatures up to 700° C. the dissociation of ethylene into acetylene and hydrogen is the most important reaction. Condensation also takes place to some extent. At higher temperatures the rate of the decomposition into carbon and methane is much greater, so this reaction plays an important part.

**ACETYLENE.** At temperatures up to 700° C. acetylene undergoes a fairly rapid polymerization to benzene and its homologs. Decomposition into carbon and hydrogen is second in importance at these temperatures while hydrogenation to ethylene, ethane and methane is least important. At slightly higher temperatures the importance of polymerization diminishes, while the decomposition into the elements and hydrogenation both increase. At still higher temperatures, such as 1100° C., the decomposition into carbon and hydrogen is the important reaction.

No discussion of the thermal reactions of propylene, diolefins, substituted acetylenes, propane, and high molecular weight tarry compounds was found.

The high molecular weight tarry compounds have been built up by synthetic reactions. For this reason they are no doubt fairly stable compounds as regards the influence of heat, and in general pass on through the apparatus and into the tar. Haber has suggested that the chief reaction of the compounds of this class is a splitting off of hydrogen.

**AROMATIC HYDROCARBONS.**—Though the formation of aromatic hydrocarbons takes place only to a limited extent in water gas machines, and to but a slightly greater extent in coal gas retorts, the tars from these processes are important sources of the commercial aromatic hydrocarbons.

The aromatic hydrocarbons contribute greatly to the illuminating value of a gas as determined in an open flame burner. However, should the calorific standard for gas service in the course of time become general, the presence of the aromatic compounds in the gas would be of far less importance to the gas manufacturer than it is to-day. These compounds contribute less to the heating value of the gas than the compounds from which they are formed. Their chief importance would then lie in the better prices obtainable for the tars containing them.

The reactions responsible for the aromatic hydrocarbons formed in the thermal decomposition of hydrocarbon oils are:

- (1)—Condensation of acetylenes,
- (2)—Dehydrogenation of naphthenes,
- (3)—Decomposition of complex compounds already containing the phenyl radical.

Toluene, xylene, ethyl benzene, and similar compounds are formed first and most easily. These by further change give rise to benzene, naphthalene, and anthracene. With high molecular weight monocyclic compounds the general course of the reaction is toward compounds of lower molecular weight. In general, monocyclic compounds tend to go to polycyclic compounds.

#### INFLUENCE OF HYDROGEN ON THE THERMAL DECOMPOSITION OF HYDROCARBONS

The idea that an oil cracked in hydrogen or in inert gases gave more valuable products has been prevalent for many years.

In so far as the work of the several investigators allows us to draw conclusions it seems that hydrogenation of hydrocarbons such as ethylene and acetylene does take place, but that it is never a reaction of great importance. The fact, however, that hydrogen is actually absorbed when oils are cracked in

atmospheres of the gas shows that hydrogenation of some sort takes place. Possibly the higher unsaturated hydrocarbons are hydrogenated more readily.

#### TRANSFER OF HEAT IN GAS MACHINES

The most striking feature of the literature which records the result of investigations of hydrocarbon decompositions is the great difference between the results of various investigators who report that they have worked at the same temperature, and, in general, under the same conditions. Irregularities too great to be attributed to the personal equation are of frequent occurrence, and these are in need of explanation.

It is often suggested that these differences are caused by the catalytic effects of the materials of construction, but without doubt the catalytic effect of contact surfaces has been overestimated. It is well known from general experience that these surfaces are always covered with a layer of hard carbon as a result of the decomposition of hydrocarbons. Hence the gases do not come into contact with an active material, but rather into contact with a dense layer of carbon deposit which is inactive as a catalyzer. Unquestionably many of the effects ascribed to *catalysis* are in reality due to the effectiveness of the heating by conduction and convection close to the surfaces of the refractory materials.

The importance of *radiant energy* in causing hydrocarbon reactions has also been over-emphasized most consistently in the literature of the gas industry. Too little attention has been paid to the *methods of making temperature measurements*, and also to the interpretation of temperature measurements made in certain ways. Thus it is obvious that a metal pyrod with a metal casing or a protective sheath of solid material such as quartz will absorb many times as much radiant energy as the gases in the heated space, and therefore indicate a temperature considerably above the true temperature of the gases. Also the conduction of heat along the metal pyrod casing is more effective than the conduction through a gas. In general, then, it would seem that the radiation does not play as important a part in transferring heat as has been taken for granted. Conduction and convection are largely responsible for this transfer, and they are helped to some extent by the dissociation reactions of the hydrocarbons. Catalysis has been greatly overrated. The influence on reaction rates supposedly brought about in this fashion can be better understood if the true mechanism of heat transfer is kept in mind. The different results of experimental investigations are also often easily understood if the shape and size of the apparatus is considered in its relation to heat transfer.

The recent work<sup>1</sup> done in connection with the commercial production of gasoline and aromatic hydrocarbons has been the most exhaustive ever attempted. However, these investigations have not been carried out from the standpoint of gas production.

It is scarcely necessary to discuss the importance of a thorough understanding of the possibilities of controlling the decomposition of hydrocarbons for the obtaining of the particular products desired.

The most profitable utilization of an oil is of extreme importance to the water gas manufacturer. The control of the cracking of an oil is the thing of first importance to the manufacturer of oil gas in any of the various processes. The effect of the presence of hydrogen on the products derived from an oil is of great importance to the water gas manufacturer and the all-oil-water-gas maker.

Also it is generally recognized that the carboniza-

<sup>1</sup> Whitaker and associates at Columbia University, and Rittman and associates, U. S. Bureau of Mines.

tion of coal and the combustion of coal and oil are allied problems, and that the results of a study of hydrocarbon decomposition are of direct application in these connections. The effect of the introduction of hydrogen into the carbonizing retorts can also be seen by a study of the data given in this paper.

Brief mention of the experimental work of a few investigators will serve to show the importance of the subject of hydrocarbon decomposition to the users of coal for gas making purposes or as a fuel.

Jones and Wheeler<sup>1</sup> have extracted solid paraffins from several British coals by means of pyridine and chloroform. Pictet and Ramseyer<sup>2</sup> have isolated hexahydrofluorene from that portion of a gas coal which was soluble in benzene. The same hydrocarbon has been identified by them in the tar obtained by the low temperature distillation of coal in a vacuum. Burgess and Wheeler<sup>3</sup> found that paraffin hydrocarbons were predominant among the primary decomposition products of coal. The same authors<sup>4</sup> found a considerable evolution of higher olefins when coal was distilled at low temperatures. E. Bornstein<sup>5</sup> discussed the decomposition of coal at temperatures up to 450° C. He found that the gaseous products consisted of 5 to 14 per cent heavy hydrocarbons, 55 to 76 per cent paraffins, and 5 to 16 per cent hydrogen. Jones and Wheeler<sup>6</sup> distilled coals at temperatures up to 450° C. in a vacuum of 5 to 40 mm. of mercury, and obtained 6.5 per cent by weight of a tar which consisted of 25 per cent olefin hydrocarbons and an equal proportion of naphthenes and paraffins. Pictet and Bouvier<sup>7</sup> have conducted experiments similar to those of Jones and Wheeler, and found a large proportion of hydroaromatic or naphthene hydrocarbons in the tars. Porter and Taylor<sup>8</sup> found that the primary decomposition products of coal were complex easily liquefiable paraffins, hydrocarbons with smaller amounts of water, carbon dioxide and hydrogen.

One of the points in the propaganda of the various recently developed low temperature carbonization schemes has been the high percentage of light hydrocarbon oils which might be recovered from the tars and used for motor spirit. The gases obtained in these processes are also rich in higher hydrocarbons. Lewes<sup>9</sup> gives the analysis of a gas which contained 10.1 per cent of the members of the paraffin series higher than methane.

White, Park, and Dunkerley<sup>10</sup> found the ethane content of the gases of low temperature carbonization processes to run from 11 per cent to 47 per cent. Parr and Olin<sup>11</sup> have found that approximately 10 per cent of a light hydrocarbon oil was obtained from tars made in low temperature carbonization experiments between 400 and 500° C.

#### PURPOSE OF THE PRESENT INVESTIGATION

It is the purpose of this investigation in general to show what results may be expected in the decomposition of an oil if temperature, rate of oil feed, and concentration of hydrogen are taken into account and carefully controlled. More specifically it is proposed to show:

1—The variation of the composition of the gases made from oil at constant temperature and pressure with changing rate of oil feed.

2—The effect of changing the temperature on the composition of gases made from oil alone at constant oil feed and constant pressure.

3—The variation in the volume of the various gases obtained per cc. of oil fed at constant temperature and pressure but with changing rate of oil feed.

4—The effect of changing temperature on the volume of various gases obtained per cc. of oil at constant rate of oil feed and constant pressure.

5—The extent to which hydrogen is absorbed at any particular concentration, and the effect of changing the concentration.

6—The influence of hydrogen of certain concentration on the number of cc. of the various gaseous components obtained per cc. of oil, and the relations between this and change of concentration of hydrogen, change of temperature, and change of oil rate.

7—The results of a study of the mean molecular weight of the olefins in the gases at certain temperature, and the influence of the presence of hydrogen and change of the rate of oil feed in this connection.

8—The proportion of aromatic hydrocarbons present in the gases and the influence of the presence of hydrogen and changing oil rate in this connection.

9—The percentages of tar formed at different temperatures and rates of oil feed, and the influence of hydrogen on tar formation.

#### PLAN AND SCOPE OF THE EXPERIMENTAL WORK

The plan of the present work was to study the decomposition of paraffin hydrocarbons under atmospheric pressure, and at a number of temperatures and varying oil rate; and under identical conditions, to investigate the effect of the presence of hydrogen of different concentrations on the decompositions of the paraffin hydrocarbons.

The working temperatures were 621° C., 723° C. and 825° C. The temperatures used in the commercial manufacture of water gas lie between 700 and 775° C., and are thus well within the temperature range of these experiments. At 927° C. two runs were made, but the separation of carbon in the furnace tube was so rapid it was impossible to keep the tube open while the adjustments for the hydrogen-oil gas runs were made. The hydrogen concentrations are discussed under the caption "The Hydrogen Concentration."

The method used was to adjust the furnace to the proper conditions and to run the oil in at the desired rate. The oil gas so made was collected. Without stopping the flow of oil, hydrogen was then admitted in proper concentration and the gas produced by cracking the oil in hydrogen collected in a second gasometer.

<sup>1</sup> *J. Chem. Soc.*, **103** (1913), 1704.

<sup>2</sup> *Ber.*, **44** (1911), 2486; *Gas World*, **56** (1911), 131.

<sup>3</sup> *J. Chem. Soc.*, **99** (1911), 649-667.

<sup>4</sup> *Ibid.*, **105** (1914), 131-140.

<sup>5</sup> *Z. angew. Chem.*, **17** (1904), 1520.

<sup>6</sup> *J. Chem. Soc.*, **105** (1914), 140-151, 2562-2565.

<sup>7</sup> *Compt. rend.*, **157** (1913), 779.

<sup>8</sup> *Proc. Am. Gas Inst.*, **1914**, 234-288.

<sup>9</sup> "Carbonization of Coal," p. 164.

<sup>10</sup> *Proc. Michigan Gas Assoc.*, **17** (1908), 83.

<sup>11</sup> "Coking of Coal at Low Temperatures," *Bull.* **79**, Univ. of Illinois Experiment Station, 1915.



The two gases were thus made under identical furnace conditions. The volumes of the tars formed were measured.

The straight oil gas runs made in connection with the research were a repetition of those previously made by Dr. C. M. Alexander (private communication), the results of whose work have not as yet been published. The experimental data of the work recorded here are in excellent agreement with those of Dr. Alexander.

#### APPARATUS AND PROCEDURE

THE FURNACE used in these experiments was designed and built by Whitaker and Alexander, and used by them in a study of the time factor in the making of oil gas.<sup>1</sup> For a detailed description of the furnace construction reference must be had to the original article.

The heating was effected by the passage of an alternating current from a single phase, 60 cycle, 50 kilowatt generator. The current passed through the carbon resistor tube of the furnace was readily controlled by means of a field rheostat. Thus a very accurate regulation of the temperature was obtained. Fluctuation limits of 1 or 2° C. were attained by careful operation.

A constant feed of oil was readily maintained by means of the static head and feed regulator. The oil was vaporized in the prevaporizer. The hydrogen gas was introduced into the sight feed just below the oil feed valve where it mixed with the oil vapors coming from the prevaporizer, and passed on into the heated tube of the furnace. The gas velocity in the tube could be calculated from its dimensions (1 in. I. D. × 38.5 in. long), and the total gas rate.

Certain features of the design of the furnace, other than the fact that it was susceptible to exact control, which made it particularly suitable for the study of the reactions of hydrocarbon decomposition both from a theoretical standpoint and from an operating standpoint, must be pointed out. It is evident that the gas in passing through the carbon tube is subjected to a set of conditions similar to those existent in the interior of the water gas carburetor and superheater; *i. e.*, heated by carbon-coated passageway walls. Though the size of the furnace tube is less than the voids in the checker bricking in the gas machine, the general conditions are the same.

Both from a theoretical standpoint and practical standpoint the study of the kinetics of these various hydrocarbon reactions is greatly to be desired as has been pointed out elsewhere in this paper. The furnace was designed in such manner as to avoid catalytic effects as completely as possible, and is therefore suitable for a study of the kinetics of such relations.

**MEASUREMENT OF GAS VOLUMES**—The gases from the runs were collected in 5-cu. ft. holders. The dimensions of these tanks were carefully taken and the volumes computed. A stationary millimeter scale was attached to the tank standard, and a rigid pointer to the movable bell so that readings could be taken at given time intervals, and the gas rates and total volumes calculated.

A wet meter was used for the measurement of the

volume and rate of the hydrogen flowing into the machine. This meter was filled with kerosene to avoid the aspiration of water vapor into the furnace. The oil level in the meter was adjusted carefully at all times, and the meter kept perfectly level. The meter was calibrated against the tank which was used for the collection of the mixed oil hydrogen gases. The hydrogen was allowed to flow into the meter, through the furnace heated to 800° C. and into the receiving tank, readings being taken, at short intervals, of the meter rate and tank rate. This calibration was checked from time to time and found not to vary appreciably.

**THE PYROD AND ITS CALIBRATION**—The temperature measurements were made with a base metal thermocouple attached to a direct reading Wilson-Maeulen instrument. The thermocouple was calibrated by checking it against the boiling point of sulfur (444.6° C.) and against the melting point of sodium chloride (800° C.). The readings of the thermocouple at these points were 425 and 775° C., respectively. Using these data a curve was plotted from which the true temperature could be read corresponding to temperatures as read from the instrument.

The temperatures at which runs were made were those observed when the pyrod projected through a suitable stuffing box into the lowest of the sight tubes. A hole the size of the end of the pyrod was made in the carbon resistor tube, and the pyrod allowed to project about 1/2 in. into the interior of the resistor tube. The upper portion of the resistor tube was about 25–30° C. colder than that part of the tube where the pyrod was inserted, due, no doubt, to the cooling effect of the incoming gases and to the endothermic reactions taking place in that part of the tube.

**THE HYDROGEN** used in these experiments was a very high-grade electrolytic gas. Analyses showed it to contain 99.9 to 100.0 per cent hydrogen.

**THE OIL** used was a water-white oil (0.8000 sp. gr.), which boiled between 150 and 265° C.

**METHOD OF OPERATION**—The furnace was first heated up well and the jacket cooling water adjusted properly. When a constant temperature 10 to 30° above the temperature at which the run was to be made had been established, the oil valve was opened and adjusted to the proper rate of flow. The temperature of the furnace was then regulated till it remained constant at the desired point. The gases formed during this preliminary operation were run to a waste tank, and the tar discarded.

As soon as all the proper operating conditions had been established, the gases were run into a gas holder and readings of the oil rate, gas rate and temperature were taken at suitable short intervals. The pressure was always atmospheric. The temperature was noted at frequent intervals, and any necessary regulations of the field rheostat were made.

When the proper amount of gas had been collected, the gas was again sent to the waste gas holder, and the tar removed from the tar drip. Hydrogen was then admitted, flowing from the compressed hydrogen tank through the reducing valve and meter and into the admixer at the top of the furnace tube. When the

<sup>1</sup> THIS JOURNAL, 7 (1915), 484–495.

rate of the hydrogen flow and all the other conditions had been adjusted, the gas passing was run into a second gas holder. Readings of the oil rate, hydrogen rate, total gas rate, and temperature were again taken at suitable intervals.

Thus an oil gas and a hydrogen-oil gas were made under exactly the same operating conditions. These gases were analyzed 18 to 20 hrs. after making. Analyses were made on low temperature, fast oil rate, gases at periods of one to two hours after making to see if the standing for longer periods caused any difference in the analytical results. No appreciable difference was found.

#### RELATION BETWEEN THE EXPERIMENTAL APPARATUS AND THE COMMERCIAL APPLIANCE

Frequently it is a difficult matter to reproduce experimental results in technical operation. It is with the object of calling attention to salient points which must be kept in mind in order that the results recorded here may be reproduced in a commercial appliance that the paragraphs which follow are written.

Experimental results show that the time factor is all important. But it must be remembered that the furnace tube used in these experiments was only 30 in. long, whereas the column of checkerbrick in the carbureter and superheater of the water gas set is many times that length. Hence even though a pyrometer may record the same temperature in this furnace and in the checkerbrick of a commercial machine it would not be expected that the gases would have the same composition.

The diameter of the furnace tube used in these experiments was 1 in. This, however, was soon carbonized so that it was more nearly  $\frac{3}{4}$  in. The interstices in the checkering of commercial machines are of greater sectional area than a circle of  $\frac{3}{4}$  in. diameter. Hence the opportunity for heat transfer in the checkerbrick is not so good as in this experimental furnace and it would be expected that a longer column of checkerbrick than was necessary in this furnace would be necessary to produce a given result, all conditions being the same.

The actual time of contact of the gases with heated surfaces is all important, but it is a very complicated function of the rate of oil feed, the amount of blue gas introduced, the volume of the checkerbrick voids, and the temperature.

Commercial operation demands that an apparatus have a reasonable gas making capacity, and for this reason the higher oil rates are most desirable. On the other hand, with high oil rates more tar is always produced than at low oil rates, which makes the use of the oil uneconomical. It is not improbable that the best results could be obtained by designing one apparatus with proper control suitable to the production of certain gaseous products, and a second apparatus which would use the tar from this first machine as the carbureting oil. An examination of the tars formed in the experimental apparatus at medium to high rates of oil feed have led to the belief that this would not be impracticable.

Methods of temperature measurement must not be neglected. Above all it must not be assumed that a particular temperature as measured will produce the same results in two different machines.

The experiments recorded in this paper merely show the possibilities in the decomposition of a hydrocarbon oil. To obtain particular results on a commercial scale would necessitate a great deal of thought as to the proper design for the machine to be used.

#### THE HYDROGEN CONCENTRATION

The introduction of hydrogen in certain concentration is a question which must be regarded from at least two standpoints; *i. e.*, the experimental and the technical or operating standpoints.

In the manufacture of carbureted water gas the oil is cracked in an atmosphere of carbon monoxide and hydrogen. The final gas is roughly  $\frac{1}{3}$  hydrocarbons,  $\frac{1}{3}$  hydrogen and  $\frac{1}{3}$  carbon monoxide. The hydrogen and hydrocarbons are thus present in the approximate ratio of 1 volume to 1 volume in the final gas. In addition there is present 1 volume of carbon monoxide, the influence of which has never been exactly determined by a comprehensive study.

In these experiments it was thought desirable to study two concentrations of hydrogen:

- (1)—1 Volume Hydrogen : 2 Volumes (oil gas + tar gas)
- (2)—2 Volumes Hydrogen : 1 Volume (oil gas + tar gas)

The experimental difficulties were such, however, that the introduction of hydrogen in exactly these proportions was practically impossible, for, with change in temperature, the amount of gas produced from a given quantity of oil at a particular rate changes, while with change in oil rate at constant temperature the amount of gas produced from a given quantity of oil changes. Also the gas formed from a certain amount of oil is different when the oil is decomposed alone or in an atmosphere of hydrogen. Furthermore, the concentration of hydrogen in the upper part of the furnace tube is much greater at any time than it is in the lower part of the tube, for as the oil vapors pass through the tube a progressive decomposition takes place with formation of a greater volume of hydrocarbon gases.

It would therefore be necessary to make several trial runs at each oil rate at each temperature to determine the proper hydrogen rate. When it is considered that each run of that sort would consume several hours' time, the impracticability of this method of procedure is apparent. Furthermore, in commercial operation the two factors which would be susceptible to control would be the rate of introduction of blue gas and the rate of introduction of the oil. So it was decided to base the hydrogen concentration arbitrarily on the oil rate. After some trials at 723° C., the following equations relating to the hydrogen rate and the oil rate were decided upon:

- (1) To approximate 1 Vol. Hydrogen : 2 Vols. (oil gas + tar gas)  

$$\frac{\text{Oil rate in cc. per minute}}{5.28} = \left\{ \begin{array}{l} \text{Hydrogen rate in liters} \\ \text{per minute.} \end{array} \right.$$
- (2) To approximate 2 Vols. Hydrogen : 1 Vol. (oil gas + tar gas)  

$$\frac{\text{Oil rate in cc. per minute}}{1.76} = \left\{ \begin{array}{l} \text{Hydrogen rate in liters} \\ \text{per minute.} \end{array} \right.$$



One set of runs only was made at 621° C. and this at the supposed ratio 1 Vol. Hydrogen : 2 Vols. Gas. The lower curve in Fig. 5 is plotted from the equation given under (1) above. The points represent the actual hydrogen rates and show how closely it was possible to adjust the hydrogen rate to that desired as calculated from the oil rate.

The upper curve in Fig. 5 shows the actual ratio of hydrogen to (oil gas + tar gas). In the furnace the hydrocarbons which compose the tar are of course gaseous and the volume of this gas is calculated on the assumption that the specific gravities of the liquid tars are 0.80 (water = 1) and that the mean molecular weight of the hydrocarbons contained in the tar is 142; *i. e.*, that the average molecule contains 10 carbon atoms.

The straight line at ordinate 0.5 is the theoretical curve for the value of the ratio of hydrogen to (oil gas + tar gas). It can be seen that the value of this ratio more nearly approximated unity than it did 0.5 in these runs.

A second series of runs with the value 2 for the ratio of hydrogen to (oil gas + tar gas), was not made for the reason that from the results at higher temperatures it was judged that the chief effect of more hydrogen at 621° C. would be to blow the vapors through the heated tube faster without producing extensive chemical change. Since there was approximately 1 volume of hydrogen to 1 volume of (oil gas + tar gas), in these runs at 621° C., that is, practically the relations existent in the carbureter and superheater of the water gas set, it was thought that this series of runs sufficed to show the possibilities of a temperature in the neighborhood of 621° C. for purposes of gas manufacture.

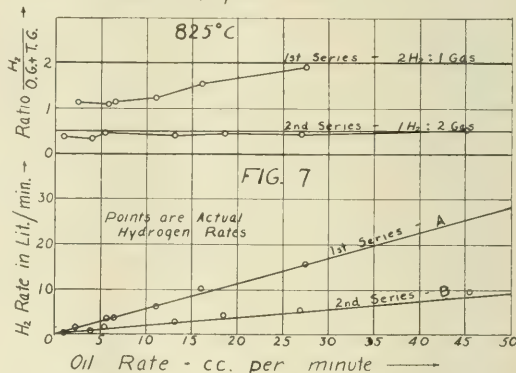
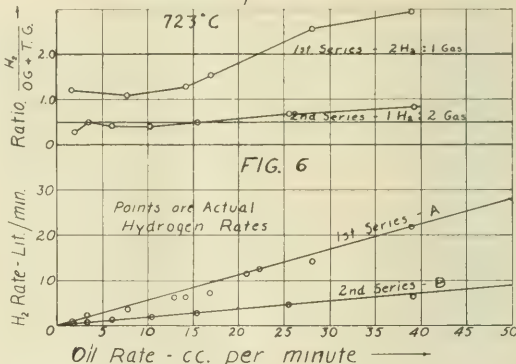
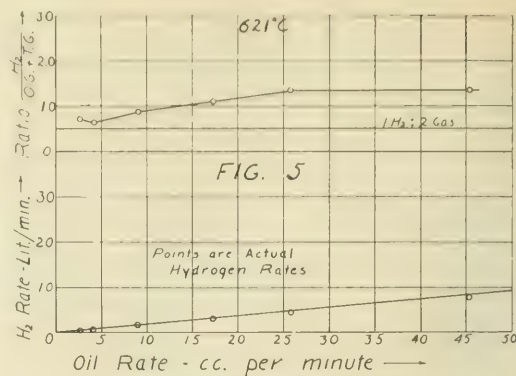
Curves A in Figs. 6 and 7 are the plots of the equation under (2) given above at 723 and 825° C., respectively, and curves B in Figs. 6 and 7 the plots of equation (1) above at those temperatures. The points show how closely the actual hydrogen rates approximated those calculated by these equations.

The lower curve in the upper half of Fig. 6 shows that the actual value of the ratio of hydrogen to (oil gas + tar gas) approximated very closely to the value 0.5 drawn horizontally on the ordinate 0.5. The upper curve in the upper half of Fig. 6 shows that at low oil rates too little hydrogen was introduced to make the value of the ratio hydrogen to (oil gas + tar gas) equal to 2.0, and at high oil rates that too much hydrogen was introduced.

The actual values of the ratio hydrogen to (oil gas + tar gas) in the second series of runs at 825° C. are shown in the curves in the upper half of Fig. 7. In the first series of runs the value of the ratio lies between 1.0 and 2.0, whereas it was intended that it should be 2.0. In the second series the desired value 0.5 is very closely approximated at all oil rates.

#### ANALYTICAL PROCEDURE FOR GASES

During the early part of the work recorded in this paper the method of gas analysis was the ordinary one employing the Hempel burette with single and double pipettes for the absorbing reagents. Thus



EFFECT OF DIFFERENT HYDROGEN CONCENTRATIONS WITH VARYING OIL RATES AT THREE TEMPERATURES  
Data for Curves Calculated on Two Bases

the carbon dioxide was removed by a solution of 1 part of KOH in 2 parts of water, the unsaturated and aromatic hydrocarbons by fuming sulfuric acid with 20 per cent free SO<sub>3</sub>, the oxygen by alkaline pyrogallol made up in accordance with Hempel's directions,<sup>1</sup> and the carbon monoxide absorption in ammoniacal cuprous chloride prepared according to Winkler.<sup>2</sup> A portion of the residual gas was then mixed with oxygen, and slowly passed back and forth over palladium black in a glass tube immersed in water at a temperature of about 85-90° C. After thus removing the hydrogen the gas mixture was exploded

<sup>1</sup> Dennis' "Gas Analysis," p. 160.

<sup>2</sup> C. Winkler, "Handbook Tech. Gas Anal.," translated by Lunge, p. 73.

over mercury, and the resulting carbon dioxide absorbed in potassium hydroxide.

"CARBON MONOXIDE"—As the work progressed it became evident that this method could be improved upon. It was difficult to understand where the carbon monoxide, varying from 0.2 per cent to 1.9 per cent as shown by the cuprous chloride absorption, could have come from. The furnace was tight, and in any case there would be a slight positive pressure outwards, so that the ingress of air in more than small amounts was out of the question. The only other possible source of oxygen was the water in the oil used. However, had the carbon monoxide arisen thus from the reaction of steam on the carbon it would have been present in larger amount at 800° C. than at 600° C. Also there should have been some relation between the percentages of carbon monoxide and carbon dioxide. But carbon monoxide, as indicated by the absorption in ammoniacal cuprous chloride, was present in largest amount at 600° C., in smaller amounts at 700° C., and least of all at 800° C. Also it was noticed that at any particular temperature the carbon monoxide tended to be highest when the oil rate was highest. However, there was no regular variation of this sort as there was with the other components of the gaseous mixtures formed. Hence it appeared that the "carbon monoxide" formation as shown by the absorption in the ammoniacal cuprous chloride was not solely a function of the furnace conditions.

F. C. Phillips<sup>1</sup> stated that cuprous chloride solution dissolved the higher members of the paraffin series to some extent. G. A. Burrell and F. M. Seibert<sup>2</sup> found that cuprous chloride solution caused a contraction of 0.5 to 0.6 per cent in Pittsburgh natural gas. They have also shown that a two-minute contact of cuprous chloride solution with pure ethane caused a loss in volume of 0.6 per cent and that in five minutes the contraction was 1.4 per cent.

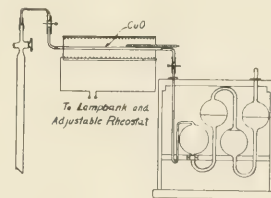
Our experimental work showed that those gases which would be expected to have the largest proportion of high molecular weight hydrocarbons, *i. e.*, those gases made at low temperatures and fast rates of oil feed, were also those which showed the highest percentages of "carbon monoxide." It appeared certain, therefore, that the contractions found on passing the gases into the ammoniacal cuprous chloride solution were in reality largely due to absorption of paraffin hydrocarbons such as ethane, propane, and butane rather than to carbon monoxide.

The use of ammoniacal cuprous chloride was therefore abandoned, and the carbon monoxide and hydrogen determined by Jaeger's fractional combustion method somewhat as described by H. C. Porter and G. B. Taylor.<sup>3</sup> In place of the vertical Nichrome resistance heater with the inverted U-tube to hold the copper oxide, a horizontal heater with a straight copper oxide tube was used as shown in the accompanying drawing. The difference in temperature between the bottom

and top of the vertical heater was great enough so that when the oxide was at the proper temperature in one part of the containing tube, it was either too hot or too cold in other parts of the tube. With the horizontal heater and the copper oxide tube running concentrically through it no such difficulty was experienced, nor did the water formed during the combustion cause any trouble.

The fractional combustion of gaseous mixtures over copper oxide consumes a little more time with gases which are low in hydrogen and high in paraffins than does the method in which the cuprous chloride pipettes and the palladium black are used. However, as the average time for carefully made analyses is not over 45 mins., this cannot be considered as a serious disadvantage.

It was found that a temperature of 275–280° C. burned the carbon monoxide and hydrogen to carbon dioxide and water without affecting the methane and other paraffin hydrocarbons present. After passing the gases over the oxide till no further contraction took place, they were allowed to cool to room temperature, and the volume read. The contraction at this



Apparatus for Fractional Combustion of CO and H<sub>2</sub> over CuO

point equals the per cent of hydrogen in the gas. The carbon dioxide was then absorbed in potassium hydroxide. This contraction is equal to the per cent of carbon monoxide in the gas. The importance of allowing the gases to reach room temperature can readily be seen. Otherwise the contact with the potassium hydroxide will cause a contraction due to the lowering of the temperature of the gas.

The method of burning the carbon monoxide and hydrogen over copper oxide has recently been discussed by G. A. Burrell and G. G. Oberfell.<sup>1</sup> Their experiences with this method were apparently similar to ours.

In the case of many of the gases obtained in the experimental work, the gas residue after the fractional combustion was small enough so that the whole of it could be mixed with oxygen and exploded over mercury. Here again the method of burning over copper oxide presents a distinct advantage over the methods first mentioned above, for in the combustion with palladium black it is necessary to mix the gas with oxygen previous to the fractional combustion of the hydrogen. Thus a much smaller proportion of the gas could be put through the partial combustion and explosion analysis, in consequence of which accuracy was sacrificed. Accuracy at this point was particularly desired in order to calculate the mean molecular weight of the paraffins.

<sup>1</sup> THIS JOURNAL, 6 (1916), 228–231.

<sup>1</sup> "Oil and Gas Levels," W. Va. Geol. Survey, 1A (1904), 552.

<sup>2</sup> "The Sampling and Analysis of Mine and Natural Gases," Bur. of Mines, Bull. 42, 46–77.

<sup>3</sup> Proc. Am. Gas Inst., 9 (1914), 255; THIS JOURNAL, 6 (1914), 845–8.



**AROMATIC HYDROCARBONS** At the outset of this work the desirability of determining the extent of the formation of hydrocarbons of the benzene series was evident. A careful survey of the literature, however, showed that none of the methods proposed had given satisfaction in the hands of all who had worked with them. It was not until the work recorded here was nearing completion that the method proposed by Hulett and developed by the Bureau of Mines<sup>1</sup> came to our attention. This method was used for the determination of the aromatics in the gases from one series of runs at 825° C.

The procedure in brief is to evacuate the apparatus with a good pump, after which the gas is admitted and the temperature and barometer readings noted. The gas is allowed to stand for some time (in these determinations 2 to 3 hrs.), in order that the phosphorus pentoxide may remove the water vapor completely, and then immersed for 10 to 15 mins. in a mush of carbon dioxide snow in acetone contained in a Dewar flask. At the end of this time the gases are sucked off by means of the pump. The bulbs are then removed from the cold bath and allowed to come to room temperature. The temperature is noted and the partial pressure of the volatilized aromatics is read on the short arm manometer. From this data the volumetric percentage of these components in the gas can be calculated. A rotary oil pump which gave a vacuum of less than 1 mm. of mercury, and that in less than a minute, was used in these experiments.

#### MEAN MOLECULAR WEIGHT OF THE OLEFINS

When the analysis and the specific gravity of a gas are known the mean molecular weight of the heavy hydrocarbons of the gas can be calculated. When, in addition to the percentages of carbon dioxide, heavy hydrocarbons, oxygen, carbon monoxide, hydrogen, methane, ethane, and nitrogen, the percentage of aromatics is known, the mean molecular weight of the olefins and acetylenes can be calculated.

In determining the specific gravity the temperature of the gas and the barometer reading should be taken, and the gas should be thoroughly shaken with water in order to saturate it with water vapor at the temperature of the room before introducing it into the specific gravity apparatus. Time should be allowed for the subsidence of any mist formed during the agitation with water.

The method used for the determination of the specific gravity was the so-called effusion method and the apparatus was similar to that described by Panertzt.<sup>2</sup> The orifice was made by pricking a piece of thin platinum foil with a needle, and then beating the foil with a small leather mallet till the tiny hole was visible only when held up to a strong light. This foil was mounted on the end of a short brass tube fitting with a carefully turned brass screw cap luted in with litharge and glycerol cement.

Certain errors are inherent in the experimental methods used. In the first place it is well known that fuming sulfuric acid absorbs higher paraffins during

<sup>1</sup> G. A. Burrell, F. M. Seibert, and I. W. Robertson, "Analysis of Natural Gas and Illuminating Gas by Fractional Distillation at Low Temperatures and Pressures," *Technical Paper*, **104**, 26-27.

<sup>2</sup> *J. für Gasbel.*, **48** (1903), 901.

the determination of the heavy hydrocarbons.<sup>1</sup> It was thought that the use of bromine water might obviate this difficulty, but analyses on 621° C. gases made by both methods checked to within 0.1 per cent showing that the two reagents were having similar effects. F. C. Phillips<sup>2</sup> says that bromine water absorbs the higher paraffins.

Disagreement between analyses made by the use of bromine water and by fuming sulfuric acid may be occasioned by the fact that bromine water does not brominate benzene. In the analyses made in these experiments there is little doubt but that the benzene would have been completely scrubbed down on account of the time and shaking necessary to obtain complete reaction between the olefins and the bromine solution. Also the proportion of benzene present in a 621° C. gas made at atmospheric pressure is not large.

The absorption of higher paraffins by the fuming sulfuric acid can be avoided in large part by the use of small portions of the reagent in an apparatus of the type described by G. B. Taylor.<sup>3</sup> It was thought, however, that the time required for analyses made in this way would be too great.

Another error inherent in the method of determining the mean molecular weight of the olefins lies in the fact that the method for aromatics does not differentiate between benzene, toluene, or xylene. An average molecular weight must be assumed here which evidently is not absolutely correct. In the calculations all aromatics have been regarded as if they were benzene, since it was believed that this hydrocarbon comprised the greatest portion of the aromatics present in the gas.

A further error lies in the fact that the paraffins were all assumed to be methane and ethane. Higher homologs of this series are without doubt present as has been shown by Burrell, Seibert, and Robertson in their analyses of carbureted water gas and coal gas by the method of fractional distillation at low temperatures.<sup>4</sup>

A certain proportion of naphthenes or polymethylenes are also no doubt present among the products of the pyrogenic decomposition of the hydrocarbons of kerosene. To what extent these are affected by the fuming sulfuric acid, and to what extent they are carried through the analysis and credited to the paraffins cannot be stated. Data on the exact behavior of the cyclobutanes, cyclopentanes, and cyclohexanes when treated with fuming sulfuric acid have not been found, if, in fact, such information is at all available.

In addition to the errors already mentioned is the experimental error in the determination of the specific gravity by the effusion method. Check determinations were always made on the time of flow, and it was found possible to get agreements to within less than 0.5 per cent.

The following analyses are cited to compare the results obtained by the usual procedure with Hempel burette and pipettes with those obtained by the use of the various modifications discussed above. These

<sup>1</sup> R. P. Anderson and J. C. Engelder, *THIS JOURNAL*, **6** (1914), 989-92; R. A. Worstell, J. A. C. S., **21** (1899), 245; Orndorff and Young, *Am. Chem. J.*, **15** (1893), 249; Burrell and Seibert, "Sampling and Analysis of Mine and Natural Gas," *Bur. of Mines, Bull.* **42** (1913), 45-47.

<sup>2</sup> "Oil and Gas Levels," *W. Va. Geol. Survey*, **1A** (1904), 522.

<sup>3</sup> *THIS JOURNAL*, **6** (1914), 845.

<sup>4</sup> Bureau of Mines, *Tech. Paper*, **104** (1915); *THIS JOURNAL*, **7** (1915), 17-21.

will be designated for the sake of brevity as the "Standard" method and the "CuO" method, respectively.

METHOD	GAS No. 24		GAS No. 24		GAS No. 25	
	Standard	CuO	Standard	CuO	Standard	CuO
Carbon dioxide.....	0.3	0.0	0.1	0.1	0.0	0.0
Heavy hydrocarbons...	48.1	48.2	47.9	49.8	49.3	50.8
Oxygen.....	0.5	0.5	0.5	0.5	0.5	0.4
Carbon monoxide.....	1.2	0.2	0.2	0.9	0.1	0.1
Hydrogen.....	11.9	11.9	12.1	9.3	9.2	10.4
Paraffins.....	37.3	37.6	37.7	38.1	37.0	37.2
Total.....	99.3	98.4	98.5	98.7	97.6	99.7

#### THE GAS RATE

The gas rates for three temperatures are plotted against the oil rates in Fig. 8. At 621° C. the gas rate increases with the oil rate up to an oil rate of 20 cc. per minute, but the introduction of more oil per minute causes no further increase in the gas rate. Apparently with a heated tube of the dimensions used here only a certain quantity of oil can be affected in a given time by heat at a temperature of 621° C. A similar limitation would be expected in a commercial machine operating at this temperature. At 723° C. the gas rate is greater with greater oil rate at all oil rates studied. Judging from the shape of the curve and from the analogy of the 621° C. curve it is apparent that an increase in oil rate above 45 to 50 cc. per minute would produce no increase in the gas rate. At 825° C. the gas rate increases with increase in oil rate as can be

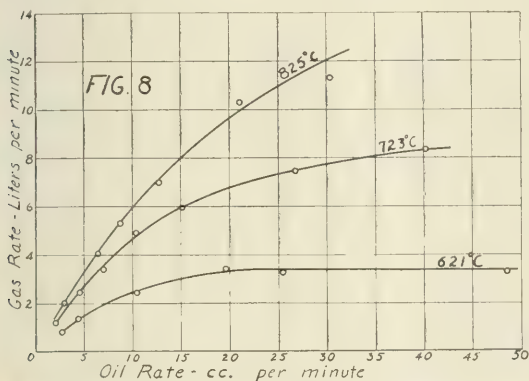


FIG. 8  
EFFECT OF VARYING GAS RATE WITH VARIOUS OIL RATES AT THREE TEMPERATURES

seen, and at the oil rates studied there is no apparent tendency for a rate to be reached beyond which there is no further increase. Obviously, however, such a point would be reached.

In comparing the gas rate curves it is interesting to note that at low oil rates the change in temperature from 621 to 723° C. has a much greater effect than the change from 723 to 825° C. At low oil rates a temperature of 723° C. is sufficient to gasify permanently the greatest portion of the oil. The slightly greater production of gas at 825° C. is largely due to the decomposition of methane into carbon and hydrogen.

As the oil rate increases, a temperature of 723° C. becomes less and less effective for the purpose of permanently gasifying the oil; 825° C. is much more effective, as can be seen from the increasing divergence between the curves.

(To be concluded in our next issue)

DEPARTMENT OF CHEMICAL ENGINEERING  
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#### THE EFFECTS OF MOISTURE INTRODUCED INTO THE DIGESTER IN THE COOKING OF SODA PULP

By S. D. WELLS

Received May 1, 1916

The work of the Forest Products Laboratory in studying the influences of the various cooking conditions in the manufacture of soda pulp from aspen indicated that in varying any one of the four variables, steam pressure, initial concentration, amount of caustic soda used per unit of wood, or duration of cooking and maintaining the other conditions constant, the amount of bleaching powder necessary to bleach the pulp to a standard white was constant for any given yield of pulp. Twenty-four semi-commercial cooks were made in studying these four variables and the yields of pulp obtained plotted

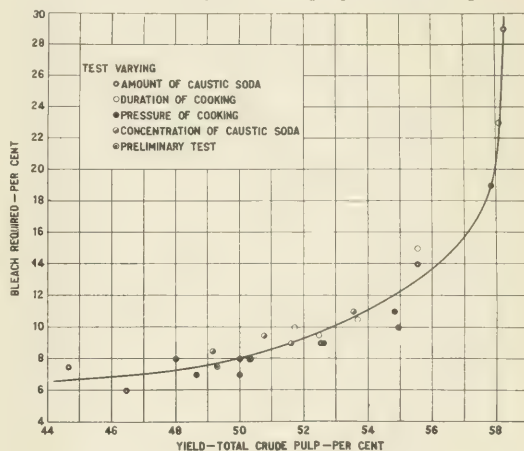


FIG. I

against the bleach consumption are shown in Fig. I obtained from *Bulletin 80* of the United States Department of Agriculture.

This curve apparently indicates that any reduction in the consumption of bleach made by altering any of the four variables mentioned cannot be brought about without lowering the yield. All the cooks made in the series, however, were in a digester of only 70 gals. capacity and the condensation during the cook was about six times as great as in a commercial sized apparatus of 3 1/2 cords capacity. A series was, therefore, run where all the conditions were maintained constant except condensation and this factor was varied by using a combination of direct steam and indirect heating by means of a jacket in the lower portion of the digester.

The results obtained developed the remarkable fact that on increasing the amount of condensation the yields of pulp were increased and at the same time the quality of the pulp was slightly improved and the bleach consumption necessary to obtain a standard white was decreased. The curves in Fig. II show the relation of bleach consumption and yield to the amount of condensation during the cook, using the following conditions:

Concentration of NaOH.....	90 g. per l.
NaOH per 100 lbs. chips.....	25 lbs.
Maximum steam pressure.....	120 lbs. per sq. in.
Duration at maximum pressure.....	4 hrs.
Time necessary to reach maximum pressure...	1 hr.



The yield of pulp was increased from 43.5 per cent to 47.1 per cent of the weight of wood used or an increase in the output of pulp from the same quantity of wood using the same quantity of cooking chemical and fuel of over 8 per cent while the quality of the pulp was improved and the bleach consumption lowered from 13 to 11 lbs. of bleaching powder per 100 lbs. of pulp.

In seeking an explanation of this phenomenon, it was necessary to study the conditions in the digester during the cook. The consumption of caustic soda as shown in Fig. III was very rapid during the first hour and a half but constantly decreased in rate and after the second hour had reached a point where only one-fourth of the original caustic was present as such.

The condensation of steam increased very rapidly during the first hour due to the fact that the contents

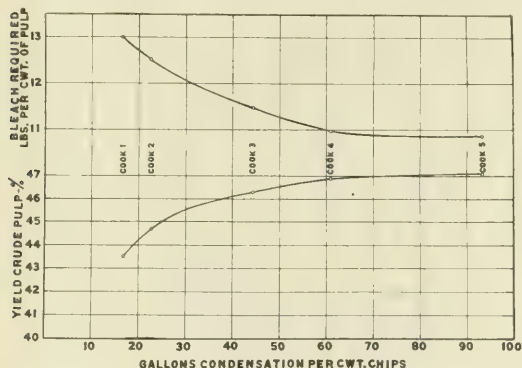


FIG. II

of the digester were being rapidly heated to the maximum temperature maintained during the succeeding 4 hrs. and the shell and lagging must necessarily be brought to the same temperature. After the first hour the rate was greatly decreased since only enough was needed to counteract the loss of heat through the shell and in steam vented to relieve gases and maintain circulation. The condensation for the five cooks of the series is shown graphically in Fig. IV.

During the 4 hrs. of maximum pressure, therefore, the concentrations of caustic (grams NaOH per liter) in the liquors were as follows:

No.	1	2	3	4	5
End of 1st hour.....	35	32	23	19	14
End of 5th hour.....	6	7	5	4	3

With the increased condensation, the pulp reduced from the outer portion of the chips was in all probability surrounded by much more dilute liquor and was therefore, attacked much less, due to the very low adsorptive power of cellulose at those concentrations, as shown by the work of Leighton.<sup>1</sup>

Aspen wood, on the other hand, has been found in our investigations to be capable of adsorbing at 100° C. as much as 20 per cent of its weight from solutions of 60 g. per liter and at the increased temperature of the cook the amount adsorbed would be considerably greater. Our experiments with aspen chips have shown that during the first hour of the cook the

caustic soda solution has penetrated the chips at nearly the original concentration. It is evident that the uncooked inner portions of the chips are capable of adsorbing sufficient caustic soda for their reduction, but on the conversion of this material to pulp the adsorptive power is so reduced that the remaining caustic soda passes back to the liquor. The increased volume due to condensation also more effectually removes the products of reduction from the wood and decreases the contamination of the pulp therefrom.

It is evident, then, that while the power of the caustic soda to reduce the ligno-cellulose is not diminished, the attack on the pulp is considerably decreased

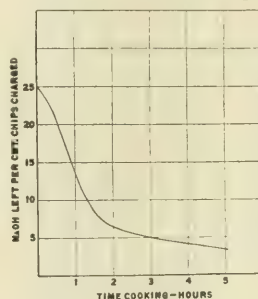


FIG. III

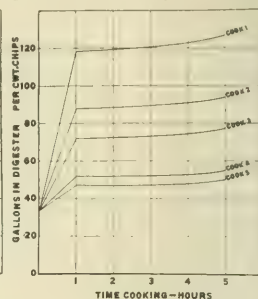


FIG. IV

and the coloring of the pulp by the products of reduction is much less, thereby decreasing the bleach necessary to obtain a standard white. While no tests on a commercial scale have yet been tried, it seems probable that the same advantages would be gained. The equivalent of the added condensation could be obtained by injecting hot water with the steam supplied, by which means perfect control could be comparatively simple. The only disadvantage would be the increased volume of the black liquor that would have to be handled in the recovery of the soda. With multiple-effect evaporators, however, the excess water could be evaporated with very small increase in the fuel consumption and the increased production of pulp would be attained at extremely small cost.

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## THE RATE OF AMMONIA DISTILLATION FROM WATER

By F. W. BRUCKMILLER  
Received March 21, 1916

In the determination of the ammoniacal nitrogen in waters, the quantity of ammonia obtained depends upon a number of factors, principal among which are the volume of the distillate saved and the rate at which the ammonia comes over.

Regarding this matter, Wanklyn,<sup>1</sup> the originator of the method, says:

"The recommendation has been given to nesslerize only the first 50 cc. of the free ammonia and to throw away the next 150 cc. Formerly, it was our custom to nesslerize all four 50 cc. tubes for the free ammonia, but that was a useless trouble, inasmuch as the first 50 cc. invariably contained three-fourths of the total free ammonia. The rule is, therefore, to nesslerize the first 50 cc. of the distillate and then add one-third. In the instance of the albuminoid ammonia, it is necessary to nesslerize each separate 50 cc. of the distillate (4) and to add the amounts together in order to arrive at the total albuminoid ammonia."

<sup>1</sup> "Water Analysis," 1896, 43.

<sup>1</sup> "The Absorption of Caustic Soda by Cellulose," *J. Phys. Chem.*, 20, 32-50.

Mason,<sup>1</sup> who has used the method extensively, says:

"Usually four 50 cc. tubes will be sufficient to carry off all the free ammonia, but it is the author's custom always to distil off six."

Stocks<sup>2</sup> says:

"In distilling ordinary waters, practically the whole of the ammonia will be present in the first 100 cc., but with sewage the whole of the ammonia may not have been obtained even after distilling 300 cc., and it is, therefore, necessary in such cases to allow the retort to cool, make up to the original volume with distilled water and continue the distillation. The albuminoid ammonia being formed by the oxidation of organic matter, is not evolved so quickly as the free ammonia, hence it may be necessary to distil several 100 cc. portions before it ceases to be evolved."

The "Standard Methods of Water Analysis" (1912 Edition) recommends the collection of three 50 cc. portions for the free ammonia, and at least four, preferably five, 50 cc. portions for albuminoid ammonia. This procedure we were using until we saw an advance copy of the Revision of the Standard Methods and learned that it was recommending a collection of four 50 cc. Nessler tubes in the distillation of the free ammonia and five in the case of albuminoid ammonia.

In order to see what influence this procedure would have upon the results obtained, we began a statistical study of the quantities of ammonia collected in each tube, as well as the total amount obtained. The results of this study are herein contained.

We have been following the revised procedure for several months, using it on all classes of water. The total number of waters examined was between 500 and 1000; the free ammonia varied from 0.002 to 2.0 parts per million, and the albuminoid from 0.002 to 4.0 parts per million. A compilation of all of the results, with regard to amount and rate of ammonia distilling, were made and the conclusions obtained were as follows:

#### NITROGEN AS FREE AMMONIA

Fourth tube averages 5 per cent of the total nitrogen

76 per cent of the waters had 100 per cent nitrogen in 3 tubes  
24 per cent of the waters had 95 per cent nitrogen in 3 tubes  
50 per cent of the waters had 50 to 55 per cent nitrogen in 1 tube  
20 per cent of the waters had 65 to 70 per cent nitrogen in 1 tube

#### NITROGEN AS ALBUMINOID AMMONIA

Fifth tube averages 5 per cent of the total nitrogen

75 per cent of the waters had 100 per cent nitrogen in 4 tubes  
25 per cent of the waters had 95 per cent nitrogen in 4 tubes  
30 per cent of the waters had 50 to 60 per cent nitrogen in 1 tube  
20 per cent of the waters had 60 to 70 per cent nitrogen in 1 tube

Those waters which had 5 per cent of the nitrogen in the last tube had a total nitrogen content of either free or albuminoid ammonia of 1 part per million or more of nitrogen. Since ordinary waters, unless grossly polluted, contain less than 1 part per million of nitrogen as free or albuminoid ammonia, we can conclude that the collection of a 4th tube in the free ammonia determination and a 5th in the albuminoid determination, under ordinary circumstances, is not necessary. Furthermore, the average per cent found in the last tube, including all samples, was only 5 per cent of the total nitrogen.

In a water containing less than 1 part per million the maximum error is 0.05 part per million; in a water containing 4 parts per million, the maximum amount found in the waters examined, the error is 0.2 part per million. In other words, in one case we would report 0.95 p. p. m. of nitrogen and in the other 3.80.

However, since the ammonia determination is not quantitative and the results are used only as a basis for determining pollution, the question to be decided is whether or not the error of 0.05 p. p. m. in one case and 0.2 in the other, would cause a change of judgment. We think it would not; that is, a water with 1 p. p. m. of nitrogen would stand as good a chance of being condemned as one containing 0.95 p. p. m., if all the other evidences pointed towards contamination.

We conclude, therefore, from this study that in order to get sufficient information upon which to base a judgment, it is not necessary, in ordinary routine water analysis, to nesslerize more than three 50 cc. portions for free ammonia, and four 50 cc. portions for albuminoid ammonia.

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### A MODIFICATION OF MCCRUDDEN'S METHOD FOR CALCIUM, FOR THE ESTIMATION OF CALCIUM AND STRONTIUM IN THE PRESENCE OF PHOSPHORIC ACID AND A SMALL AMOUNT OF IRON

By O. B. WINTER

Received August 11, 1915

The method<sup>1</sup> generally used in estimating calcium and strontium, when both are present in a solution, is to precipitate them as the oxalates, burn to the oxides, change to the nitrates, separate the calcium nitrate from the strontium nitrate by means of absolute alcohol and ether, and then determine each element separately. If phosphoric acid and iron are also present in the solution with the calcium and strontium salts, the separation becomes much more difficult since calcium, strontium and iron phosphates are quite insoluble in a neutral or alkaline solution. In this latter case, the phosphoric acid and iron are removed before the calcium and strontium are determined. This is usually accomplished by precipitating<sup>2</sup> the phosphoric acid as ferric phosphate, and the excess of iron as ferric subacetate. However, when there is a large amount of phosphoric acid in the solution, this method becomes tedious because the bulky, gelatinous precipitate formed causes the solution to filter very slowly, and it is almost impossible to wash all of the calcium and strontium salts out of this precipitate.

McCrudden has worked out a method<sup>3</sup> for "The quantitative separation of calcium and magnesium in the presence of phosphoric acid and small amounts of iron, devised especially for the analysis of foods, urine and feces." By this method the calcium is precipitated very slowly as the oxalate in a boiling solution containing a small amount of free hydrochloric acid. This gives rise to a condition in which the calcium oxalate comes down very coarsely crystalline, and apparently no soluble salts are carried down by occlusion.

The above method was found accurate for the estimation of calcium, but in trying it out on a strontium

<sup>1</sup> Examination of Water, 1913, 62.

<sup>2</sup> Water Analysis, 1912, 11.

<sup>3</sup> U. S. Dept. of Agr., Bureau of Chemistry, Bull. 162, 44.

<sup>4</sup> Perkin, "Methods in Qual. Analysis," p. 76.

<sup>5</sup> J. Biol. Chem. 7 (1909), 83.



solution, it was found that this element ran low, but not so much so as was anticipated. Several different modifications of the method were attempted and finally it was shown that the addition of alcohol would insure complete precipitation of strontium. The following method gave very satisfactory results for both calcium and strontium:

Dilute the solution containing the calcium or strontium, or both, to about 200 cc. and add a few drops of alizarine and ammonium hydroxide until the solution is faintly alkaline. Now add dilute hydrochloric acid until the solution is faintly acid. To this solution add 10 cc. of 0.5 *N* hydrochloric acid and 10 cc. of 2.5 per cent of oxalic acid, and boil until the precipitate becomes coarsely granular. Then add saturated ammonium oxalate solution, a few drops at a time with constant stirring, until about twice the amount necessary to precipitate all the calcium and strontium has been added. Cool the solution, add, with constant stirring, 8 cc. of 20 per cent sodium acetate solution and about 15 cc. of 95 per cent alcohol, and allow to stand from 4 to 18 hours. Filter and wash the precipitate a few times with 1 per cent ammonium oxalate solution, several times with 1 per cent ammonium oxalate solution containing 20 per cent by volume of alcohol, and finally a few times with water containing 20 per cent by volume of alcohol. Now burn the precipitate to the oxide, dissolve in nitric acid, dehydrate, separate the calcium nitrate<sup>1</sup> from the strontium nitrate by means of absolute alcohol and ether, and determine each element in the usual manner.

That this modified method gives quantitative results is shown in the accompanying table, which gives the analyses of synthetic solutions of calcium and strontium salts. The amount of calcium in these solutions was determined by precipitating it as the oxalate<sup>2</sup> in a neutral solution and then burning to the oxide, after first removing the phosphoric acid with ferric chloride<sup>3</sup> and the excess of iron as ferric subacetate. The strontium in the solutions was estimated as the sulfate<sup>4</sup> and calculated to the oxide.

P <sub>2</sub> O <sub>5</sub> + No. Fe <sub>2</sub> O <sub>3</sub>	RESULTS BY MODIFIED MCCRUDDEN METHOD			
	GRAM CALCIUM OXIDE (CaO)		GRAM STRONTIUM OXIDE (SrO)	
	Present	Found	Present	Found
1 Absent	....	....	0.0493	0.0494 0.0496 0.0498
2 Absent	....	....	0.1464	0.1460 0.1467 ....
3 Present	....	....	0.0991	0.0995 0.0994 ....
4 Present	0.0908	0.0907 0.0911	0.0732	0.0728 0.0730 ....
5 Absent	0.1004	0.0997 0.1003	0.0495	0.0490 ....
6 Present	0.0454	0.0450		

#### SUMMARY

I—McCrudden's method with the modifications given in this paper may be used for determining calcium or strontium.

II—This modified McCrudden method is accurate and convenient for determining calcium and strontium when both are present in a solution containing phosphoric acid and a small amount of iron.

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<sup>1</sup> U. S. Dept. of Agr., Bureau of Chemistry, *Bull.* 162, 44.

<sup>2</sup> Treadwell-Hall, "Analytical Chem.," "Quant. Analyses," 1st Ed., 2 (1909), 65.

<sup>3</sup> Perkin, "Methods in Qual. Analysis," p. 76.

<sup>4</sup> Treadwell-Hall, "Analytical Chem.," "Quant. Analyses," 1st Ed., 2 (1909), 66.

## BIOCHEMICAL CHANGES IN COTTONSEED IN STORAGE<sup>1</sup>

By J. B. RATHIER

Received March 25, 1916

The investigation here reported is an outgrowth of a study of the effect of storage on the vitality of cottonseed planned and conducted by the Department of Agronomy of the Arkansas Experiment Station. The field work gave opportunity to study changes in the seed with reference to the possible deterioration from the standpoint of the feeder of live stock and the manufacturer of cottonseed oil. With this in mind, samples of cottonseed collected in the work on the vitality of cottonseed were examined as described below.

No mention of the biochemical changes which take place in stored cottonseed has been found in the literature. It is common knowledge, however, that cottonseed will heat and deteriorate in storage under certain conditions. This heating is undesirable from the standpoint of the oil mill because it leads to the production of low-grade cottonseed oil, dark in color and high in free fatty acids. There is a larger loss in refining such oil, and as cottonseed oil is sold to the refiners on the basis of that factor, the oil mills constantly watch for heating in their storage bins, and move the heated seed out as rapidly as possible. *A priori*, then, cottonseed that has heated would be expected to be high in free fatty acids. The work of various investigators on the deterioration of corn (maize) in storage<sup>2</sup> indicates that cottonseed would probably increase also in total acidity under similar conditions.

#### EXPERIMENTAL

The field work of this investigation was conducted at Morrilton, Arkansas, during the seasons of 1914 and 1915, by Mr. M. S. Baker of the Department of Agronomy of this Experiment Station. Morrilton is in a typical cotton section of the state, and the soil selected was as nearly uniform as possible.

A five-bale lot of seed cotton, from native Mebane's Triumph seed, was harvested in mid-season, while dry, and stored the same day in an oil mill seed bin. After a storage period of 21 days it was ginned, and the seed (5000 lbs.) stored in a pile 12 ft. by 12 ft. by 6 ft. in an oil mill seed bin for a period of 77 days. Samples were taken immediately after harvest, when the seed was ginned, and whenever the temperature of the seed seemed to warrant it. In sampling the cottonseed a sampler was used which took the sample from top to bottom of the bin at the point desired. Four thermometers were placed in different parts of the bin and accurate records kept of the changes in temperature. The samples were forwarded to the laboratory in air-tight containers, and as soon as possible after their arrival a portion of each was ground for analysis. Moisture, fat, free fatty acids in fat, crude protein, albuminoids, and total acidity determinations were

<sup>1</sup> Full details of these and additional experiments will be published as a Bulletin of the Arkansas Experiment Station.

<sup>2</sup> See Black and Alsberg, *Bur. Plant Ind.*, U. S. Dept. Agr., *Bull.* 199; Besley and Baston, U. S. Dept. Agr., *Bull.* 102; and references there given.

made on each sample. For reasons to be discussed elsewhere, all analyses were begun immediately after grinding the seed. Whenever it was found necessary to repeat free fatty acid, albuminoid, or total acidity determinations, freshly ground portions of the seed were used. The method for the determination of total acidity was similar to that used by Besley and Baston.<sup>1</sup> The other methods were those of the Association of Official Agricultural Chemists<sup>2</sup> with such modifications as the work demanded. All results are the average of two or more concordant determinations.

#### CHANGES IN COTTONSEED IN STORAGE

Absolute uniformity in composition from sample to sample is not to be expected in work of this nature. Aside from any variation in the closeness of ginning of the seed, which would affect the composition more

moisture, during this time, provided that the seed cotton is harvested dry.

During the period of storage as cottonseed the seed heated, the maximum temperature developed being 109° F. Samples were taken in the heating portion of the seed, and at the same time in the unheated portion, in order to determine whether any changes observed were due to aging or to the heating. During this period the moisture dropped to 10.94 per cent, a total drop of 4.53 per cent from the original water content of the seed. There was a slight increase in the percentage of fat and protein, probably due to this loss of moisture. There appeared to be little or no tendency for the protein to hydrolyze in the heating seed during this time.

It is likely that there is little real difference between the crude protein and the albuminoids in the samples,

TABLE I—PERCENTAGE COMPOSITION OF COTTONSEED AT DIFFERENT TIMES DURING STORAGE

								TOTAL ACIDITY			
								As Cc. N			
DATE			TEMP. WHEN	MOISTURE	CRUDE	FREE FATTY ACIDS		Stearic	Alkali	CRUDE	ALBU-
SAMPLED	STORED AS	LAB. NO.	SAMPLED ° F.	Per cent	FAT Per cent	(As Stearic Acid) Per cent of Fat		Acid % of Fat	per Kg Seed	PROTEIN Per cent	MINOIDS Per cent
Sept. 30	Seed Cotton	2095	75	16.47	17.45	1.78		.....		20.09	19.92
Oct. 1	Seed Cotton	2096	63	16.49	19.24	1.17		.....		19.66	18.62
Oct. 4	Seed Cotton	2099	77	14.92	18.61	1.56		.....		19.77	18.75
Oct. 7	Seed Cotton	2100	75	14.97	18.19	1.55		.....		18.63	17.50
Oct. 16	Seed Cotton	2106	71	12.92	19.33	1.18		.....		18.50	18.50
Oct. 19	Seed Cotton	2107	74	13.11	19.32	2.83		.....		20.00	18.63
Oct. 22	Seed Cotton	2110	75	14.22	18.82	2.25		.....		19.79	19.87
Oct. 22	Cottonseed	2111	72	13.77	18.16	2.26		.....		19.28	19.13
Oct. 28	Cottonseed	2114	70	13.45	18.64	2.59		.....		18.78	18.33
Nov. 4	Cottonseed	2122	72	12.87	16.56	2.88	4.80	28		17.66	17.75
Nov. 10	Cottonseed	2123	80	12.72	18.34	1.94	4.02	26		19.44	19.06
Nov. 13	Cottonseed	2124	91	10.75	19.83	1.55	4.70	28		20.59	19.06
Nov. 16	Cottonseed	2126	99	13.35	18.54	2.53	4.60	31		19.02	18.93
Nov. 17	Cottonseed	2127	102	12.22	19.61	4.14	4.60	32		18.93	18.88
Nov. 17	Cottonseed	2128	75(a)	12.64	19.10	2.53		30		19.27	18.44
Nov. 20	Cottonseed	2134	106	13.28	19.37	4.33	7.00	48		19.50	19.25
Nov. 20	Cottonseed	2136	71(a)	12.12	19.48	1.75		28		19.37	18.50
Nov. 20	Cottonseed	2137	107	11.74	19.74	4.18	6.00	42		19.50	19.62
Nov. 25	Cottonseed	2140	107	11.54	19.81	4.44	6.30	44		20.08	19.28
Nov. 25	Cottonseed	2141	66(a)	12.10	19.63	1.81		28		19.99	19.56
Nov. 26	Cottonseed	2143	109	10.75	19.31	8.55	6.20	42		19.08	18.78
Nov. 29	Cottonseed	2151	108	11.98	18.88	7.21	8.70	58		18.63	18.56
Dec. 3	Cottonseed	2154	102	10.38	19.73	11.89	13.10	91		20.43	19.19
Dec. 3	Cottonseed	2156	66(a)	11.71	19.62	2.18		.....		18.25	18.47
Jan. 7	Cottonseed	2171	42(a)	11.30	19.34	2.43		.....	27	20.56	19.87
Heated Cottonseed from Oil Mill Seed Bin .....		2044	92	29.07	9.71	54.01	58.50	200		19.09	14.00
		2045	97	30.30	11.35	50.50	41.10	164		19.06	13.20
		2046	103	24.07	9.00	59.64	55.52	176		19.67	13.63
		2048	111	29.77	10.77	39.04	39.04	148		20.06	12.88
LOT	SAMPLED AT	ANALYZED									
No. 6	Harvest	15 mo. later	1995	(b)	8.71	18.94	1.65	.....	26	20.44	20.00
(c)	End of Storage	12 mo. later	2040	(b)	8.29	19.14	1.78	.....	40	20.44	20.06
No. 8	Harvest	15 mo. later	2016	(b)	8.05	19.55	1.75	.....	38	19.48	18.75
(d)	End of Storage	14 mo. later	2042	(b)	9.00	18.24	3.43	.....	50	19.22	18.87

(a) Taken from parts of the pile which had never heated.

(b) These lots of cottonseed showed no tendency to heat at any stage.

(c) Lot 6 stored 120 days.

(d) Lot 8 stored 120 days.

or less, there are a large number of other factors which may affect the percentage of fat<sup>3</sup> and possibly the percentages of other constituents of the seed.

The results of the chemical examination of the samples are shown in Table I and Figs. I and II.

During the storage as seed cotton the moisture decreased from 16.47 to 13.77 per cent. There was no significant change in the percentage of fat, crude protein or albuminoids, although they all appeared to increase slightly. The minimum percentage of free fatty acids, obtained with No. 2096, was 1.17, and the maximum, with No. 2107, was 2.83 per cent. There thus appears to be a slight rise in the percentage of free fatty acids during the period of storage as seed cotton. As seed cotton is ginned nearly always within a few weeks of the time of harvest, it is probable that there is little change in composition, except in loss in

the wide divergencies from the mean being probably due to errors of analysis and to inherent inaccuracies in the method for the determination of albuminoids. In Fig. II the difference between the crude protein and the albuminoids is plotted under the title "Non-protein."

The most significant changes that took place during the period of storage as cottonseed were the increase in the free fatty acids and the total acidity. The free fatty acids increased from 2.26 per cent in No. 2111 to 11.89 per cent in No. 2154. Increase in total acidity accompanied in each case the increase in the free fatty acids. The total acidity increased during the heating of the seed from 28 cc. of normal alkali per kilogram of seed in No. 2122, to 91 cc. in No. 2154. These changes are shown graphically in Fig. I, the total acidity being calculated in terms of free fatty acids in the fat of the respective samples. From these and other results to be published elsewhere it

<sup>1</sup> Loc. cit.

<sup>2</sup> Bureau of Chemistry, U. S. Dept. Agric., Bull. 107, revised.

<sup>3</sup> J. Agr. Res., 3, 27



appears that the free fatty acids in cottonseed have an initial value of less than 2 per cent of the fat, and the total acidity of not more than 26 cc. of normal alkali per kilogram of cottonseed. Even a sample of cottonseed analyzed 15 months after harvest (No. 1995) was within these limits.

It will be noted that the greatest acidity was found after the heating had passed its maximum intensity.

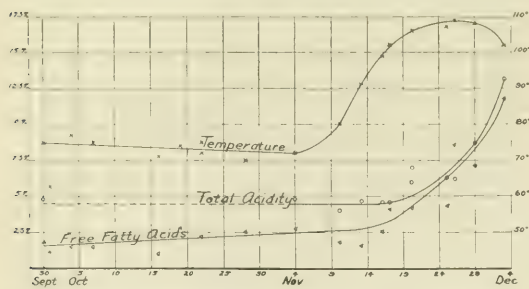


FIG. I—CHANGES IN THE ACIDS OF "HEATING" COTTONSEED

In this connection the following experiments are of interest.

Samples of cottonseed were taken from a lot in an oil mill seed bin where the seed was heating, at temperatures similar to those at which the above samples were taken. The samples were stored in air-tight containers in the laboratory, thus approximating the conditions in the center of a pile of heating cottonseed as far as the absence of air is concerned. The samples were analyzed at the end of 12 months. The results are given in Table I (Nos. 2044, 2045, 2046, and 2048).

While, unfortunately, analyses of the samples made at the time of sampling are not available, it is reasonable to assume that the seed had not changed more than the above samples taken at the same temperature. The hydrolysis of the fat and protein was found to have taken place to a very marked extent. The free fatty acids varied from 50.50 per cent in No. 2045 to 70.94 per cent in No. 2048, while the albuminoids were only 65 per cent of the crude protein in the case of No. 2048 and correspondingly low in the other samples. The total acidity reached a maximum of 200 cc. with No. 2044, corresponding to 58.50 per cent of free fatty acids in the fat of the same sample.

It is probable, therefore, that the hydrolysis of the fat and protein, as well as the production of total acidity, continues in heat-damaged seed even when the temperature has gone down, provided the air continues to be excluded. The heating of cottonseed even to a comparatively slight extent leads to a loss to the cotton oil mill, due, in the case studied, to the hydrolysis of more than 10 per cent of the fat. A large amount of heating, or storage of heat-damaged seed in the absence of air, causes hydrolytic changes in the protein and fat which may amount to 33 per cent of the former and 70 per cent of the latter, as well as an increase of 77 per cent in the total acidity. Such cottonseed is practically worthless except for the lowest grades of cottonseed oil, and the resulting

cottonseed meal useless to the farmer except as a fertilizer.

#### SOURCE OF THE ACIDITY OF HEATED COTTONSEED

The total acidity of cottonseed might come from the fat by hydrolysis, from the carbohydrates by decomposition forming various organic acids, and possibly, but not likely, from the proteins by decomposition. It will be noted that the total acidity increases with the free fatty acids in the samples examined. By calculating the total acidity in terms of free fatty acids in the fat of the respective samples a relation between the two is brought out: the results of such calculations appear in Table I, and a curve plotted from the data is shown in Fig. I.

In the unheated cottonseed the total acidity was greater on an average by about 2 per cent than the free fatty acidity, but in the case of Nos. 2142 and 2143 it was 3.75 and 2.35 per cent less. With these exceptions the fatty acid acidity increased directly as the total acidity. The increase in the total acidity in these samples is probably due to the formation of free fatty acids to a large extent, and only in a minor degree to the decomposition of other constituents of the seed than the fat. Besley and Baston believe that the acidity of corn comes from the germ, which is richest in fat, while Black and Alsberg state that the acidity may come from the carbohydrates in the case of the same cereal. The facts that the badly heat-damaged corn had an acidity of only 50 to 90 cc. as compared with 200 cc. for badly heat-damaged cottonseed, and that the germ of corn contains much readily hydrolyzable fat, accords with the view held by the writer that the acidity of cottonseed, except in fresh samples, comes in large part, if not almost entirely, from the fatty acids formed from the fat by agencies within the seed.

#### EFFECT OF AGE ON THE COMPOSITION OF COTTONSEED

In order to determine whether the acidity noted was due to the aging of the seed alone or to the heating,

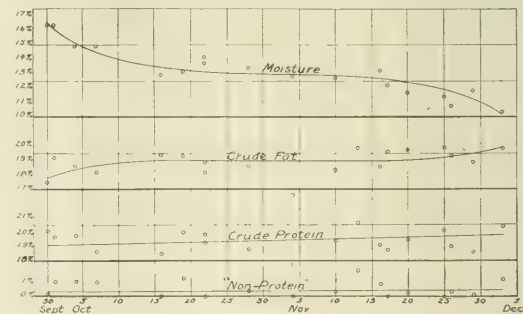


FIG. II—CHANGES IN SOME CONSTITUENTS OF "HEATING" COTTONSEED

Samples 2128, 2136, 2141, and 2156 were taken from unheated parts of the cottonseed at the same time samples were taken from the heated part. The samples were analyzed as already described and the results are shown in Table I.

There were no significant differences in the percentages of moisture, fat, protein, or albuminoids in

the heated and the corresponding unheated samples. The fatty free acids and the total acidity, however, are in each case higher in the heated samples than in the unheated ones. The free fatty acids remained in the latter within 0.45 per cent of the mean for these samples—2.06 per cent—but the free fatty acids in the heated samples increased from 2.70 per cent in No. 2130 to 11.89 per cent in No. 2154. The total acidity varied in the same way as the free fatty acids. The minimum for the unheated seed was 26 cc. of normal alkali per kilogram of seed with No. 2123, the maximum 32 cc. with No. 2128, and the average 28 cc. For the heated seed the minimum was 32 cc. with No. 2127, the maximum 91 cc. with No. 2154, and the average 51 cc. The total acidity of the unheated samples increased only slightly with increase in length of storage, while that of the heated seed increased about 300 per cent. A sample taken from the unheated area at the end of the storage period—No. 2171—contained only 2.43 per cent free fatty acids and 27 cc. acidity, figures essentially the same as those obtained on the freshly ginned seed of this lot. Samples from two lots of cottonseed—Nos. 1995 and 2016—sampled at harvest and stored in the laboratory for 15 mos. showed 1.65 and 1.75 per cent free fatty acids in fat and 26 and 38 cc. total acidity. Samples of the same lots of seed stored in a seed bin for 3 mos. and then kept in the laboratory for 12 mos. before analysis—Nos. 2040 and 2042—showed 1.78 and 3.43 per cent free fatty acids in fat, and 40 and 50 cc. acidity, respectively. Increase in acidity and free fatty acids in stored cottonseed is due to the heating of the seed and not to aging. Dry cottonseed may be kept for a year or longer without deterioration.

#### SUMMARY AND CONCLUSIONS

I—Dry cottonseed stored in an oil mill seed house in a 5000 lb. lot in a pile 12 ft. by 12 ft. by 6 ft., dried out in storage and then heated. During the heating the free fatty acids increased nearly 500 per cent, and the total acidity nearly 375 per cent. There was no apparent tendency for the protein to hydrolyze during the storage period.

II—Even a short heating of cottonseed causes the hydrolysis of about 10 per cent of the fat of cottonseed, and an increase in the total acidity, while long heating or storage of heated seed in the absence of air may cause 70 per cent of the fat, and 33 per cent of the protein to hydrolyze, and lead to the production of 700 per cent more total acidity than normal seed contains. Such cottonseed is worth little except as a source of soap stock and fertilizer.

III—The source of the acidity of fresh cottonseed is the fat only in part, but in heated cottonseed it is probably the fat almost entirely. Free fatty acids in fresh samples of cottonseed averaged less than 2 per cent of the fat, and the total acidity not more than 26 cc. in terms of normal alkali per kilogram of cottonseed.

IV—Increase in the acidity and the free fatty acids in stored cottonseed is due to heating and not to the aging of the cottonseed.

ARKANSAS EXPERIMENT STATION, FAYETTEVILLE

#### VANILLA EXTRACT<sup>1</sup>

By J. R. DEAN AND J. O. SCHLOTTERBECK<sup>2</sup>

Received January 3, 1916

Before going into a discussion of the tincture or extract of vanilla, it seems logical to consider, for a moment, the composition and nature of the crude material from which the extract is prepared.

The vanilla bean is the source of vanilla extract and is the fruit of the plant *Vanilla planifolia* (Andrew). This climbing, perennial plant belongs to the orchid family and is indigenous to Central and South America and the West Indies, but is cultivated also in Reunion, Seychelles, Madagascar, Comores, Ceylon, Java and Tahiti. The most highly prized beans are cultivated in Mexico in the vicinity of Vera Cruz. While the different varieties differ in some details, the best cured beans of commerce, as a rule, are from 8 to 10 in. (20 to 25 cm.) in length and from  $\frac{1}{8}$  to  $\frac{1}{4}$  of an inch (4 to 8 mm.) thick, drawn out at their ends and curved at the base. They are rich dark brown in color, of a waxy nature to the touch, deeply rifted lengthwise, and are often covered with frost-like crystals of vanillin.

#### COMPOSITION OF THE BEANS

The beans contain vanillin, secondary aromatic compounds, resins, organic acids, volatile oil, fixed oil, sugar, gum, tannin, wax and water. The percentage analysis of two varieties of beans, according to König, is as follows:

	I	II
Water.....	25.85	30.94
Nitrogenous bodies.....	4.87	2.56
Reducing sugar.....	7.07	9.12
Fat and wax.....	6.74	4.68
Non-nitrogenous bodies.....	30.50	32.90
Cellulose.....	19.60	15.27
Ash.....	4.73	4.53

Vanillin is included in the above table under the "non-nitrogenous bodies" and is the chief flavoring agent of the bean. Chemically, vanillin is the methyl ester of protocatechuic aldehyde. It is soluble in hot water, alcohol, ether, chloroform and some volatile oils, but only slightly so in cold water. At 81 to 82° C. vanillin melts and sublimates at high temperatures without decomposition. Heated in a current of carbon dioxide, vanillin can be distilled under pressure of 15 mm. of mercury. It is present in vanilla beans to an amount varying from 1 to 3 per cent, and, curiously enough, the higher prized beans do not contain the most vanillin. This has been shown by Tiemann and Haarmann<sup>3</sup> as follows:

BEANS	Mexican	Bourbon	Java
Per cent Vanillin.....	1.69	2.48	2.75

The green vanilla beans do not contain vanillin and are devoid of the fragrance of the ripe and cured beans. Vanillin is formed in the bean during the process of curing by hydrolysis from coniferin, a glucoside found in various parts of the plant and elsewhere in the vegetable kingdom. Coniferin is first split

<sup>1</sup> A report of the work done during 1914–15 at the University of Michigan on the Fellowship granted for the purpose by the Flavoring Extract Manufacturers' Association and published by them in September, 1915, in the minutes of their 6th Annual Convention, held in Cleveland, Ohio, in July, 1915.

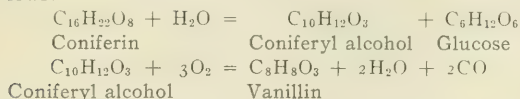
<sup>2</sup> College of Pharmacy, University of Michigan, Ann Arbor, Mich.

<sup>3</sup> Ber., 8 (1875), 1118; 9 (1876), 1287.



into coniferyl alcohol and glucose by means of an enzyme. The coniferyl alcohol is then oxidized to vanillin by an oxidase present in the beans. The beans are cured naturally if left on the vines, but the beans cured on the vines are not as fine as those which are pulled green and cured by artificial means. The curing process consists of repeated sweatings and dryings obtained by the heat of the tropical sun. In some of the other countries, especially in Reunion, the beans are cured by dipping into hot water and then drying. The former, or Mexican process, is said to produce a much finer bean than the latter, which is often called the Bourbon process.<sup>1</sup> It has been possible to obtain vanillin from other parts of the vanilla plant than the beans. This has been shown by Jos. Behrens, who was able to obtain vanillin from the leaves of the vanilla plant by hydrolysis with dilute acid.<sup>1</sup> That the production of vanillin in the bean is an enzyme action has been shown by obtaining two green beans from Mexico and heating one to 80° C. in order to destroy the natural enzyme present, and then submitting both beans to a curing process. The bean which had not been heated produced vanillin while the heated one did not.

The chemical reaction occurring during the formation of vanillin in the bean is supposed to be as follows:



Vanillin was first separated from vanilla beans in 1858 by Goble and first prepared synthetically by Tiemann and Haarmann in 1874<sup>2</sup> from coniferin by means of chromic acid. That the value of vanilla beans cannot be determined by their vanillin content has long been known and is evident from the fact that the most highly prized varieties do not contain the most vanillin. The chemical reaction which produces the vanillin in the beans is believed by some to continue even after the beans are tied up into bundles. This would account for the well known custom of storing the beans for one or two years after being received from the plantation. It might be of interest also to know that vanillin is not limited in nature to vanilla beans alone but that it is found in Siam benzoin,<sup>3</sup> in asafoetida,<sup>4</sup> in crude beet sugar,<sup>5</sup> in asparagus,<sup>6</sup> in dahlia tubers,<sup>7</sup> and in many other plants, in resins, in balsams, and other substances.

Synthetic vanillin is produced on a large scale and is identical with the natural product. It was first made from coniferin by oxidation with chromic acid. Now it is largely obtained from the eugenol or oil of cloves by means of alkaline potassium permanganate.

SECONDARY AROMATIC COMPOUNDS—It is well known that an extract of vanilla beans is superior in flavor to a simple solution of vanillin, and it is claimed that

the additional flavor of the extract is due to several secondary aromatic flavoring compounds which are present in the beans in very small amounts. This additional flavor has been said to be due to piperonal (heliotropin),<sup>1</sup> and others claim the presence of several other aromatic aldehydes, alcohols and esters. But besides the statement that piperonal is present, there is no definite scientific statement to be found in the literature in regard to either the Mexican or the Bourbon beans. Walbaum has separated anisic aldehyde, anisic alcohol and anisic acid from Tahiti beans, and has denied the presence of piperonal in Tahiti beans.<sup>2</sup>

The whole complex of the secondary flavoring compound is often spoken of as the "Balsam" of the beans, and it is no doubt made up of a large number of compounds more or less different in the different varieties of beans if not also in the different lots of the same beans.

A volatile oil has been obtained from vanilla beans, but no more can be found in the literature about it than about the secondary flavoring compounds; it is no doubt a part of the balsam.

RESIN—The resins of vanilla beans are said by some investigators to be present in amounts varying from 4 to 18 per cent, while others say that they are present in an amount equal to that of the vanillin.<sup>3</sup> They were at one time thought to be of great flavoring value and to make the difference between an extract of vanilla and a simple solution of vanillin. This has been disproven lately, however, and it is now known that these bodies, whatever they are, are odorless and have anything but a pleasant taste.<sup>4</sup> We are able to separate a dark red sticky substance that was soluble in alcohol and alkalies and insoluble in water that seemed to us as being the substance usually called the resins. The alcoholic and alkaline water solutions of the substance were dark red in color. The alkaline water solution was slightly acidified with acetic acid and lead acetate was added when a precipitate was obtained that was in every respect similar to the precipitate obtained in the lead number determinations. This substance was tasteless and odorless.

It has been claimed that vanilla beans contain two different resins, one acid and the other neutral.<sup>5</sup> Absolute alcohol dissolves a yellowish substance from the beans that is not soluble in dilute alcohol and it is not possible to obtain the coloring matter of the beans in absolute alcohol although it is soluble in dilute alcohol to a more or less extent. Thus it would seem that there are two substances present, both of which are of a resinous nature, and that at least one of them is largely the lead-precipitating material of the bean, and is also a part of the coloring matter.

The chief function of the resins, however, is as fixative for the delicate flavoring compound and it is well known that an extract which contains but a small amount of these resins will not retain its value as

<sup>1</sup> *Tropenplanzer*, 1899, 299.

<sup>2</sup> *Ber.*, 8 (1875), 1123.

<sup>3</sup> *Ibid.*, 11 (1878), 1635.

<sup>4</sup> *Ibid.*, 19 (1886), 705.

<sup>5</sup> *Ibid.*, 13 (1880), 335, 662.

<sup>6</sup> *Ibid.*, 16 (1883), 44, 18.

<sup>7</sup> *Ibid.*, 39 (1906), 4147.

<sup>1</sup> "Der Pflanzen chemie," Vol. 1, p. 89.

<sup>2</sup> "Festschrift of Otto Wallach," 1909, 649.

<sup>3</sup> *American Perfumer*, Nov., 1908, 167.

<sup>4</sup> "Alois von Isakovics," 1914, Minutes of the F. E. M. A.

<sup>5</sup> *Ber.*, 9 (1876), 1289.

long as an extract that contains a larger amount of them. Their ability to hold on to the aromatic compound is great and was no doubt the cause of the long mistaken idea about their flavoring value.

Alcohol and alkalis dissolve the resins readily, but they are almost insoluble in all of the other solvents and entirely so in water. When the alcohol is removed from an alcoholic solution of the resins by evaporation the resins are precipitated in a very fine state of subdivision and are light brown in color. On filtering and drying they darken and finally turn almost black.

#### GRINDING VANILLA BEANS

There are various acids present in the vanilla bean, such as oxalic and vanillic, but they are of no flavoring value except when they are present in the form of esters. It is, however, very likely that these acids, which are of no value in a new extract, become very valuable when the extract has been aged, due to the formation of esters.

Before employing vegetable drugs in the various pharmaceutical preparations, it generally becomes necessary to reduce them to a state of subdivision more or less fine, according to the nature of the material. The moisture present in the beans makes their reduction very difficult and still it is imperative that they be reduced to a rather fine state of subdivision in order to obtain a uniform and sufficient extraction. It is the custom of some manufacturers to reduce the beans to a very fine state by first cutting into small pieces and then passing them between steel rollers, which are set fairly close together. Others obtain a rather fine degree of subdivision by grinding the beans in some suitable mill, as a sausage grinder for example, after the beans have been mixed with quite a large amount of fine white sand or granulated sugar. Still another method is to cut the beans by means of rapidly moving vertical knives until a suitable state of subdivision is obtained. Grinding or pounding the beans has a tendency to press out the soft pulp, which soon retards the reduction of the tough fiber and requires the expenditure of much time and labor. In all processes in which grinding, pounding or rolling are used for the reduction of the beans, quite a little heat is developed during the process and is doubtless detrimental because of loss of flavor by volatilization. Comminution of the beans by passing between steel rolls is very efficient, but objectionable on account of the great amount of heat developed. Much can be said in favor of this process and it is possible that the objectionable heating of the beans could be overcome by cooling the rollers with cold water circulating through them. It is claimed that the process of cutting the beans, with the vertical knives, overcomes this heating difficulty and leaves the beans practically in their original condition, no pulp being expressed and a uniform product being obtained which is superior to that produced by other methods.

#### DRYING VANILLA BEANS

This difficulty of reducing vanilla beans to a suitable state of subdivision is well known and one that is

bound to cause more or less trouble on account of the nature of the material. Vanilla beans contain moisture in an amount from 10 to 50 per cent and it is desired to extract from them, not only the vanillin and other aromatic compounds, but also as much of the resins and other extractive matter as is possible and still hold the alcohol low enough in strength to obtain maximum coloring matter. A very good extraction can be obtained with a 50 to 60 per cent alcoholic menstruum, but still it is not complete. The higher the alcoholic content of the menstruum, the greater is the extraction of the resins, but if the alcohol exceeds 65 per cent, the lower the amount of coloring matter which is extracted. When the beans have been dried, however, it is possible to obtain a far better extraction of both the resins and the coloring matter and, at the same time, overcome the difficulty of reducing the beans to a fine state of subdivision. In order to determine the most desirable method of drying, and the effects produced on the beans, the following experiments were carried out on a good quality of Mexican beans which contained about 22.5 per cent of moisture.

No. 1.—One hundred grams of chopped beans were placed in a glass tube, which was contained in an oven and heated at 122° F. (50° C.) for eight hours. By means of an air pump a slow current of dried air was passed through the heated beans, the air being washed on leaving the tube by passing through dilute alcohol. The loss in weight amounted to about 20 per cent at the end of 8 hours, which was about 90 per cent of the total moisture present. When the alcohol, through which the air had passed, was carefully evaporated, only a trace of vanillin was found.

No. 2.—Experiment No. 2 was the same as No. 1, except that the drying was done at room temperature. The loss in weight in 8 hours was about 10 per cent; in 20 hours, about 14 per cent, and in 48 hours, about 18 per cent, which was about 80 per cent of the total moisture present. The amount of vanillin removed here was about the same as in No. 1.

No. 3.—One hundred grams of the same beans were spread out in a thin layer and exposed to the air at room temperature. The loss in 24 hours was about 14 per cent; in 48 hours, 18 per cent, or about 18 per cent of the total moisture present.

No. 4.—One hundred grams of the same beans were placed in a glass tube through which a strong current of air was blown, the whole being kept at the room temperature. The loss in 8 hours was 20 per cent, or about 90 per cent of the total moisture present. As in experiments Nos. 1 and 2, the air was passed through washing towers which contained dilute alcohol and dilute potassium hydroxide solutions, respectively. The air current was under such pressure that it was impossible to completely wash it of volatile aromatic substances, since it still smelled strongly of vanilla even after it had passed through both solutions. The mixed solutions were then freed from alcohol, acidified and extracted with ether. On evaporating the ether, the residue remaining was dark brown in color, had a rather strong vanilla odor and contained a great number of well defined crystals of vanillin. The method of drying was as efficient as the one in which heat was used, but quite obviously, it would not be practical with a high-grade bean because of material loss of flavor.

On the large scale, the drying at room temperature can be easily affected by spreading the chopped beans in thin layers on tables and turning the drafts from electrical fans over them. Or the beans could be



placed on shelves in a small room through which a current of air is drawn. By this method the temperature could be regulated by either heating the entire room or by allowing only heated air to enter. An arrangement of the shelves in such a way that only alternate ones extend clear to the side walls, on each side, would force a more complete circulation of the air over the beans, since the air would have to go over the entire length of the shelves in order to descend.

The beans dried in the above experiments were used, along with similar but undried beans, to make several extracts in order to see if the drying had in any way altered their value from a flavoring, as well as from an analytical, standpoint. The dried beans were very brittle, which made it easy to reduce them to a fine powder. Their aroma seemed different from that of the undried beans, being rather strong and harsh when compared with undried beans. The process of extraction consisted of a one week's maceration followed by a slow percolation. Complete extraction was naturally not obtained, owing to the short duration of the process, but all of the extracts were made at the time and under the same conditions and hence

In the case of the "Lead Number,"<sup>1</sup> however, we were able to obtain some variations in extracts from dried and undried beans but none of great importance. The greatest increase was from 0.6324 (No. 12) to 0.8095 (No. 24) which is an increase of 0.17 plus and was obtained from a dried bean extract. But such a great increase was not constant throughout the entire number of extracts and could not be taken as typical. The lead numbers of the undried bean extracts varied from 0.6324 (No. 12) to 0.7485 (No. 21) and averaged 0.6951 for the seven extracts. Those of the dried bean extracts varied from 0.7438 (No. 25) to 0.8095 (No. 24) and averaged 0.7741. This gives an average increase of only 0.079, a value too small to be of any great importance.

In determining the lead numbers of this, the alkali and a part of the menstruum series, it was not possible to obtain clear lead acetate filtrates and we had to content ourselves with rather cloudy solutions of the unused lead acetate. The lead precipitates in most of the cases were also unnatural, both in color and appearance. It was necessary to centrifuge most all of the samples in order to obtain a solution that would

TABLE I—EXTRACTION EXPERIMENTS (SERIES 2)

Extr. No.	Percentages Alcohol	Vanillin	Lead No.	TOTAL Red	COLOR Yellow	Ratio of Red to Yellow(a)	BEAN	ADDITION	REMARKS	EXTRACT
12	50	0.23	0.6324	22.5	75.0	1: 3.3	Fresh			Clear
13	50	0.23	0.6379	15.0	52.5	1: 3.5	Fresh	Sand	Sugar in percolator	Clear
14	50	0.23	0.7219	17.5	62.5	1: 3.5	Fresh	Sand	No sugar	Clear
15	50	0.23	0.7472	25.0	92.5	1: 3.7	Dried			Clear
16	50	0.23	0.8034	25.0	87.5	1: 3.5	Dried	Sand and Sugar		Clear
17	50	0.23	0.8011	25.0	87.5	1: 3.5	Dried	Sand, no Sugar		Clear
18(b)	35	0.23	0.6905	17.5	50.0	1: 2.8	Fresh			Cloudy(b)
19	40	0.23	0.6955	17.5	55.0	1: 3.1	Fresh			Cloudy
20	45	0.23	0.7390	25.0	75.0	1: 3.0	Fresh			Clear
21	50	0.23	0.7485	25.0	77.5	1: 3.1	Fresh			Clear
22	35	0.23	0.7560	22.5	67.5	1: 3.0	Dried			Cloudy
23	40	0.23	0.7581	25.0	77.5	1: 3.1	Dried			Clear
24	45	0.23	0.8095	25.0	90.0	1: 3.6	Dried			Clear
25	50	0.23	0.7438	25.0	90.0	1: 3.6	Dried			Clear
26(c)	60	0.22	0.442	22.0	117.0	1: 3.6	Fresh			Clear
27	40	0.20	0.433	25.0	50.0	1: 2.0	Fresh			Clear
28	40	0.26	0.552	30.0	100.0	1: 3.3	Fresh	Sand		Cloudy
29	40	0.26	0.510	42.5	110.0	1: 2.6	Same as 28			Clear
30	40	0.26	0.438	20.0	60.5	1: 3.0	Fresh	Sand	Macerated for 5 mo.	Clear
31	40	0.21	0.415	25.0	90.0	1: 3.6	Fresh		Macerated 30 hrs. at 110° F. (c)	Clear
32	40	0.16	0.460	27.5	72.5	1: 2.6	Dried		Macerated 15 hrs. at 110° F.	Clear
33	50	0.23	0.608	49.0	100.0	1: 2.5	Fresh		Macerated 3 mo. 75% glycerin in menstruum	Clear
33A	50	0.23	0.658	38.0	102.0	1: 2.7	Fresh		Same as 33 after 6 mo.	Clear
34	62	0.21	0.506	25.0	110.0	1: 4.4	Fresh Tahiti			Clear

(a) Extract color. (b) Extracts 18 to 26 contain 20 per cent sugar. (c) Extracts 26 to 33A were made from the same Mexican bean.

are comparable. In the case of the dried beans, an allowance was made for the absence of the moisture in weighing out the samples. Menstrua of varying strengths were also used on both dried and undried beans, and also the value of packing the beans with sand and sugar, both independently and together, was studied.

The analytical results obtained from these extracts are given in Table I, extracts Nos. 12 to 25, inclusive. The percentage of vanillin remained the same in the entire number of extracts, in this experiment, regardless of the variations in the method of extraction or the use of dried beans. The extraction of vanillin seems to be fairly simple, even with a low percentage of alcohol, but it is not complete and the dregs still contained some undissolved. That part of the vanillin which was not removed by the menstruum was doubtless contained in the beans in such a way that the menstruum could not get in contact with it, for neither drying nor grinding increased the amount of vanillin in the extract.<sup>1</sup>

<sup>1</sup> The vanillin was estimated by the Folin colorimetric method, THIS JOURNAL, 4 (1912), 670

filter at all and some stood this action for an hour without producing a solution that would filter clear. This cloudiness of the lead acetate filtrates made the exact determination of the unused lead a little troublesome and in some cases almost impossible, and, no doubt, accounts for the variations obtained from very similar extracts (No. 24 and No. 25, for instance), but the determinations were all made in duplicate, the average being taken as the true value, and in most cases the duplicates were very close. On the whole, the values obtained were certainly near enough for all practical purposes, notwithstanding the trouble encountered in obtaining them.

The "Total Color"<sup>2</sup> of the extracts was the most varied constant of all and is the best guide for the degree of extraction. Unlike the vanillin and lead number, the color values are greatly influenced by the amount of alcohol in the menstruum, increasing as the alcohol approaches 65 per cent, and falling off as the alcohol exceeds 65 and approaches 95 per cent. The undried bean extracts gave values for red vary-

<sup>1</sup> U. S. Dept. Agr., Bureau of Chem., Bull. 132, 110; *Ibid.*, 137, 120.

<sup>2</sup> *Ibid.*, 152, 148.

ing from 15 (No. 13) to 25 (No. 21) and for yellow, from 50 (No. 18) to 77.5 (No. 21). The dried bean extracts gave values for red from 22.5 (No. 22) to 25 (No. 23, etc.) and for yellow, from 67.5 (No. 22) to 92.5 (No. 15). Thus it is easily seen that a dried bean will give up more of its color to a given amount of alcohol than will an undried bean, especially in regard to the yellow. The color is the most difficultly extractable part of the bean and is of commercial value but the drying of the beans does not make such a great amount of difference, at least, hardly enough to justify the drying of the beans for that purpose alone.

It might be added here that it was impossible to obtain the lead filtrate color values, as is the custom, on account of the cloudy filtrates mentioned above. The ratio of red to yellow, in the tables, is of little value in an analysis so long as it passes the requirement of not being less than 1 : 2.2, and in our work means very little or nothing.<sup>1</sup>

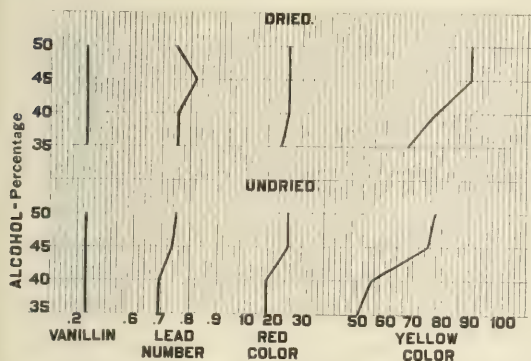
The flavor of these extracts, made from the undried and dried beans, seemed to be about equal where the same amount of alcohol had been used. The period

This result leads to the conclusion that drying vanilla beans is of service where it is done at room temperature and with a slow current of air. The differences obtained in the lead numbers, color values, clarity and flavor, were not exceedingly great but when summed up they make quite a contrast between the two extracts, everything being in favor of the dried beans.

#### DEFINITE MOISTURE CONTENT

As has been stated before, vanilla beans contain various amounts of moisture and it is generally the rule that the most prized beans contain the most moisture. This moisture is that left in the beans in the curing process and is certain to cause more or less reduction of the alcoholic strength of the menstruum used to extract them, which naturally reduces the extractive power of the menstruum. Drying the beans at a low temperature and with a slow current of air has been found to be a good means of overcoming the influence of this moisture but drying may not be always desirable or possible and some other means would have to be resorted to in order to obtain the same result. This is best done by regulating the amount of alcohol in the menstruum to suit the amount of moisture in the beans and will accomplish about the same result as the drying. The idea here is that the moisture of the beans amounts to just that much water, and enough absolute alcohol must be added to convert this water into a hydro-alcoholic mixture of the same alcoholic strength as that of the menstruum. Thus, if 100 lbs. of beans are to be worked up which contain 25 per cent moisture, there is added with the beans some 3 gallons of water in excess to that allowed for in the formula and, if a 50 per cent menstruum is being used, 3 gallons of 95 per cent or absolute alcohol ought to be added to convert the moisture into a 50 per cent hydro-alcoholic mixture.

Some manufacturers make use of a 60 or 65 per cent alcoholic menstruum to extract the beans and then reduce the alcoholic strength of the otherwise finished extract to 40 or 45 per cent by the addition of water. This method ought to prove of service, not only in producing a more complete extraction and a more uniform product, but also in being able to make use of the higher strength alcohol for the extraction and still finishing the extract at a comparatively low alcoholic content. This method is based on the well known fact that once a substance, especially organic extractive matter, is in solution in alcohol it is possible to reduce the strength of the alcohol considerably without precipitating the dissolved substance. In using such a method, however, it is necessary to avoid too great a reduction of the alcohol for this would produce too great a concentration of the dissolved material and a separation would in time take place. In making such a reduction of the alcoholic strength, of the otherwise finished extract, it is desirable to know the amount of alcohol present so as to avoid too great a reduction in order to avoid any future separation. A reduction from 60 to 40 per cent will produce a separation in the course of a year, especially if the extract has been cooled to a low temperature. A much smaller reduction ought to prove of more service even if



ANALYTICAL RESULTS OBTAINED FROM VANILLA EXTRACTS MADE FROM DRIED AND UNDRIED BEANS

of maceration, however, was so short that the maximum flavor was not obtained and it was very difficult to detect any difference between them. It seemed possible that the undried bean extracts were a little more aromatic than the dried bean extracts but the difference, if any, was certainly small. In order to be certain about this, we prepared two extracts from the same beans, both dried and undried, by packing with sand and macerating for two months before percolation. The menstruum contained 50 per cent alcohol and the maceration was carried out at room temperature in glass percolators. These extracts had a fine delicate aroma and it seemed certain that the one made from the dried beans was superior to the undried bean extract. The flavor of the dried bean extract was clearly more pronounced and seemed on the whole to be better. It is certain that the flavor of the dried bean extract was not inferior to the undried bean extract.

<sup>1</sup> This constant is determined by comparing the color of the extract, after suitable dilution, with standard colored glass slides. The numbers under red and yellow in the tables denote the amount of standard red and yellow estimated to be present in the total color complex of the extracts. These values are determined in a Lovibond tintometer, and are entirely empirical in nature, being of service only as a means of comparison.



it is necessary to make the extraction with a lower percentage of alcohol, say 50 or 55 per cent and then reducing to 40 or 45 per cent. It is obviously necessary to make a stronger than 10 per cent extract when such a method is employed so that the finished product will represent the soluble matter from 10 grams of beans in 100 cc. of the extract. It is also of great importance to have the water added very slowly and under constant agitation in order to prevent a cloudy product, which is certain to form if the water is added quickly.

We made some experiments along this line that seem very conclusive. The beans were extracted first with 95 per cent or straight alcohol and the percolates thus obtained were diluted with an equal volume of water. In half of the samples the water was added all at once and in the others the water was added very slowly and with frequent agitation. All of these percolates were then poured back into their respective percolators and, after a week's maceration, were repercolated. In every case where the water was added quickly we obtained a cloudy extract; and in every case where the water was added slowly we obtained

We prepared eight extracts, four from dried and four from undried beans, using alcoholic menstrua varying from 35 to 50 per cent (Table I, extracts No. 18 to No. 25, inclusive). The beans were the same as used in all of the other experiments. The C. F. Sauer Co. also prepared twenty-eight extracts for us which were made from four varieties of beans and with menstrua varying from 30 to 62 per cent alcohol (Table II, extracts from No. 40 to No. 67). The object of this experiment was to see if the different amounts of alcohol would make a difference in the analytical constants of the finished extracts.

By reference to Table I it will be seen that the vanillin remained the same in all of the eight extracts which we prepared regardless of the amount of alcohol in the menstruum. In the lot of twenty-eight extracts, Table II, the percentage of vanillin varied slightly in the four different series of extracts but the variations were not great enough to be of any importance. In fact it was found quite generally that the vanillin remained constant, or nearly so, in every series of experiments where the same bean was used

TABLE II—MENSTRUUM EXPERIMENTS (WITHOUT SUGAR)

BEAN	Per cent Moisture	Extr. No.	PERCENTAGES Alcohol Vanillin	Lead No.	EXTRACT Red	COLOR Yellow	FILTRATE COLOR Red Yellow	RATIO Extract	RED TO YELLOW Filtrate	REMARKS ON EXTRACT Color	CONDITION
M. M.	35	40	30 0.23	0.613	15.0	46.0	...	1:3.0	...	Light	Slightly turbid
		41	35 0.23	0.597	15.0	50.0	...	1:3.3	...	Light	Slightly turbid
		42	40 0.22	0.592	15.0	47.5	...	1:3.1	...	Light	Slightly turbid
		43	45 0.23	0.625	16.0	50.0	...	1:3.1	...	Light	Slightly turbid
		44	50 0.23	0.613	12.0	50.0	1.0 5.0	1:4.0	1:5.0	Light	Clear. Precipitate
		45	62 0.22	0.572	16.0	57.0	1.0 5.0	1:3.8	1:5.0	Light	Clear
		46	57 0.21	0.613	16.0	56.0	1.0 4.4	1:3.7	1:4.4	Light	Clear
J. P. T.	22.5	47	30 0.21	0.833	17.0	50.0	...	1:2.8	...	Light	Clear
		48	35 0.21	0.796	16.0	54.0	...	1:3.4	...	Light	Slightly turbid
		49	40 0.21	0.773	16.0	56.0	...	1:3.4	...	Light	Slightly turbid
		50	45 0.22	0.726	20.0	69.0	...	1:3.4	...	Light	Clear
		51	50 0.21	0.724	18.0	72.0	1.0 5.0	1:3.8	1:5.0	Light	Clear. Precipitate
		52	62 0.21	0.700	19.0	68.0	1.0 5.0	1:3.6	1:5.0	Light	Clear
		53	57 0.21	0.700	19.0	68.0	1.0 5.0	1:3.6	1:5.0	Light	Clear
Mexican Cuts	13.5	54	30 0.23	0.950	31.0	83.0	...	1:2.7	...	Dark	Slightly turbid
		55	35 0.23	0.871	44.0	95.0	...	1:2.15	...	Dark	Slightly turbid
		56	40 0.22	0.855	36.0	94.0	...	1:2.6	...	Dark	Slightly turbid
		57	45 0.23	0.830	44.0	94.0	...	1:3.15	...	Dark	Clear
		58	50 0.23	0.892	49.0	106.0	2.0 7.8	1:2.16	1:3.9	Dark	Clear. Precipitate
		59	62 0.21	0.822	46.0	112.0	2.4 10.0	1:2.4	1:4.1	Dark	Clear
		60	57 0.20	0.814	45.0	112.5	2.4 10.0	1:2.5	1:4.1	Dark	Clear
Bourbon	25	61	30 0.23	0.648	26.0	73.0	...	1:2.8	...	Dark	Very turbid
		62	35 0.23	0.651	24.0	73.0	...	1:3.1	...	Dark	Clear
		63	40 0.23	0.662	25.0	82.0	...	1:3.3	...	Dark	Slightly turbid
		64	45 0.23	0.640	25.0	83.0	...	1:3.3	...	Dark	Clear
		65	50 0.23	0.616	24.0	75.0	2.0 7.8	1:3.1	1:3.9	Dark	Clear
		66	62 0.25	0.612	27.0	94.0	1.0 4.5	1:3.4	1:4.5	Dark	Clear
		67	57 0.23	0.599	27.0	95.0	1.4 5.6	1:3.4	1:4.0	Dark	Clear

a clear extract. The total color and lead numbers of all of these extracts were about the same but the clarity of the products was very different, showing the effects of the two methods of dilution.

The moisture of the beans can be easily determined on small samples by direct drying at 100° C. (212° F.) and then weighing. Or the determinations can be made on a larger sample by distillation in petroleum oil and calculating from the amount of water in the distillate.<sup>1</sup>

#### EFFECTS OF VARYING AMOUNTS OF ALCOHOL

It has been shown that extracts made from a dried bean will give constants that vary more or less from extracts made from the same but undried beans and, also, that almost the same result can be obtained from an undried bean if the alcoholic strength of the menstruum is altered to suit the moisture content of the bean. There remains, however, a little more to be said in regard to the constants obtained from the same beans with varying amounts of alcohol.

regardless of all modifications in the method of extraction.

The lead numbers of the eight extracts in Table I were almost, but not quite, constant. There were some variations but they were not of a definite nature, neither increasing nor decreasing regularly with the variations in the alcoholic content of the menstrua. In the lot of extracts recorded in Table II we noted a slight decrease in the lead numbers with an increase of the alcohol in the menstrua, except in the case of the M. M. bean extracts where the values remained almost constant. This decrease in the lead numbers was small and not large enough to be of any commercial importance, from an analytical standpoint, but still it was large enough to be measured and to be noticeable in the table of results. The smallest variation was in the M. M. bean samples and was from 0.625 to 0.572, the whole series averaging 0.602. The J. P. T. bean extracts varied from 0.833 to 0.700 and averaged 0.736. The Mexican cuts gave extracts that varied from 0.950 to 0.814 and averaged 0.862.

<sup>1</sup> U. S. Dept. of Agr., Bur. of Plant Ind., *Bull.* 99, and *Circ.* 72.

The Bourbon bean extracts varied from 0.662 to 0.599 and averaged 0.632. The smallest variation in any one series was 0.053 and the largest variation in any one series was 0.136.

The total color of the extracts was increased, up to a maximum amount, with an increase of alcohol in the menstruum. This was true in all but a very few exceptions, and those were minor ones, the differences being small. All that has been said before in regard to the general nature of the color of the extracts applies here as well. In some of the samples we were able to obtain the lead acetate filtrate color values but they are of little importance.

In the extracts made from the Mexican cuts the ratio of red to yellow, in some cases, was below the Federal requirement of being not less than 1:2.2. Three of these extracts gave ratios of 1:2.15, showing an excessive amount of red in the color complex. This is doubtless due to the nature of the beans, produced by the curing process, and not to the presence of caramel in the beans, as has been sometimes claimed, for we were not able to detect the presence of caramel in either the beans or the extracts.

As has been said before, the primary object of this experiment was to see what the effects would be on the vanillin content, the lead number and the total color of the extracts made from the same beans with varying amounts of alcohol. From the whole number of extracts it seems certain that the vanillin content is altered only very slightly, if at all; that the lead number is decreased to a small degree and that the total color and clarity of the extract is increased up to a maximum by an increase of alcohol in the menstruum, up to about 65 per cent.

The flavoring value of the extracts made with the various amounts of alcohol were about the same where the extracts were prepared in a short time but in the samples which were macerated for two months before percolation, it was easily seen that the extract prepared with the 60 per cent menstruum was superior to that made with the 50 per cent menstruum. The color of the 60 per cent extract was darker than the 50 per cent extract and the extract showed a less tendency to precipitate when it was subjected to a low temperature. There does not seem to be much uniformity in opinion among manufacturers as to the most desirable amount of alcohol to be used in making vanilla extract but from our experiments it seems certain that 60 per cent alcohol produces a much finer extract than can be obtained with 50 per cent alcohol. The 60 per cent alcohol extract had a more delicate flavor, was stronger and had a darker color than the 50 per cent extract. The lead number, however, was slightly reduced by the use of the higher amount of alcohol.

#### USE OF AN ALKALI

It is well known that a complete extraction of vanilla beans with alcoholic menstrua is not possible and that the dregs left after percolation always contain more or less valuable material. Only a part of the resin is soluble in dilute alcohol and the same is true with 95 per cent alcohol. No matter what strength

alcohol is used for the extraction, a part of the extractive matter is lost, due to its insolubility. These constituents are, however, soluble in alkalies and therefore in alkaline menstruum will remove a far greater amount of them than will a neutral or acid menstruum.

At first thought it might appear that the use of an alkali in an extract of vanilla is an adulterant. It is, however, on theoretical grounds the logical thing to do, because of the acid nature of vanilla beans. The use of acids and alkalies in alcoholic menstrua for the extraction of vegetable drugs has found practical application in a number of cases and makes possible some pharmaceutical preparations that would be unsatisfactory without them. A well known example of the use of an acid is in fluid extract of blood

TABLE III—ALKALI EXPERIMENTS (SERIES 1)

Extr. No.	Per cent $K_2CO_3$	Per cent Vanillin	Lead No.	TOTAL Red	COLOR Yellow	Ratio Red to Yellow
1A.....	0.00	0.22	0.5669	25.0	77.5	1:3.1
B.....	0.00	0.22	0.5286	15.0	52.5	1:3.5
C.....	0.00	0.22	0.5682	27.5	87.5	1:3.1
D.....	0.00	0.22	0.5669	25.0	87.5	1:3.5
Av.....		0.22	0.5651	23.1	76.2	1:3.3
2A.....	0.04	0.22	0.7144	20.0	75.0	1:3.7
B.....	0.04	0.22	0.6571	20.0	75.0	1:3.7
C.....	0.04	0.22	0.7226	25.0	82.5	1:3.3
D.....	0.04	0.22	0.6311	25.0	80.0	1:3.2
Av.....		0.22	0.6813	22.5	78.1	1:3.4
3A.....	0.08	0.22	0.6474	25.0	72.5	1:2.9
B.....	0.08	0.22	0.7506	25.0	75.0	1:3.0
C.....	0.08	0.22	0.7267	25.0	85.0	1:3.4
D.....	0.08	0.22	0.6693	27.5	87.5	1:3.1
Av.....		0.22	0.6985	25.6	80.0	1:3.1
4A.....	0.12	0.22	0.7540	25.0	77.5	1:3.1
B.....	0.12	0.22	0.7923	25.0	80.5	1:3.2
C.....	0.12	0.22	0.6830	27.5	77.5	1:3.1
D.....	0.12	0.22	0.6789	30.0	85.0	1:2.8
Av.....		0.22	0.7320	26.9	80.0	1:3.0
5A.....	0.16	0.22	0.7855	27.5	77.5	1:2.8
B.....	0.16	0.22	0.7554	27.5	82.5	1:3.0
C.....	0.16	0.22	0.7363	27.5	90.0	1:3.0
D.....	0.16	0.22	0.7691	32.5	92.5	1:2.8
Av.....		0.22	0.7615	29.4	85.6	1:2.9
6A.....	0.20	0.22	0.7089	30.0	77.5	1:2.6
B.....	0.20	0.22	0.7895	27.5	82.5	1:3.0
C.....	0.20	0.22	0.8360	37.5	97.5	1:2.6
D.....	0.20	0.22	0.8073	37.5	100.0	1:2.6
Av.....		0.22	0.7854	33.1	89.4	1:2.7
7A.....	0.24	0.22	0.8018	27.5	80.0	1:2.9
B.....	0.24	0.22	0.6325	30.0	82.5	1:2.7
C.....	0.24	0.22	0.7472	40.0	125.0	1:3.1
D.....	0.24	0.22	0.7554	47.5	120.0	1:2.5
Av.....		0.22	0.7342	36.2	102.0	1:2.8
8A.....	0.28	0.22	0.7786	32.5	80.0	1:2.1
B.....	0.28	0.22	0.7977	37.5	87.5	1:2.3
C.....	0.28	0.22	0.8674	45.0	117.5	1:2.6
D.....	0.28	0.22	0.8264	47.5	122.5	1:2.3
Av.....		0.22	0.8175	40.6	102.0	1:2.5
9A.....	0.32	0.22	0.8073	40.0	87.5	1:2.2
B.....	0.32	0.22	0.7991	42.5	92.5	1:2.2
Av.....		0.22	0.8032	41.2	90.0	1:2.2
10A.....	0.36	0.22	0.8360	37.5	92.5	1:2.4
B.....	0.36	0.22	0.8169	42.5	95.0	1:2.2
Av.....		0.22	0.8264	40.0	93.7	1:2.3
11A.....	0.40	0.22	1.015	37.5	95.0	1:2.5
B.....	0.40	0.22	0.9794	40.0	97.5	1:2.5
Av.....		0.22	0.9972	38.7	96.2	1:2.5

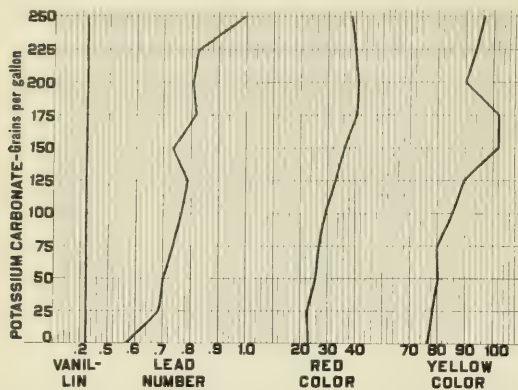
root where the acid is necessary to dissolve the alkaloids, and, of the use of an alkali, in fluid extract of senega where the alkali is used to dissolve the pectins. The use of an alkaline menstruum has also found some application in the preparation of vanilla extract and it should produce an extract that is higher in both color and lead number values than could be produced from the same beans with a neutral menstruum. The question at once arises: Will the alkali modify the flavor or will it intensify the flavor?

It was for the purpose of answering these questions that some 34 extracts containing various amounts of potassium carbonate were prepared. They were made in ten different lots containing the alkali in amounts varying from 25 grains (0.04 per cent) to 250 grains (0.4 per cent) to the gallon. At the same time we



prepared four extracts without alkali to be used as standards for comparison. The menstruum used in all of the extracts was 50 per cent alcohol, for it was not for the purpose of reducing the amount of alcohol in the menstruum that the experiment was made, but, on the contrary, it was a hope that a faintly alkaline menstruum would more completely extract the bean and thereby increase both the physical constants and the flavoring powers of the extracts. The analytical results of this experiment appear in Table III.

The vanillin content was the same in all of these extracts. The alkali neither increased nor decreased it. This would indicate again that the vanillin of



ANALYTICAL RESULTS OBTAINED FROM VANILLA EXTRACTS MADE FROM MEXICAN BEANS AND FIFTY PER CENT ALCOHOLIC MENSTRUUM CONTAINING VARYING AMOUNTS OF POTASSIUM CARBONATE

the beans is quite easily extracted, up to a certain limit, and that what remains undissolved is held in the beans in such a way as to make its extraction very difficult.

The lead number values showed a rather marked increase with the increasing amounts of alkali. The standard extracts averaged in lead number 0.565 and the samples containing the maximum amount of alkali averaged 0.997, an increase of 0.432 or about 76 per cent. The intervening samples gave values between these and were, with a few exceptions, greater the larger the amount of alkali employed. In no case was the amount of alkali used sufficient to render the finished extract alkaline. Extracts No. 9 contained the theoretical amount of potassium carbonate needed to neutralize the acidity of the beans, calculated from the acidity of the standard extracts, but it was found that these extracts were still acid and that an excess of the theoretical amount of alkali did not overcome the acidity of the beans but extracted more and more from the beans. This is shown by the increase of the lead numbers up to the maximum amount used and the fact that these extracts were still acid.

The color of the extracts increased, up to a maximum, with the increasing amounts of alkali and would indicate that this is also of an acid nature, favorably acted upon by a small amount of alkali. The samples containing 0.28 per cent of potassium carbonate gave the maximum amount of color, which was 40.6 red and 102.0 yellow against 23.1 red and 76.2 yellow

low in the standard samples. The clarity of the extracts was also greatly improved by the presence of the alkali and increased directly with the increasing amounts of alkali used.

Thus it is easily seen that the lead number, the color values and the clarity of the extracts were increased in definite progression by the use of the alkali. It was found, however, that the flavor of these extracts was not equal to that of the standards and seemed to decrease with each additional amount of alkali. These extracts possessed a flavor that is foreign to a good extract of vanilla. The flavor might be described as being of greater "body" but clearly lacking in the delicate aroma which is so characteristic of a good and pure extract.

The cause of this off flavor is not fully clear but it is doubtless due the action of the alkali on the resins, forming potassium salts having a peculiar taste and flavor. Vanillin itself is acid in nature and can be neutralized with an alkali but neutralized vanillin has a taste not much different from that of unneutralized vanillin and far different from the taste of the extracts made with alkali. The addition of an acid to the extracts, made with the alkaline menstrua, overcame the disagreeable taste but also threw out of solution the extra material which the alkali had dissolved and left an extract about the same in color and taste as those made without alkali.

In view of the formation of foreign flavor, the use of an alkali in the preparation of pure extract of vanilla is not favored.

(To be concluded in our next issue)

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## THE DETECTION OF NATURAL AND ARTIFICIAL PIGMENTS IN OLEOMARGARINE AND BUTTER

By LEROY S. PALMER AND WALTER E. THRUN  
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### INTRODUCTION

The natural yellow color of butter and of the body-fat of dairy cattle, the latter being characterized by its intense color in the case of the Guernsey and Jersey breeds, is now known<sup>1</sup> to arise from the direct transfer of the yellow pigment, carotin, from the feed to the milk and body-fat. During the season of the year when the food of the dairy cow is more or less devoid of carotin and the butter, in consequence, loses its natural yellow color, the law permits the butter manufacturer to add certain harmless pigments to the butter in order that the consumers' demand for yellow butter throughout the year may be satisfied. Most of the various brands of "butter color" on the market for this purpose are solutions of annatto in some vegetable oil, usually cottonseed oil. Certain other pigments<sup>2</sup> are also permitted for butter coloring, but they are not in common use at the present time.

<sup>1</sup> Leroy S. Palmer and C. H. Eckles, "Carotin: The Natural Yellow Pigment of Milk Fat, etc.," *J. Biol. Chem.*, **16** (1914), 191-249; *Missouri Agr. Research, Bulls.* **10** and **11** (1914).

<sup>2</sup> Among the permissible vegetable pigments are turmeric, saffron, marigold and safflower. The only yellow or orange coal-tar dyes allowed under the Federal Law are Naphthol Yellow S and Orange I.

The Federal Law also permits the use of the above-mentioned pigments for coloring oleomargarine, but at the same time imposes an additional tax of 10 c. per lb. on the colored product. Oleomargarine mixed with highly colored butter to give it a yellow color, or manufactured from beef fat with a high natural yellow color for the same purpose is also subject to the color tax. Many states have statutes with clauses to this effect. For example, the Missouri statutes declare that, "to add to or mix with oleomargarine any artificial coloration that causes it to look like butter of any shade of yellow," renders the person so doing an oleomargarine manufacturer in the eyes of the law.

Although the Federal Law permits the use of coloring matter in the manufacture of oleomargarine, more than half the states of the Union have statutes which prohibit the sale of oleomargarine with any color whatever, either natural or added. It is not possible for the manufacturers of oleomargarine to comply with the letter of this law because practically all beef fat contains some natural yellow color, although it may not be possible to see this color until the fat is rendered and viewed in the clear, liquid condition. The pigment of the natural beef fat is carotin, as previously stated. Its presence in the natural state in all beef fats makes it necessary for the court to decide how much natural yellow color is permissible under the law. The points for the chemist to determine in the case of suspected samples of oleomargarine are: (1) whether the oleomargarine has admixed with it sufficient butter to give it the color found, and (2) whether the color is natural to the fat, or has been added. The material presented in this paper was the result of an effort to arrive at a satisfactory answer to the second of these questions in the case of several suspected samples of oleomargarine.

#### EXPERIMENTAL

Satisfactory tests for most of the permissible dyes and vegetable pigments, including annatto, are given in all the text-books dealing with food analysis, and also in the official methods of the Association of Official Agricultural Chemists. Although a negative test for the usual artificial pigments employed in butter coloring would probably permit the conclusion that the coloring matter present was natural to the butter or oleomargarine, no simple, direct test for the natural pigment of animal fats is given.

Leach,<sup>1</sup> however, gives two tests for the detection of the coloring matter of the carrot when added to butter or oleomargarine; *i. e.*, Cornelison's<sup>2</sup> and Moore's<sup>3</sup> tests. Inasmuch as the carotin of butter and beef fat is now known to be chemically and physiologically identical with the carotin of carrots, one of two conclusions seemed obvious: either (1) the natural carotin of butter and beef fat exists in a different state than carotin added artificially to these fats,

or (2) the tests are not specific for added carotin, as they are supposed to be.

#### CORNELISON'S TEST

Cornelison's test consists of shaking 10 g. of fat with 10 to 20 g. of 99.5 per cent acetic acid and adding a few drops of concentrated nitric and sulfuric acids, respectively, to 5 cc. portions of the clear acid extract. According to Leach, this test applied to natural yellow butter gives a colorless extract, which remains colorless on adding nitric or sulfuric acids, while the acid extract from butter colored with carrot color is yellow, and remains yellow on addition of the nitric acid, but with sulfuric acid gives a pink color on standing.

Reference to Cornelison's original article shows that the statement in Leach does not agree with the results stated by Cornelison in one very essential point, namely, that although Cornelison found the acid extract of natural butter to be colorless and to be unaffected by nitric acid, when treated with sulfuric acid the same faint pink coloration resulted as in the case of the extract of butter colored with carotin from carrots. Leach's statement of Cornelison's tests is further contradicted, and Cornelison's results substantiated by the following experiment:

Ten cc. portions of natural yellow butter fat and colorless oleomargarine fat, colored with carotin from carrots,<sup>1</sup> were shaken in separatory funnels with 10 to 20 g. of 99.5 per cent acetic acid. The acid layer was drawn off when it became perfectly clear on standing. It had a faint yellow color in each case, that from the oleomargarine possibly being a little more intense than that from the butter, due undoubtedly to the somewhat greater original color of the oleomargarine. The addition of 3 drops of concentrated nitric acid to 5 cc. of each extract completely destroyed the yellow color. The addition of 3 drops of concentrated sulfuric acid to 5 cc. of each extract produced a faint pink color, which, on standing for a few minutes, persisted for some time.

#### MOORE'S TEST

Attention was next directed to Moore's test. The conclusion that would be drawn from the statement in Leach in regard to this test is that it was devised as a modification of Martin's<sup>2</sup> general test, making it applicable as well for the detection of carotin. Leach states that "Carotin (the coloring matter of the carrot root) does not impart its color to the alcohol layer in Martin's test." "Moore has pointed out this exception, and shown that with carotin present, the alcohol layer in Martin's test remains colorless as in the case of uncolored butter." Reference to the original papers by Martin and Moore makes it difficult to understand how this conception of the relation between the two tests could have arisen. Mar-

<sup>1</sup> This was done by contact of the rendered, melted oleomargarine with dried carrot pulp for several hours, with frequent shaking. The fat was filtered before using.

<sup>2</sup> Edward W. Martin, "Detection of Artificial Coloring Matter in Butter Oleomargarine, Fats, Oils, etc.," *Analyst*, **12** (1887), 70. Five grams of fat are shaken with 25 cc. of a reagent made by mixing 15 parts alcohol and 2 parts carbon disulfide. The alcohol layer which separates on standing contains any artificial coloring matter present in the fat.

<sup>1</sup> Albert E. Leach, "Food Inspection and Analysis," 3rd Ed., by Andrew J. Winton, 1914, 536, 537. John Wiley & Sons, New York.

<sup>2</sup> R. W. Cornelison, "A Method for Detecting Synthetic Color in Butter," *J. Am. Chem. Soc.*, **30** (1908), 1478.

<sup>3</sup> Russell W. Moore, "A Test for Carrot Color in Butter," *Analyst*, **11** (1886), 163.



tin's test, which is given by Leach, was in reality published a year later than Moore's test, and was, moreover, a modification, making Moore's test applicable to the detection of a number of coloring matters, such as annatto, turmeric, aniline yellow, naphthol yellow, etc., and also included carotin. Martin states this specifically, and, in addition, states that "the natural color of fats, oils, butter, etc., in no instance colored the alcohol." However, reference to Moore's original paper shows that his test was, in a certain sense, a modification of an earlier test by Martin<sup>1</sup> for detecting annatto in oils and fats, in which the annatto is extracted from the fat with dilute caustic alkali.<sup>2</sup>

Martin's general test for artificial coloring matter has undoubtedly proved a useful one for the preliminary detection of the presence of artificial pigments.<sup>3</sup> Martin's test is not applicable, however, to the detection of either natural or added carotin in fat. Leach is correct in his statement in regard to this, but not in his statement that the exception for added carotin was pointed out by Moore.

Moore's test for added carotin in butter fat and other fats, as given in the original article, is to dissolve 10 g. of fat in barely sufficient carbon disulfide, and to add to this 20 cc. of 90 per cent alcohol. A drop of dilute ferric chloride solution is now added and the tube containing the whole shaken. According to Moore, in the case of lard colored artificially with carotin from carrots<sup>4</sup> the addition of the ferric chloride caused the alcohol layer to "absorb the color from the carbon disulfide layer until the tints of the two layers were reversed," while "natural butter, without artificial coloring matter, will not be decolorized by this treatment even after standing for several days." Moore states that he obtained the same results with beef fat, mutton fat, olive oil, and lard, colored by warming them for several hours in contact with ground carrots, as he did in the case of the lard tested as noted above. No mention is made, however, of trying the test on butter fat colored by carotin in this manner, the assumption being that the action would be similar.

To anyone familiar with the properties of carotin, particularly its relative solubility in different solvents, the principle which is supposed to be the basis of Moore's test is at once seen to be open to question. One of the well-established properties of carotin is its much greater solubility in carbon disulfide than in alcohol. That the mere addition of a drop of dilute ferric chloride solution should cause a reversion of this property would be questionable even if the carotin were merely dissolved in carbon disulfide; that this should occur when the matter is further compli-

cated by the incorporation of the carotin in fat would be even more questionable.

Several preliminary trials of Moore's test were made on butter fat with a natural yellow color. The results differed from Moore's in two respects: (1) the test was found to be specific for the carotin of natural yellow butter; (2) the phenomenon involved in the test was found to be merely a complete decolorization of the pigment in the fat, and not a transfer of the carotin from the fat to the alcohol layer. Although the alcohol layer had a yellowish tint at the conclusion of the tests, no carotin was found to be present. An attempt to recover carotin as unsaponifiable matter, after saponification of the fat which was in solution in the alcohol, gave negative results. The yellow color of the alcohol layer, which led Moore to believe that carotin had been extracted by the alcohol and ferric chloride, is undoubtedly caused by the ferric chloride itself. Moore, himself, stated that the pigment in the alcohol layer in his test failed to give a green coloration with ferric chloride,<sup>1</sup> which is one of the properties of carotin given by Husemann.

Carotin is an unsaturated hydrocarbon and loses its color on oxidation. Dissolved in fat, however, it is very stable towards all the ordinary laboratory reagents, such as most metallic salts, alkalies, dilute acids, both mineral and organic, and glacial acetic acid. That it should be decolorized so readily in Moore's test through the agency of the ferric chloride seemed worthy of more extended study. Numerous tests on samples of butter fat with a natural yellow color showed that the decolorization of the carotin could be brought about much more readily if a better contact was secured between the carotin and the ferric chloride than is given by Moore's test. For example, 1 or 2 drops of 1 per cent aqueous ferric chloride solution added to a solution of 5 cc. of fat in 25 cc. of hot absolute alcohol caused an almost instantaneous decolorization of the fat, which separated colorless when the alcohol cooled, or if sufficient water was added to cause the separation to take place. Especially striking, however, was the reaction which was found to take place when a very small crystal of pure ferric chloride was added directly to 5 cc. of hot, melted fat. On shaking, the ferric chloride dissolved in the fat, and the yellow color was rapidly replaced by a beautiful green color. When the fat was shaken with 10 cc. of methyl or 95 per cent ethyl alcohol the green color was extracted and the fat was found to have been completely decolorized. If more ferric chloride was added than necessary to decolorize the fat, the green color did not appear; instead, the fat remained yellow, due to the excess ferric chloride in solution. On extracting this with alcohol the fat was found to have been decolorized, the ferric chloride going into the alcohol layer and the fat separating colorless.

The green coloration seen in the above test was

<sup>1</sup> It seems probable that Moore's test grew out of his attempt to test for carotin with ferric chloride, according to its property (as stated by Husemann) of giving a green coloration with this reagent when in alcoholic solution. Instead, he got a decolorization of the fat. Moore does not state the origin of the test in his original paper.

<sup>1</sup> Edward W. Martin, "Detection of Annatto in Butter, etc.," *Analyst*, 10 (1885), 163.

<sup>2</sup> This method is still in common use for extracting annatto from fats.

<sup>3</sup> The use of ether, acetone, etc., in the place of ethyl or methyl alcohol in the reagent, as suggested by Martin in his original paper, would not be possible if a separation of the fat from the solvent is desired, because the reagent made with either, acetone, or other fat solvents would dissolve the fat or oil completely.

<sup>4</sup> Prepared according to Husemann's method. August Husemann, "Ueber Carotin und Hydrocarotin," *Liebigs Ann.*, 117 (1861), 200.

found to be due to the ferrous chloride formed from the ferric chloride by the reducing action of the carotin, the carotin, at the same time, being oxidized and decolorized. Ferrous chloride solutions are characterized by their green color, as is well known. Husemann<sup>1</sup> first pointed out that carotin has an action on ferric chloride, when he recorded his observation that "Eisenchloride erteilt der weingeistigen Lösung eine bei auffallendem Lichte grünlich erscheinende dunklere Färbung." He obviously overlooked the decolorization of the carotin in the test, and also that alcohol itself reduces ferric chloride, methyl alcohol solutions being especially characterized by their green color. We have found that the reduction of ferric chloride to ferrous chloride by carotin may be strikingly shown by dropping a crystal of the ferric salt on a freshly prepared amorphous residue from the chloroform extract of carrot pulp. The ferric chloride turns a beautiful green; and the aqueous solution of the reduced iron salt gives a strong test for ferrous ions on addition of potassium ferricyanide, care being taken that the ferric chloride used alone shows no precipitate of "Turnbull's blue" on addition of the ferricyanide. The yellow carotin residue, to which the ferric chloride is added, is seen to be colorless when the ferrous chloride is washed off with water, in which carotin is insoluble.

With Moore's tests so greatly simplified, and the basis of the reaction established, attention was directed to showing whether carotin added artificially to fat would act differently from the carotin natural to fat. For this purpose butter fat naturally nearly free from carotin and rendered fat from white oleomargarine were colored by warming the melted fat with carrot pulp,<sup>2</sup> with frequent shaking. The yellow fats prepared in this way, together with freshly rendered Jersey-cow body-fat, which had a high natural yellow color, were subjected to Martin's test, to Moore's test as given by Leach, and also to the several modifications of this test mentioned above. Identical results were secured in each test with all the fats. Martin's test failed to extract the carotin, but the ferric chloride caused a decolorization in all the tests in which its use was involved. The green coloration of the fat, when just sufficient ferric chloride was added directly to the fat to cause the oxidation of the carotin, was just as striking in the cases of added carotin as in the cases of the fats naturally colored by this coloring matter. The conclusion drawn from these results was that it is not possible to differentiate by this method between the carotin natural to butter fat and beef tallow (oleomargarine) and carotin that has been added artificially to these fats.

It was found possible, however, to detect the presence of both carotin and other pigments, such as annatto, when present in the same fat. This is due to the fact that annatto and all other pigments not natural to fat can be practically quantitatively extracted from fat by Martin's method if the fat is

shaken with several successive portions of Martin's reagent. Several tests of this character were made, and it was found that when the extract was no longer colored in Martin's test any coloring matter that remained in the fat could be readily identified as carotin by the modified Moore's test. Annatto, which belongs to the same class of vegetable pigments as carotin, was also found to be decolorized by ferric chloride. When dissolved in fat, however, its oxidation was not found to be as rapid as that of carotin. The very fact that it does respond to the same test, however, makes its extraction from the fat by Martin's or some other reagent necessary before testing for the presence of carotin.

#### AUTHOR'S TEST

The following method, summarizing what has been given above, is recommended for the detection of artificial and natural (carotin) pigments in butter fat and oleomargarine.

Shake 10 cc. of rendered, melted fat with successive 25 cc. portions of Martin's reagent (15 parts 95 per cent alcohol and 2 parts carbon disulfide) until no more color is extracted. Test the extracted coloring matter for annatto or other pigments by one or more of the approved methods. Drain off *all* of the alcohol from the fat, and test the pigment remaining in the fat for carotin by adding a small crystal of pure ferric chloride to the hot, melted fat. After thorough shaking, extract with 10 cc. of methyl or 95 per cent ethyl alcohol. If the pigment was carotin the fat which separates will, when melted, be seen to be completely decolorized. If just sufficient ferric chloride is added to cause complete decolorization the ferrous chloride formed will impart a beautiful green color to the fat.

#### DISCUSSION

One of the most interesting results of this brief study is the impossibility of differentiating between the natural yellow coloring matter of butter fat and beef tallow, and the same coloring matter added artificially to these fats. The conclusion that would naturally be drawn from this result is that the carotin of butter fat and beef fat exists there in simple solution. The question of how this pigment exists in animal fats was not investigated in the studies of the general question of yellow animal pigments recently published by one of us.<sup>1</sup> The assumption was that a simple solution of the pigments existed in the fats. That assumption seems to be substantiated by the tests made in the present study.

Mention of the fact that the carotin natural to butter fat and beef fat has a small amount of xanthophyl associated with it has been purposely avoided throughout the paper for fear of confusing the main problem. Although xanthophyl is abundant in all vegetable matter containing carotin, it comprises such a small proportion of the total coloring matter of butter fat and beef fat, even under the most favorable conditions, that it can be practically left out of consideration. Moreover, xanthophyl appears to be as completely decolorized by ferric chloride as carotin. The

<sup>1</sup> *Loc. cit.*, p. 226.

<sup>2</sup> Some carrots were peeled, ground up, and boiled with water. The pulp was pressed, dried, ground up as finely as possible, and used for coloring the fat.

<sup>1</sup> Leroy S. Palmer and C. H. Eckles, *loc. cit.*



existence of xanthophyl to an appreciable extent in carrots and the ready solubility of xanthophyl in fat makes it reasonably certain that it was present in the fat in the cases of artificial coloration with carotin, in which as complete oxidation of the pigments by the ferric chloride resulted as in the cases involving the natural pigment only.

From the viewpoint of the analyst it is unfortunate that it does not appear possible to detect the presence of carotin added artificially to butter fat or oleomargarine. This conclusion may be a hasty one, however. Although it will probably never be possible to differentiate between natural and added carotin in fats, it may be possible, should the food laws ever require it, to tell whether carotin has been added to fat. While no attempt has been made to work out any tests in this connection it is suggested that the possibilities of determining whether carotin has been added lie in the fact that xanthophyl is naturally present in animal fats in very small proportion of the total pigment, while it is present in much greater proportion in all the vegetable matter containing carotin which might be used as a source of carotin for the artificial coloration of fat; furthermore, it would not be possible to extract the carotin from these sources without, at the same time, extracting the xanthophyl. Accordingly, butter fat or oleomargarine containing added carotin would likewise contain a much greater proportion of xanthophyl than is natural to these fats. It is doubtful if any simple test can be devised for determining the relative proportion of carotin and xanthophyl in fat. The solution of the problem would probably have to involve a separation of the total pigment from the fat and a subsequent separation of the extracted pigment into its carotin and xanthophyl portions by means of one of the relative solubility properties of these two classes of pigments. These properties are discussed fully in the studies on animal pigments previously published from this laboratory. As the question is not one of immediate moment the reader interested in the question is referred to the publications mentioned.

The strong reducing action of carotin on ferric chloride, which is the basis of the method for the detection of carotin, suggested that other reducible ferric salts might be similarly affected and accordingly serve equally well for the detection of carotin. This was found to be the case. Ferric nitrate was found to oxidize and decolorize carotin in butter fat but the test using this salt could not be simplified as in the case of ferric chloride, owing to the insolubility of ferric nitrate in fat. It was found necessary to add some reagent which would dissolve both the fat and the ferric nitrate, such as acetone. No green coloration accompanied the decolorization of the carotin in this test, but instead there was a suspension of a reddish brown iron oxide formed from the ferric nitrate.

#### SUMMARY

I—It is pointed out that the detection of carotin (the natural yellow pigment of animal fats) in oleo-

margarine is made necessary by the oleomargarine laws of many states.

II—Cornelison's test for carotin artificially added to fat is shown to be quoted wrongly in Leach's "Food Inspection and Analysis."

III—The relation between Martin's test for artificial pigments in fats and Moore's test for carotin added artificially to fat, as given in Leach's "Food Inspection and Analysis," is shown to be confused, and the true relation is pointed out.

IV—It is shown that Moore's test for carotin in fat or oleomargarine is not alone specific for carotin added artificially, but is equally specific for the carotin natural to animal fats.

V—It is shown that the carotin is not dissolved out of the fat in Moore's test, as stated by Moore, but is merely decolorized by the ferric chloride added. The reaction involved is shown to be a reduction of the iron and the simultaneous oxidation of the carotin.

VI—Modification and improvements in Moore's tests are given. A method is also suggested for detecting both natural and artificial pigments (other than carotin) in the same fat.

VII—The relation of Moore's test to the question of the natural state of carotin in fat, and the possibility of determining whether carotin has been added to butter fat or oleomargarine are discussed.

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## CULTIVATION AND CANNING OF MANGOES IN INDIA

By TARINI CHARAN CHAUDHURI<sup>1</sup>

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The mango tree, *Mangifera indica*, is a large evergreen and native of the south of Asia. It grows in the Tropical Himalayas at 1,000 to 3,000 ft. above sea level, from Kumaun to Bhutan, Bengal and Southern India. It has been known and cultivated all over India from very remote ages. It is profusely connected with Sanskrit mythology and some religious rites of the Hindus and finds a place in the old Hindu tales and folklore. Mention is made of it by most of the foreign travelers in India. F. Jordanus notes the remarkable quality of the fruit about 1328 A. D., and Baber, the founder of the Moghul Empire in India, speaks of the excellence of the mango. Later on, Gracia de Orta, in the year 1563, states that the fruit is so delightfully tasteful and highly refreshing that, when in season,<sup>2</sup> no other fruit can sell. There are numerous varieties<sup>3</sup> of mangoes in India, the best and most widely grown being Fazlee, Langra and Bombay. The plants can be grown from the seed or stone of the fruit; but it is found that on the same soil the seedlings rarely produce fruit equal in size, taste and flavor

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<sup>2</sup> The general flowering period of mango trees is from December to February, and the principal ripening season for mangoes is from May to the middle of August. Watt, D. E. P., Vol. 5, 147.

<sup>3</sup> Woodrow, "The Mango, Cultivation and Varieties," II, 1911; Firminger, *Mango-Gard. Ind.*, 1904, 256-61.

to the parents. The usual method of cultivation and propagation is by *inarching*. Maries states that the best place for mango plantation is a raised, well-drained piece of land with a good depth of soil. The nature of the soil, however, does not appear to interfere much with the growth of the tree. It is found that in Bengal it succeeds equally well on a rich, deep, river deposit, on clayey or on sandy soil; while in Gwalior good trees are grown on *Kankara*—a soil with a large proportion of lime or stone nodules.

For purposes of inarching, the stones of the fruit when the mango is ripe in season are usually sown, and when the plants have become one year old, they are potted out to be grafted by inarching with desirable trees. This is done during setting-in of the rains in the second year of the growth of the seedling, the union being usually complete at the growth of the rainy season. The essential principle in this method of grafting consists in bringing the cambium of the stock and the scion together before the graft is completely severed, the parts being fastened carefully so as to exclude air and water and to keep the plant and the mother tree healthy during the short growing period. It is to be noted that the scion and the stock should be of the same thickness. The best season for planting out the young grafts is in the early part of the rainy season. Firm states that shade is necessary during the following six months, and the intervening land between the rows of grafts is cultivated with moderate irrigation and rich manuring and crops grown until the mango trees have attained the flowering size. Generally speaking, in five years the trees should bear a considerable quantity of fruit.

The principal localities in India where good mangoes are said to be produced are Mazagon in Bombay and Durbhanga; but the finest varieties of the fruit in extensive scale are grown at *Malda in Bengal*. In Assam, on the other hand, the fruit ripens very badly and is extremely diseased, the mango weevil being very destructive to the fruit.<sup>1</sup>

Besides being eaten as a ripe fruit in India, numerous preparations are made of it. When green, it is peeled, cut into slices, and after removing the stone, it is put into curries or made into sauces, chutnies or pickles of various kinds. When young and green it is boiled, strained, mixed with milk and sugar and thus prepared as the custard, known as *mango-phul*. When it is cut into pieces and dried, it is known as Indian *amchoor*; and when very young, small pieces are taken in salad. So, also, ripe mango is used in curries and salads; and the mango juice, expressed and dried in thin cakes, is known as Indian *amsath*. In recent years, pickles and chutnies are largely exported to Europe, Africa and elsewhere. Watt believed that if mangoes, in fresh condition, could be conveyed cheaply into England, a trade as extensive as the fruits of the West Indies might be immediately anticipated.<sup>2</sup>

The use of this fruit cannot be considered as a mere

luxury. It is thought to be a necessity by medical authorities from medicinal and dietetic points of view. In medicine, the ripe fruit is considered invigorating, fattening, laxative and diuretic. It is a current view that in many cases fresh ripe mangoes, eaten in large quantities, give rise to troublesome boils, and on abstaining from taking mangoes, the eruptions heal up. Gibson and Issabella, of the Medical College in the Philippine University,<sup>3</sup> conclude that if a mother eats sufficient mangoes, the boils appear in her sucking infant, the cause being mainly attributed to the richness of the gums in mango juice.

The present writer has examined the Bengal mangoes both as regards their gum content and physiological influence. The juice of this fruit contains a small percentage of gums and is rich in sugar. In 63 cases of men, women and children, who were overfed with mangoes (Fazlee and Langrah) for 7 days, not one case of eruption occurred. These two varieties of mangoes, especially preserved in pure sugar syrup, while possessing all the medicinal and dietetic value, is absolutely free from any such objection.<sup>2</sup>

The modern methods of preserving fruit may be briefly classified under five heads: (1) heat or cold storage; (2) drying; (3) excluding air; (4) adding a third substance which acts as a preservative; (5) pickling in suitable liquors.

Each of these methods, considered individually, is unsatisfactory for preserving mangoes. Sometimes the combination of (3), (4) and (5) is applied. But the aim of scientific canning is not only to preserve the fruit but to retain all the delicacies of the fresh ripe fruit, *viz.*, the natural color, taste and flavor. To preserve the mango with all its delicacies requires a thorough familiarity of the character of the fruit and also the climatic condition of the country where the preserves have to be stored, for the selection of the proper process depends roughly on these factors. It has been found that no cut-and-dried process or combination of processes can preserve the mangoes in fresh condition. The writer announces that with regard to mangoes, which are sensitive fruits, he has been successful almost to the ideal standard by first sorting the ripe fruit suitable for canning and estimating its degree of sweetness and then determining the strength of the crystalline sugar syrup which has to be so regulated that it does not impart any additional artificial sweetness to the fruit. A different temperature is also used for different varieties of mango, according to the durability of the flavor and stiffness or softness of the slices. In this process no preservative substance which may act prejudicially on the fruit, immediately or after a period of storage, is used.<sup>3</sup>

GHORAMORA,<sup>3</sup> RAJSHAH, INDIA

<sup>1</sup> *The Philippine Journal of Science*, 1915.

<sup>2</sup> In Malda, the poor people, as a matter of moral right, live almost exclusively on mangoes of the garden owners. On inquiry the writer has almost no information of pimples, boils or cancers, excepting the usual stray cases.

<sup>3</sup> The Hindustan Fruit Preserving Co., Malda, Bengal (India), are now working on these lines.

<sup>1</sup> M. Lefroy, *Agr. J. India*, I, II, 164.

<sup>2</sup> Watt, C. P. I., 1908, 765.



THE INHIBITING ACTION OF CERTAIN SPICES ON THE GROWTH OF MICROORGANISMS<sup>1</sup>

By FREDA M. BACHMANN

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A laboratory study of the preservative action of spices was first made by Hoffman and Evans in 1911. They reported that as a result of their experiments they found certain spices to have considerable antiseptic properties. They found cinnamon most effective in inhibiting the growth of organisms; cloves and allspices next in effectiveness; and the other spices of little value as preservatives. They used pure cultures of some of the bacteria and yeasts, but depended on chance inoculation for mold growth. Apple sauce, to which varying amounts of spice were added, was exposed for several days. The yeasts and bacteria were grown in sterile broth to which cinnamic aldehyde, eugenol, or benzoic acid was added. The present work was undertaken to confirm the results of Hoffman and Evans and to collect more data on the subject.

## METHOD

For the greater part of the work, pure cultures of organisms were used. Species of the common molds, *Rhizopus*, *Penicillium*, *Aspergillus*, and *Alternaria*, which are frequently found on spoiled preserves, and of the bacteria, *B. coli*, *B. prodigiosus*, and *B. subtilis*, were the organisms used in most of the experiments. The *Aspergillus* was obtained from tomato butter which had spoiled; the *Penicillium* from a growth on canned peaches.

For the greater part of the work, agar has been used as a nutrient medium. The molds grow best on Thaxter's potato hard agar, which consists of potato broth with 3 per cent agar and 2 per cent glucose. The bacteria were grown on ordinary nutrient agar. The spice in some form was introduced into the agar before it solidified. To compare readily the growth on a spiced medium with that on a medium without the spice, it was found convenient to use some kind of a double plate. The double plate described by Frost<sup>2</sup> in his studies on antagonism of organisms was first used. Here the Petri dish is divided through the center by a glass rod which is sealed to the bottom of the dish by means of collodion. It is then sterilized. The one objection to this method for the present studies is that in sterilization the collodion sometimes shrivels to such an extent that the rod is no longer well sealed to the plate, so that some of the agar poured in on one side is likely to run underneath the rod into the opposite side of the dish. A modification of this method seemed desirable.<sup>3</sup> For studying the amount of diffusion, it was found satisfactory to cover one-half of the bottom of the Petri dish with a piece of cheese-cloth and then sterilize the dishes. Agar containing no spice was then poured into the dish and when solid, the cloth with the ad-

herent agar removed by means of a sterile forceps, thus leaving agar on only one-half of the plate. The spiced agar was then poured into the side opposite the plain agar. In such plates, whatever inhibition of growth there is on the side where there is no spice is due to the amount of spice which diffuses through the medium and to whatever volatilizes. To distinguish between diffusion and volatilization in inhibiting growth, it was necessary to use still another kind of double plate, one in which there could be no diffusion through the medium. Small, thin glass watch crystals were sterilized in the Petri dishes and later the spiced agar poured into the watch crystal and the plain agar in the Petri dish. In plates prepared in this way the inhibition of growth on the plain agar could be due only to the amount of spice which volatilizes. The organisms have also been grown on spiced agar slants and in spiced bouillon. The latter is not always very desirable because the spice may cause a cloudiness which makes a very small amount of growth difficult to detect. Cooked apples to which spice, or vinegar, or both, were added, have also been used as a medium.

Spice was introduced in the form of ground spice, the alcoholic extracts, the essential oils, and the active principles. The ground spice and the alcoholic extracts were introduced directly into a definite amount of agar. The essential oils and the active principles were diluted with water. Amounts of this emulsion were introduced into the liquefied agar. The emulsion was very thoroughly shaken each time before transferring any of it to the agar.

To inoculate the plates with molds, a suspension of the mold spores in sterile water was streaked across the agar with the platinum loop. In this way a very even amount of growth was obtained all along the streak in the control plates. However, in order to make certain that a greater amount of growth on the side farthest from the spiced agar would not be due to heavier inoculation, the streak was made by drawing the loop from the center to the circumference, thus placing the greater number of spores near the spice. All the cultures have been grown at room temperature.

## EFFECT OF ALCOHOLIC EXTRACTS OF SPICE

The alcoholic extracts were prepared by the laboratory of pharmacy. The spices were extracted with alcohol and the extract evaporated so that 1 cc. of the extract represented 1 g. of the spice. Controls in which the same amount of 95 per cent alcohol was used were made for comparison. The results given in Table I are from plates where the spiced and unspiced agar were in contact and were taken one week after inoculation.

There is considerable difference in the amount of spice which prevents mycelial growth and the amount preventing germination of spores. Frequently in plates in which the agar in one-half of the dish contained sufficient alcoholic extract of a spice to prevent germination of the spores, the mycelium which had covered the side without spice grew readily across

<sup>1</sup> Published with permission of the Director, Wisconsin Experiment Station.

<sup>2</sup> William D. Frost, "The Antagonism Exhibited by Certain Saprophytic Bacteria against the *Bacillus Typhosus* Gaffky," *J. Inf. Dis.*, **1** (1914), 641.

<sup>3</sup> W. D. Frost and Freda M. Bachmann, "Another Use of the Double Plate Method," *Science*, N. S., **43** (1916).

the center over the spiced agar. This is indicated in the accompanying tables by the abbreviation "myc." The amount and kind of growth on the spiced agar is

TABLE I

The plus (+) sign indicates growth, and zero (0) no growth. The abbreviation "myc" indicates that when mycelial filaments were used for inoculation a growth of the mold resulted, but that the same amount of spice prevented germination of the spores. The negative results in the columns marked "No" are due to the diffusion and volatilization of the spice on the opposite side of the plate, i. e., on the side containing the spice.

ORGANISM	DILUTION	CINNAMON		CLOVES		MUSTARD		ALCOHOL	
		No	Yes	No	Yes	No	Yes	No	Yes
<i>Rhizopus</i> .....	1:7	0	0	0	0	+	0	+	0
	1:14	+	myc	+	0	+	+	+	+
	1:70	+	+	+	0	+	+	+	+
	1:140	+	+	+	myc	+	+	+	+
	1:700	+	+	+	+	+	+	+	+
<i>Aspergillus</i> .....	1:10	0	0	+	+	+	+	+	+
	1:100	+	+	+	+	+	+	+	+
	1:200	+	+	+	+	+	+	+	+
<i>Penicillium</i> .....	1:7	0	0	0	0	+	+	+	+
	1:70	+	myc	+	0	+	+	+	+
	1:140	+	+	+	0	+	+	+	+

entirely in proportion to the amount of spice used. Where the mycelium has grown over the spiced agar from the side without the spice, the growth is frequently not so thick, but otherwise appears to be fairly healthy and produces abundant fruiting branches. Where there is more spice the growth is thin, much stunted and in *Rhizopus*, no sporangia are formed.

That there is considerable diffusion of the spice in the form of alcoholic extracts is evidenced by the amount and shape of the growth on the non-spice side. It will be seen from Table I that where a 1:7 or 1:10 dilution of cinnamon or cloves in agar was used, there was no germination of spores even on the side containing no spice. With 1:14 dilution of cloves on one side, there was germination of the spores of *Rhizopus* only farthest from the spice agar and the resulting growth was crowded near the rim of the Petri dish (Fig. I). With somewhat less spice, as in a dilution of 1:70 of extract of cloves, the growth



FIG. I. Petri dishes. Each contains two kinds of agar. S-side contains spiced agar. Broken line shows line of inoculation. m, mold growth

of *Rhizopus* on the non-spiced side is triangular, tapering toward the center as shown in Fig. II. If the interference with growth on the non-spiced side were due for the most part to the volatilization of the spice on the opposite side, it would seem that the limited growth which does occur would not always have this triangular shape, nor would it be so crowded toward the rim of the Petri dish farthest from the spiced agar.

There is considerable difference in the sensitiveness of any one mold to the different spices. The extract of cloves, according to Table I, is seen to be ten times as efficient as cinnamon in inhibiting the growth of *Rhizopus*. Mustard in alcoholic extract appears to

be of little value in inhibiting the growth of any of these molds. There was very little difference between the plates in which alcohol and those in which alcoholic extract of mustard was used. It is also evident from Table I that there is considerable difference in the sensitiveness of different molds to the alcoholic extract of any one spice. *Rhizopus* is very much less sensitive than either *Aspergillus* or *Penicillium* to the extract of cinnamon. *Penicillium*, on the other hand, is more sensitive to the extract of cloves than *Rhizopus*.

## EFFECT OF GROUND SPICE

To determine the effect of ground spice, a weighed amount of the spice was introduced into a definite quantity of agar and then sterilized. The spiced agar was then poured into a watch glass set in a Petri dish. Agar without spice was poured into the Petri dish around the watch glass. Bacteria or mold spores were placed on the spiced agar and on that without spice. The antiseptic properties of cinnamon, cloves, allspice, and nutmeg were tested with the organisms noted in Table II:

TABLE II—RESULTS ONE WEEK AFTER INOCULATION

ORGANISM	DILUTION	CINNAMON		CLOVES		ALLSPICE		NUTMEG	
		No	Yes	No	Yes	No	Yes	No	Yes
<i>Alternaria</i> ...	1:25	+	0	+	0	0	0	+	+
	1:50	+	0	+	+	+	0	+	+
	1:100	+	0	+	+	+	+	+	+
<i>Penicillium</i> ...	1:25	+	0	+	0	0	0	+	+
	1:50	+	0	+	+	+	0	+	+
	1:100	+	0	+	+	+	+	+	+
<i>Rhizopus</i> ....	1:25	+	+	+	0	0	0	+	+
	1:50	+	+	+	+	+	myc	+	+
	1:100	+	+	+	+	+	+	+	+
<i>Aspergillus</i> ...	1:25	+	0	+	0	+	0	+	+
	1:50	+	0	+	+	+	+	+	+
	1:100	+	0	+	+	+	+	+	+
<i>B. prodigiosus</i>	1:25	+	+	+	0	+	0	+	+
	1:50	+	+	+	+	+	0	+	+
	1:100	+	+	+	+	+	+	+	+
<i>B. coli</i> ....	1:25	+	0	+	0	+	0	+	+
	1:50	+	+	+	+	+	0	+	+
	1:100	+	+	+	+	+	0	+	+
<i>B. subtilis</i> ...	1:25	+	0	+	0	+	0	+	+
	1:50	+	0	+	0	+	0	+	+
	1:100	+	+	+	0	+	0	+	+

Cinnamon appears to have more antiseptic properties generally than either allspice or cloves. Cinnamon has little antiseptic value toward *Rhizopus*, but is valuable in preventing the growth of *Alternaria*, *Penicillium*, and *Aspergillus*. Cloves are about as effective as allspice for *Rhizopus* and *Aspergillus* but somewhat less so for *Alternaria* and *Penicillium*. Nutmeg has little or no value as a preservative even in large amounts. *B. prodigiosus* appears to be only slightly sensitive to spices, while *B. subtilis* did not grow on even a 1:100 dilution of cloves and of all-spice.

## EFFECT OF SPICE AND VINEGAR

To determine the effect of vinegar and vinegar and spice and sugar, steamed apples were half covered with:

- (1) Vinegar, Sugar, and Cinnamon in such amounts as could be used in spicing apples
- (2) Vinegar and Cinnamon
- (3) Water, Sugar, and Cinnamon
- (4) Water and Cinnamon
- (5) Water
- (6) Vinegar
- (7) Vinegar, Sugar, Cinnamon, and Cloves
- (8) Vinegar, Cinnamon, and Cloves
- (9) Water, Sugar, Cinnamon, and Cloves



The same proportion of spice and vinegar or spice and water was used in each tube. The material was then inoculated with mold or yeast. After one week there was a good growth of mold in 3, 4, 5 and 9, that is, in all the tubes except those containing the vinegar. The vinegar was not diluted and contained 5.9 per cent acetic acid. The apples, after standing in the vinegar, spice, and sugar for 6 weeks, were not too sharply acid to taste well, so it does not seem that the vinegar was stronger than might often be used in spicing fruit. However, it is evident that in these tubes the vinegar was the preservative, rather than the spice. The formation of gas bubbles in the tubes without vinegar indicated the growth of the yeast in those tubes. The amount of cinnamon and cloves used, although sufficient for flavoring purposes, served to retard only slightly the first growth of molds and yeasts.

#### EFFECT OF CINNAMIC ALDEHYDE AND EUGENOL

In Table III are the results of experiments using the active principles of cinnamon and cloves, cinnamic aldehyde and eugenol. These substances were diluted with water, the mixture thoroughly shaken and some of this emulsion introduced into melted agar, which was then poured into plates. The data are based on growth on spiced agar slants in test tubes and in plates divided with watch glasses. The growth on the spiced agar in test tubes and in plates was the same in each experiment and hence but one column is necessary to indicate the growth in both. In the first column under each spice are the results of inoculating the agar without spice in the Petri dish. The negative results in these columns are due to volatilization of the spice in the watch glasses.

TABLE III—RESULTS NINE DAYS AFTER INOCULATION

ORGANISM	DILUTION	CINNAMIC ALDEHYDE		EUGENOL	
		No	Yes	No	Yes
<i>Rhizopus</i> .....	1:2000	+	0	+	myc
	1:5000	+	myc	+	+
	1:10000	+	+	+	+
<i>Penicillium</i> .....	1:2000	0	+	+	+
	1:5000	0	0	+	+
	1:10000	0	0	+	+
<i>Aspergillus</i> .....	1:2000	0	0	+	+
	1:5000	0	0	+	+
<i>Alternaria</i> .....	1:2000	+	0	+	0
	1:5000	+	myc	+	+
<i>B. prodigiosus</i> ....	1:1000	+	0	+	+
	1:2000	+	0	+	+
<i>B. coli</i> .....	1:1000	0	0	+	+
	1:2000	0	0	+	+
<i>B. subtilis</i> .....	1:1000	0	0	+	0
	1:2000	0	0	+	+

It is quite evident from the above that cinnamic aldehyde has strong antiseptic properties. It is not only effective when directly introduced into a medium, but the amount which volatilizes in dilutions up to 1:2000 is sufficient to inhibit the growth of *Penicillium*, *Aspergillus*, *B. coli* and *B. subtilis* on the agar without spice. There was no growth of *B. prodigiosus* on the agar containing cinnamic aldehyde in a dilution of 1:2000, yet after one week enough of the spice had volatilized so that when the plate was reinoculated a good growth resulted. The organism failed, however, to produce any pigment. The spores of *Aspergillus* failed to germinate on the agar without spice, but when after two days the spiced agar, dilution 1:5000, was reinoculated with mycelial filament, a fair amount of growth appeared. Eugenol

has much less value as an antiseptic. *Rhizopus* and *Alternaria* are more sensitive to it than any of the other organisms studied.

#### EFFECT OF THE OILS OF ALLSPICE AND NUTMEG AND THE OLEORESIN OF BLACK PEPPER

The oleoresin of black pepper was found to have no antiseptic value in dilutions of 1:200 for the molds and in dilutions of 1:1000 for the bacteria. The same is true of the oil of nutmeg except for *Rhizopus*, which did not grow in a dilution of 1:200 but grew well in a dilution of 1:500. The oil of allspice appears to have considerable value: *Rhizopus* spores failed to germinate in a dilution of 1:5000 but grew readily in 1:10000 dilution; *B. prodigiosus* and *B. coli* were not affected by it in dilutions of 1:1000; *B. subtilis* is more sensitive to it and did not grow when the dilution was 1:1000.

#### GENERAL OBSERVATIONS AND CONCLUSIONS

When plain and spiced agar are in contact there is always some diffusion of the spice, whether it is in the form of alcoholic extract, essential oil, or ground spice. There is also always a certain amount which volatilizes. In plates where the plain and spiced agar are in contact, the inhibition of growth of the organisms on the plain agar is partly due to both diffusion and volatilization of the spice. In such plates, when the amount of spice is great enough, the growth on the agar without spice is crowded near the edge of the Petri dish farthest from the spice, tapering along the streak with the broadest part of the growth farthest from the spice. This is true of both molds and bacteria but is more striking in the molds. The shape of this growth is due entirely to the diffusion of the spice. In plates where the spice is in watch glasses, so there can be no diffusion, the growth on the agar without spice may be more or less stunted but it is evenly distributed along the line of inoculation.

The amount of growth is dependent on the amount of spice used and in the case of molds on the material used for inoculation. The spores of *Penicillium*, *Aspergillus*, *Alternaria* and *Rhizopus* are much more sensitive to spice than the mycelium and fail to germinate, where if mycelial filaments are used for inoculation, a good growth results. The spores may push out stunted germ tubes no longer than the width of the spore or very often they fail to give any of the first indications of germination. There is no enlarging of the spore due to taking up water. From the practical side of food preservation this fact is of interest since chance inoculation is probably almost always due to spores. However, if the spice is not evenly distributed and the spores germinate in some part of a food material where there is less spice, the mycelium will readily grow over other parts and the food become covered with mold.

Frequently the amount of spice used is found to allow a good growth of the mycelium of molds, but to prevent sporulation, or at least only a few spores may be produced. The mycelium with more spice may be very poorly developed. This is very often found in *Rhizopus*. In such a growth there are many

protuberances on a hypha as if it had started to branch at various places: these are very irregular in shape but usually quite short and broad at some places and narrower in others: there is little protoplasmic content in the hyphae where the growth is considerably stunted. A number of scattered oil globules may be all that can be seen. There is no slimy protoplasm in many of the hyphae and the branches often appear to be merely empty cell walls. In other hyphae there is evident plasmolysis resulting in a shrunken protoplast. It has not been determined whether the morphology of the bacteria is changed when these are grown on or near a spiced medium. *B. prodigiosus* fails to produce any pigment if the amount of spice is large. Although several transfers of this colorless growth are grown on spice, when the organism is transferred again to a medium without spice, the pigment is produced as before.

It does not appear from the extent of the present study that spices, as used in the kitchen, in the usual amounts for flavoring purposes in spiced cakes, exert a very considerable preservative effect. Where cinnamon, cloves, and allspice are used in large amounts, the growth of molds may be retarded. In spiced fruit where a large amount of the spice is used, the preservative effect may be much greater. This effect may be greater too when the spice is combined with vinegar. It seems entirely possible, as suggested by Hoffman and Evans, that the active principles, at least cinnamic aldehyde, could be used in such dilutions as to prevent the growth of many microorganisms and yet in small enough quantities not to spoil the flavor of the product. Further studies on the action of spices on microorganisms are necessary before very positive and general statements of the practical value of them as preservatives can be made. Pepper and nutmeg have little effect on the growth of microorganisms. A mixture of nutmeg and water boiled for a half hour and left exposed to the air for chance inoculation was covered with various molds in less than a week. Cloves and allspice in large amounts are quite effective in preventing the growth of molds and bacteria, and cinnamon is the most effective of the spices; this is true of the ground spices, their essential oils, and the alcoholic extracts. The bacteria used in this study are less sensitive for the most part than the molds, but there is evidently considerable difference in the sensitiveness of various species of bacteria just as there is a difference in the sensitiveness of molds.

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## SEPARATION AND ESTIMATION OF POLYSULFIDES AND THIOSULFATE IN LIME-SULFUR SOLUTIONS

By S. D. AVERITT

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In recent years there have been quite a number of articles written on the composition and analysis of lime-sulfur solution. The writer first became interested in the problem in 1911 when he was Associate Referee on Insecticides for the Association of Official

Agricultural Chemists. Methods for the analysis of lime-sulfur solution were then being considered and coöperative work being done. The methods<sup>1</sup> proposed by the Referee at that time have since become known as the Zinc Chloride Methods.

In January of that year there was issued by the Michigan Agricultural Experiment Station a bulletin by J. E. Harris in which were published methods for the analysis of lime-sulfur solution since become known as the Iodine Methods.<sup>2</sup>

After having worked the two samples of lime-sulfur submitted for coöperative work by both methods it was found that there was a marked discrepancy between the thiosulfate figures by the two methods. One of the samples submitted was a straight lime-sulfur solution made with pure chemicals and the calcium calculated from the iodine titrations checked the determined calcium. The other sample had sodium thiosulfate added and the calculated and determined calcium would not check until the added sodium thiosulfate had been deducted from the thiosulfate figure.

In the case of the straight lime-sulfur solution, using the thiosulfate as determined by the proposed methods (zinc chloride) the calculated calcium would not check the determined calcium.

The proposed methods gave concordant results, however, and it was recommended that they be made official. This recommendation was approved for final action by the Association the following year.

The next year (1912), as Referee, the writer in his report<sup>3</sup> brought out the facts in regard to the two methods, having first satisfied himself that the iodine titration methods gave accurate results for thiosulfate.

The Association instructed the Referee to compare the two methods in 1913. This was done, and in his next report<sup>4</sup> more evidence was submitted in favor of the iodine titration methods. There was strong opposition<sup>5</sup> to the iodine methods, however, with the result that there are at this time no official methods for the analysis of commercial lime-sulfur solutions.

Taking the position that it is desirable that methods of analysis should not only be accurate but that they should possess in addition, workableness, freedom from tediousness, and as far as possible give at least a measure of insight into the character of the substance under examination, the writer in this paper hopes to make a contribution that will at least tend to solve the problems in the analysis of commercial lime-sulfur solutions.

The direct iodine titration of a lime-sulfur solution meets all of the above requirements, and while the zinc chloride methods may be so modified as to give accurate results, they can never be freed from tediousness and to the busy analyst this is an objection that

<sup>1</sup> Bureau of Chemistry, *Bull.* 152, p. 68.

<sup>2</sup> Michigan Experiment Station, *Tech. Bull.* 6.

<sup>3</sup> Bureau of Chemistry, *Bull.* 162, p. 27.

<sup>4</sup> *Jour. A. O. A. C.*, 1, No. 1, p. 50.

<sup>5</sup> Bureau of Chemistry, *Bull.* 162, p. 38; *Jour. A. O. A. C.*, 1, No. 1, p. 76.



weighs heavily against them. Consequently he will invariably resort to rapid methods even if their use involves a reasonably negligible loss of accuracy.

Without reviewing the substances that may possibly occur on boiling lime and sulfur of different degrees of purity in widely varying proportions with different kinds and amounts of water, it is sufficient to state that in commercial concentrates as sold upon the market the main constituents are calcium polysulfides and calcium thiosulfate. The other things are present in traces or very small quantities.

The total sulfur is easily and accurately determined, thus leaving the accurate determination of polysulfide and thiosulfate sulfur as the main problems. Of these, the determination of thiosulfate sulfur is the more important since with an accurate determination of total sulfur the polysulfide by difference is sufficiently accurate for all practical purposes.

A quick method for the determination of polysulfide is given and if the total sulfur is taken as the sum of polysulfide and thiosulfate, the analysis of a commercial lime-sulfur solution becomes a matter of two hours or less with a surprisingly small amount of manipulation. The writer believes from his experience that more accurate or at least just as accurate analyses are obtained as by the longer methods.

#### SEPARATION OF POLYSULFIDE AND THIOSULFATE SULFUR AND THEIR DETERMINATION IN LIME-SULFUR SOLUTION

In this investigation several interesting and important facts were developed. The one of prime importance is that hydrogen sulfide may be boiled off from a very slightly acid solution without decomposing the thiosulfate, thereby rendering its subsequent titration with iodine possible.

Next in importance is the fact that an excess of soluble sulfide ( $\text{Na}_2\text{S}$ ) will convert tetrathionate into thiosulfate as follows:



This is a well known reaction and affords a means of determining the tetrathionate formed in the titration of a thiosulfate as the excess of added sulfide may be decomposed with weak hydrochloric acid using methyl orange or methyl red as indicator. The hydrogen sulfide is then boiled off, the solution cooled and titrated with iodine.

Chapin<sup>1</sup> makes use of tetrathionate to determine sulfides. The above reaction is just the reverse. Standard  $\text{Na}_2\text{S}$  could be used but the writer found some difficulty with the end-point and thought it best to add an excess and decompose it with HCl, as already described, and boil off the hydrogen sulfide.

Another observation of considerable importance was that with certain limitations sodium nitroprusside could be used as an internal indicator for sulfides with a remarkable degree of accuracy.

#### DETERMINATION OF THIOSULFATE SULFUR

**PREPARATION OF SAMPLE FOR ANALYSIS**—From 5 to 20 g. of the lime-sulfur solution, depending upon concentration, are accurately weighed and made to

200 cc. in a graduated flask with freshly boiled and cooled distilled water well mixed and transferred to small bottles, filling them full and sealing. These may be kept as long as necessary, opening them when needed for analysis. Aliquots of 10 cc. are used for the determinations.

#### DESCRIPTION OF METHODS

Four methods were employed in this investigation, two of which have not heretofore been used, so far as the writer is able to learn from the literature upon the subject. These methods will be designated as A, B, C and D.

**METHOD A**—This was essentially the method of Harris by direct titration with iodine. Ten cc. of the sample prepared for analysis are run into a wide-neck Erlenmeyer flask of about 200 cc. capacity having a bottom 7 to 8 cm. in diameter, about 15 cc. of freshly boiled and cooled distilled water added and titrated immediately with  $N/10$  Iodine, the addition of which should be fairly rapid at first with constant shaking. When the yellow color due to the polysulfide becomes very faint, or better when the solution becomes barely white, a very small crystal of sodium nitroprusside is added and the solution vigorously shaken until the purple color develops distinctly. The color is then discharged with a few more drops of standard iodine, added quickly but carefully. This is the *mono-sulfur equivalent titration*. The burette reading is then taken and the titration continued until a small drop produces a faint coloration in the liquid. This is the end of the thiosulfate titration and the difference between the total amount of iodine used and that used for the mono-sulfur equivalent represents the thiosulfate present in the solution. ( $1 \text{ cc. } N/10 \text{ I} = 0.0016 \text{ S as mono-sulfur equivalent and } 0.0064 \text{ S in thiosulfate.}$ )

**METHOD B**—The procedure was the same as in (A) except that  $N/10$  HCl is used instead of iodine for the mono-sulfur equivalent titration, using one drop of methyl orange or methyl red as the indicator, which should not be added until near the end-point or until the solution becomes white. The titration is carried to a faint but distinct end-point. A little freshly boiled and cooled distilled water is now added, the hydrogen sulfide boiled off until no test is given with moistened lead acetate paper, the solution cooled, and titrated with standard iodine either with or without starch as indicator.

**METHOD C**—The procedure was as in (A), no attention being paid to the mono-sulfur equivalent titration, consequently no sodium nitroprusside added. Care should be taken not to go over the end-point for thiosulfate more than a small drop of standard iodine. To the solution is then added one drop of ammonium hydroxide and a solution of sodium sulfide of approximately  $N/5$  strength added until a drop of the solution gives a test for sulfides when applied to a drop of nickel sulfate solution on a touch plate. One drop of methyl orange is now added and the solution brought to very faintly acid with weak HCl, the  $\text{H}_2\text{S}$  boiled off, the solution cooled and titrated as in (B). The sodium sulfide should be added from a measuring pipette and a blank run for thiosulfate on the amount used (usually not over 1-3 cc.).

**METHOD D** (Thompson and Whittier<sup>1</sup>)—Here the procedure was as follows: A 10 cc. aliquot (as in the other methods) is run into a 200 cc. beaker, 15 to 20 cc. water added, then a slight excess of approximately  $N/10$  ammoniacal cadmium chloride to precipitate the sulfide. The solution is then diluted to 100-125 cc. with freshly boiled and cooled distilled water and allowed to stand about one hour with frequent stirring. The solution is then filtered and the precipitate washed with water, the filtrate neutralized with weak sulfuric acid, using a

<sup>1</sup> THIS JOURNAL, 8 (1916), 151.

<sup>1</sup> Delaware College Experiment Station, Bull. 105, June, 1914.

drop of methyl orange or methyl red as indicator and titrated with standard iodine with starch as indicator.

#### EXPERIMENTAL

Four samples were used in this work: Nos. 1 and 2 were made in this laboratory, using pure lime and sulfur and distilled water; No. 1 was about half the strength of the usual commercial lime-sulfur solution, No. 2 being somewhat weaker. Nos. 3 and 4 are commercial concentrates, bought upon the market and representing the product of two prominent manufacturers located in different sections of the country; the guaranteed specific gravity was 33° B.

Table I shows the accuracy of the thiosulfate titrations after boiling off  $H_2S$  from the very slightly acid solution.

TABLE I—EFFECT OF BOILING A SOLUTION OF THIOSULFATE  
10 cc. Standard Sodium Thiosulfate Used in Each Case

ADDITIONS	TREATMENT	CC. ST. I Required	
None	Not boiled	9.82	9.83
1 drop N/10 HCl	Boiled	9.83	9.83
1 drop N/10 HCl and $H_2S$	$H_2S$ boiled off	9.83	9.83
1 drop N/10 HCl, $H_2S$ and $CaCl_2$	$H_2S$ boiled off	9.83	9.83

The addition of calcium carbonate and barium chloride were without effect upon the titration. The standard thiosulfate was diluted to 50 cc. with freshly boiled and cooled distilled water in all cases, and the boiling was continued until tests for  $H_2S$  with moistened lead acetate paper were negative. The solutions were then cooled and titrated.

The fact that a very slightly acid solution of thiosulfate is not decomposed by boiling is the basal feature of Method B and one of the main points in Method C. The other feature of Method C is the conversion of tetrathionate to thiosulfate by a soluble sulfide. In order to test this point, 5 cc. of standard  $Na_2S_2O_3$  were titrated with standard I, requiring 4.73 cc. After conversion as outlined in Method C, 4.75 cc. of standard I were required. This was repeated: 5 cc. standard  $Na_2S_2O_3$  required 4.70 cc. standard I, and after conversion 4.72 cc. standard I were required. From these results it would seem that the accuracy of Method C could not be questioned.

All figures in the remaining tables are given in percentages as calculated in the records of the work.

TABLE II—COMPARISON OF THIOSULFATE SULFUR DETERMINED BY  
DIFFERENT METHODS

SAMPLE	METHOD	DETERMINATIONS						AVERAGE
1	A	2.30	2.30	2.24	2.30	2.37	.....	2.30
	B	2.24	2.24	2.30	.....	.....	.....	2.26
	C	2.30	2.28	2.31	2.30	2.30	.....	2.30
	D	2.28	2.22	2.26	.....	.....	.....	2.25
2	A	1.91	1.97	1.91	1.97	.....	.....	1.94
	B	1.97	1.97	1.97	1.91	.....	.....	1.95
	C	1.91	1.97	1.91	.....	.....	.....	1.93
	D	1.97	1.97	1.91	.....	.....	.....	1.95
3	A	0.84	0.86	0.94	0.86	0.84	0.84	0.86
	B	0.84	0.84	0.84	0.84	.....	.....	0.84
	C	0.84	0.84	0.86	.....	.....	.....	0.85
	D	0.94	0.94	.....	.....	.....	.....	0.94
4	A	0.87	0.87	0.91	0.87	.....	.....	0.88
	B	0.86	0.84	0.86	0.84	.....	.....	0.85
	C	0.84	0.89	0.89	.....	.....	.....	0.87
	D	0.91	0.84	.....	.....	.....	.....	0.87

It would seem from an inspection of Table II that from the standpoint of accuracy alone there could scarcely be a choice of methods, although in Sample 1, Methods B and D give slightly lower averages. If, however, individual determinations are considered, it will be seen that no figure is without exact or at

least very close duplicates in one or more of the other methods. The agreement in the other samples, with the single exception of the seemingly high figures by Method D in Sample 3 is all that could be expected or desired. In regard to the apparently high figures by Method D on Sample 3, it should be stated that all of the first weighing was exhausted and considerable decomposition had occurred in the original sample on account of a defective stopper so that no more work on it was attempted.

When factors other than accuracy are considered, a choice of methods is not only easy but highly desirable. Method A requires but one titration and that with one reagent (*Standard Iodine*). Method B requires two titrations with two reagents (*Standard HCl* and *Standard Iodine*). Methods C and D each require three titrations with two and three different reagents. In point of ease of manipulation and time required, Method A stands in a class apart from the others. From an experience extending over several years in its use, the writer unhesitatingly states that four or five determinations may be made by Method A in the time required to make one determination by any of the other methods. Method D is the most tedious and time-consuming of all the methods. As stated above, there has been strong objection to Method A. Just recently in *THIS JOURNAL*<sup>1</sup> it was stated that this method "cannot be regarded as trustworthy." The writer of that article produced no original data in support of this statement and had evidently overlooked the collaborative work of a dozen chemists presented to the Association of Official Agricultural Chemists in the Report on Insecticides in 1913,<sup>2</sup> in which also, as a part of the report, was a discussion of his reference.<sup>3</sup> That this criticism does not apply to a straight lime-sulfur concentrate is clearly demonstrated not only in that report but also in the present paper.

In this connection it should be stated that, in Method B, after titrating with standard HCl, the precipitated sulfur was filtered off in one or two cases with each sample and  $BaCl_2$  added before boiling off  $H_2S$ . In no case was there any perceptible precipitate of  $BaSO_4$  until after the titration with iodine: a very slight precipitation was then noticeable in all cases and since it is extremely doubtful if any sulfite could exist in a lime-sulfur solution, certainly no more than a trace, this precipitate is probably due to a very slight oxidation of tetrathionate to sulfate by an excess of iodine and for this reason it is recommended, in Method A, to prevent a regional excess of iodine by titration just moderately fast with constant shaking. That this oxidation is negligible in the analysis, however, is shown by the closeness of the agreement between Method B and Method A, and that within the experimental error all the methods agree in the amount of thiosulfate indicated. The use of N/10 iodine solution would probably be conducive to somewhat closer end-points.

<sup>1</sup> *THIS JOURNAL*, 8 (1916), 181.

<sup>2</sup> *Jour. A. O. A. C.*, 1, No. 1, p. 59.

<sup>3</sup> Bureau of Chemistry, *Bull.* 162, p. 38.



## DETERMINATION OF POLYSULFIDE SULFUR

In the longer methods of analysis the precipitated zinc sulfide, cadmium sulfide or precipitated sulfur from the iodine titrations is digested in caustic soda, oxidized and precipitated as barium sulfate. This is a long tedious process and often unsatisfactory results are obtained.

It has been known for several years that the precipitated sulfur in Methods A and B may be filtered, washed and weighed directly. In the iodine titration (Method A) the total sulfide sulfur is precipitated as follows:



In the hydrochloric acid titration it is necessary to add the mono-sulfur equivalent sulfur to the precipitated sulfur in order to get the total. In that titration it is very probable that the following reactions occur:

- (1)  $\text{CaS}_x + 2\text{HCl} = \text{CaCl}_2 + \text{H}_2\text{S} + (x-1)\text{S}$ ;
- (2)  $\text{CaS}_x + \text{H}_2\text{S} = \text{Ca}(\text{SH})_2 + (x-1)\text{S}$ ;
- (3)  $\text{Ca}(\text{SH})_2 + 2\text{HCl} = \text{CaCl}_2 + 2\text{H}_2\text{S}$ .

As an indication of the occurrence of these reactions it was noted that until the solution becomes white there is no very strong odor of  $\text{H}_2\text{S}$ . After this point in the titration is reached, however, the odor of  $\text{H}_2\text{S}$  becomes very strong, showing that it is being formed rapidly as indicated by Equation (3).

A method of weighing the precipitated sulfur, which the writer has found to give accurate and quick results, is as follows: Wash a 7 cm. ashless filter several times with suction, put in drying oven for half an hour at 94 to 96° C., place in wide mouth weighing bottle and weigh at once. Filter the precipitated sulfur on the weighed filter, washing well with suction. Dry in oven for 45 minutes to one hour and weigh as before. The difference is the weight of sulfide sulfur. This has been found to give constant weight when the amount of sulfur is not too large.

In a previous article<sup>1</sup> attention was called to this method of weighing the precipitated sulfur from the iodine titration and a comparison of the results with those obtained by oxidation and weighing as barium sulfate was shown.

After the titrations, if the solutions are allowed to stand a few hours, the sulfur collects and is readily filtered. If, however, it is desired to filter at once,

sulfate and polysulfide figures, in Table IV is shown the total sulfur as determined by oxidation and precipitation as  $\text{BaSO}_4$  and as the sum of polysulfide and thiosulfate sulfurs. The determined total sulfur is the mean of two determinations. The sum of the polysulfide and thiosulfate sulfurs consists of the average of all thiosulfate determinations by the four methods as shown in Table II; the polysulfide sulfur is the average of all figures by both methods, as shown in Table III.

TABLE IV—TOTAL SULFUR

SAMPLE No.	DETERMINED SULFUR Duplicates		AV.	THIOSULFATE AND POLYSULFIDE SULFUR	
1.....	11.96	11.94	11.95	11.89	
2.....	10.28	10.26	10.27	10.22	
3.....	25.03	25.14	25.08	25.02	
4.....	25.48	25.42	25.45	25.43	

When a straight lime-sulfur solution is titrated with iodine (Method A) it is quite easy, when desirable, to use as a check upon the work the determined lime (CaO) and the lime as calculated from the titrations since the iodine is reacting with the calcium (Ca). The mono-sulfur equivalent multiplied by  $1\frac{3}{4}$  is equivalent to the lime (CaO) in combination as polysulfide; the thiosulfate sulfur multiplied by  $\frac{7}{8}$  is equivalent to the lime (CaO) in combination as thiosulfate: the sum is equivalent to total lime (CaO). The average of the mono-sulfur equivalent by Method A and the average of the thiosulfate by the same method as shown in Table II are used in the calculations: the determined lime (CaO) is the mean of two determinations.

TABLE V—SHOWING THE VALUE FOR LIME (CaO) AS ACTUALLY DETERMINED AND AS CALCULATED FROM THE IODINE TITRATIONS (METHOD A)

Sample No.	MONOSULFUR EQUIVALENT DETERMINATIONS		THIO-SULFATE AV. SULFUR	PERCENTAGE LIME DETERMINED							
				Calculated (a)	Duplicates		Av.				
1	2.01	1.99	2.01	1.96	1.95	1.98	2.30	5.47	5.39	5.42	5.41
2	1.71	1.71	1.72	1.71	1.71	1.94	4.70	4.64	4.81	4.72	
3	5.02	5.02	5.06	4.99	4.99	5.02	0.86	9.53	9.52	9.62	9.57
4	5.32	5.29	5.29	5.29	5.30	0.88	10.04	10.11	10.08	10.10	

(a) Calculated from two preceding columns as noted in text.

(a) Calculated from two preceding columns as noted in text.

Acknowledgments are due Dr. A. M. Peter, of this Station, for having called attention to the fact that an excess of iodine oxidizes tetrathionate to sulfate,<sup>1</sup> and to the possibility of titrating tetrathionate directly with a soluble sulfide, as well as for helpful suggestions and criticisms in the preparation of the manuscript.

The suggestion that the reactions between tetrathionate and soluble sulfides is quantitative, as noted in the larger works on chemistry, is due to Chapin's paper.<sup>2</sup>

## SUMMARY

I—The experiments described and data presented in this paper afford new proof that calcium polysulfide in solution can be quantitatively decomposed by iodine solutions and thus eliminated from a solution containing thiosulfate, preparatory to the accurate determination of the latter.

II—It is shown that the same end may be accomplished by means of dilute HCl and elimination of the  $\text{H}_2\text{S}$  formed by boiling.

<sup>1</sup> Ber., 48, 2088; Chem.-Ztg., 1908, 1203.

<sup>2</sup> THIS JOURNAL, 8 (1916), 151.

TABLE III POLYSULFIDE SULFUR AS DETERMINED BY WEIGHING SULFUR DIRECTLY

SAMPLE IODINE NO. TITRATION	HYDROCHLORIC ACID TITRATION		SAMPLE IODINE NO. TITRATION	HYDROCHLORIC ACID TITRATION	
1	9.58	7.58 + 2.01 = 9.59	3	24.16	18.96 + 5.12 = 24.08
	9.54	7.66 + 2.01 = 9.67		24.04	19.08 + 5.12 = 24.20
	9.64			24.16	19.12 + 5.12 = 24.24
Average 9.59		9.63		24.12	24.17
2	8.28	6.58 + 1.72 = 8.30	4	24.56	19.20 + 5.40 = 24.60
	8.26	6.56 + 1.72 = 8.28		24.52	19.16 + 5.40 = 24.56
Average 8.27		8.29		24.54	24.58

add 2 or 3 drops of weak hydrochloric acid and warm on water bath until the sulfur collects. Care must be taken that no sulfur is lost in the washing. No more care is necessary, however, than a good analyst would naturally bestow upon it.

In order to illustrate the accuracy of both the thio-

<sup>1</sup> Jour. A. O. A. C., 1, No. 1, p. 95.

III—It is shown that sodium nitroprusside can be used as an internal indicator to show the end-point of the disappearance of the sulfide in the titration with iodine.

IV—This work affords further evidence of the interesting fact that when an iodine solution or a dilute acid is carefully added to a solution containing calcium polysulfide and thiosulfate, the polysulfide can be quantitatively decomposed before the thiosulfate is attacked.

V—A rapid accurate method of weighing the pre-

cipitated sulfur in the iodine and hydrochloric acid titrations of a lime sulfur solution is proposed.

VI—Two methods (B and C), not heretofore used for the determination of thiosulfate in lime-sulfur solutions, are described, both being theoretically and practically sound and accurate.

VII—The accuracy of the iodine titration method (or Harris method) for the analysis of such solutions is confirmed.

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## LABORATORY AND PLANT

### THE FLOW OF VISCOUS LIQUIDS THROUGH PIPES

By W. K. LEWIS

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The carrying capacity of pipes for water under various pressure drops has been experimentally studied by many engineers and while the results are not very concordant on account of the extreme sensitiveness to varying conditions, none the less our knowledge of the resistance to flow of water through pipe lines is relatively satisfactory and complete. On the other hand, practically no work has been published on the resistance to flow through pipes of liquids other than water despite the fact that information of this sort is of vital importance to the chemical engineer. Davis, in his "Handbook of Chemical Engineering," points out the extremely small carrying capacity of pipes for viscous liquids such as sulfuric acid and glycerin as compared with their capacity for water, but he gives no suggestions as to methods of estimating the size of pipes required for specific cases. There are in this country thousands of miles of pipe lines transmitting mineral oils as well as the piping systems of chemical plants handling acids, solvents, and all sorts of liquids in large quantities. While a wealth of information along this line is undoubtedly available to the engineers of individual corporations, the lack of any published figures and the importance of the whole problem led this laboratory to undertake an investigation along these lines which has extended over the last four years. After certain preliminary work, a series of tests was made studying the flow of mineral oils of varying viscosity at relatively low velocities. The results of this work are reported as Series A. Later, in order to supplement the results of these first experiments by study of flow at higher velocities, another separate investigation was carried out which is reported as Series B. While the results are limited to relatively small pipes and low viscosities, certain generalizations can be drawn which are so well confirmed that their use, even beyond the scope of the present experimental range, seems justified, especially as a working basis upon which to develop further investigation.

#### NOMENCLATURE

P = pressure drop in grams/cm<sup>2</sup>. or lbs./sq. ft.  
μ = { coefficient of absolute viscosity in  
sec. dynes/cm<sup>2</sup>. or sec. pounds/sq. ft.

l = length of the pipe in cm. or ft.  
r = radius of pipe in cm. or ft.  
ρ = density of the fluid.  
V<sub>c</sub> = { mean velocity at point where sinuous flow  
changes to parallel flow, cm./sec. or ft./sec.  
V<sub>m</sub> = mean velocity in cm./sec. or ft./sec.  
f = hydraulic frictional coefficient.

#### GENERAL DISCUSSION

It has long been known that, for the flow of fluids through capillary tubes up to 4 or 5 mm. in diameter, the formula of Poiseuille,  $P = \frac{8\mu l V_m}{gr^2}$ , holds quantitatively. Though for the flow of liquids other than water through large tubes or pipes, quantitative data have not been published, the paths along which the particles of liquid travel have been studied qualitatively by introducing air or dyes into the fluids and photographing the effects produced by forcing them through glass containers of various shapes and sizes.<sup>1</sup> These observations show that at low velocities liquids move in straight lines parallel to the axis of the tube, but when the velocity is sufficiently increased, the lines of flow become distorted, the filament forming violent eddies of constantly changing form and position. At the walls of the container there is always a film of liquid which is retarded by the friction of the solid surface, so that it continues to move in straight lines. The mean velocity of the fluid, at the point where the change in type of motion takes place, is commonly known as the critical velocity and all flow below this point is called parallel, direct, or viscous motion, while that above is known as turbulent, indirect, or sinuous flow.

From this it is obvious that at least two different laws must govern the flow of fluids, the one above and the other below the critical velocity, with the possibility of a third for an intermediate state. Poiseuille's law would be the one to use below the critical point, since his formula applies entirely to straight line motion. For flow above the critical point, we have but one suggestion as to the manner in which flow may take place, from observation of the formulae for the flow of steam, air, and water above the critical rate. These equations may all be written  $P = \frac{\int \rho l V_m}{gr}$ .

<sup>1</sup> H. S. Hele-Shaw, *Engineering*, 65 (1898), 420-444, 477, 510



and it is surprising to find that they all have approximately the same constant,  $f$ , and also nearly the same value of  $n$ . It would seem possible, then, that this formula may be general and hence apply to any fluid, but this is an hypothesis which can be verified only by experiment.

#### SERIES A<sup>1</sup>

Two horizontal lines of pipe were built, one consisting of standard 1-in. pipe 136 ft. long, and the other

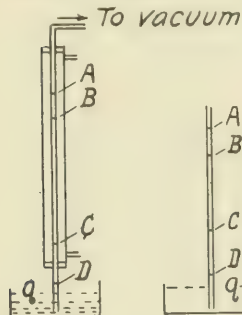


FIG. I

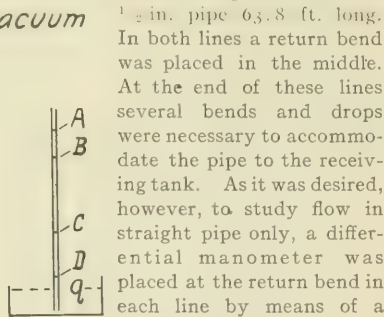


FIG. II

1-in. pipe 63.8 ft. long. In both lines a return bend was placed in the middle. At the end of these lines several bends and drops were necessary to accommodate the pipe to the receiving tank. As it was desired, however, to study flow in straight pipe only, a differential manometer was placed at the return bend in each line by means of a T separated from the bend by a close nipple, and an ordinary manometer was attached at a point near the end of the system, before the bends or drops were introduced. The pressure recorded by these manometers was subtracted from the pressure registered by a gauge at the beginning of the line and thus the pressure drop throughout the straight pipe was obtained.

TABLE I—RESULTS OF TYPICAL RUNS (SERIES A)

Run No. (c)	Coeff. Visc. $\rho$	Dens. of Fluid $\rho$	DELIVERY THROUGH PIPE			Per cent Deviation from Obs.	PRESSURE DROP (a)		
			Lbs. per Min.	Calc. (d)	Obs.		Lbs. per sq. in.	Dynes per sq. cm.	
11	0.938	0.95	31.25	256.0	248.0	3.1	10.8	74.3	
24	0.917	0.95	39.80	318.0	316.0	0.6	13.12	90.3	
39	0.920	0.95	65.50	520.0	520.0	0.0	21.7	156.0	
43	0.920	0.95	50.00	397.0	397.0	0.0	16.45	113.0	
54	0.920	0.95	11.20	88.5	89.0	0.6	3.67	25.2	
64	0.790	0.91	8.33	66.8	66.2	0.6	12.0	82.5	
69	0.718	0.91	11.91	91.4	94.9	-3.8	14.9	102.2	
74	0.670	0.91	16.75	131.3	133.0	-1.3	18.58	127.5	
79	0.620	0.91	22.42	179.0	178.0	0.6	22.45	154.1	
98	0.308	0.89	4.28	32.1	33.9	-4.6	4.89	33.6	
107	0.304	0.89	6.95	57.0	55.3	3.0	8.49	58.3	
133	0.310	0.89	14.1	120.0	112.0	6.7	18.28	125.5	
143	0.261	0.88	50.0	415.0	397.0	4.4	5.32	36.5	
148	0.246	0.88	82.5	676.0	656.0	3.1	8.17	56.0	
154	0.235	0.88	97.0	810.0	770.0	5.2	9.37	64.3	
158	0.227	0.88	112.5	1000.0	894.0	11.8	11.2	77.9	
160	0.224	0.88	115.8	1125.0	919.0	22.4	12.25	84.2	
187	0.081	0.85	156.2	5480.0	1243.0	293.0	22.0	151.0	
167	0.218	0.88	123.5	1519.0	983.0	53.5	16.23	111.3	
171	0.217	0.88	133.2	1810.0	1060.0	69.8	19.25	132.1	
175	0.215	0.88	144.3	2130.0	1148.0	85.2	23.35	153.5	
181	0.086	0.86	96.8	1978.0	770.0	156.0	8.52	58.5	
182	0.084	0.85	111.5	3090.0	888.0	250.0	8.40	57.6	
185	0.082	0.85	139.5	4450.0	1108.0	331.0	17.48	120.0	

(a) The conversion factor for changing lbs. per sq. in. to dynes per sq. in. is  $6.87 \times 10^4$ .

(b) The conversion factor for changing lbs. per min. to cc. per sec. is 7.95.

(c) In Runs 1-60 and 95-187, the 1-in. standard steam pipe was used. The 1/2-in. standard steam pipe was used in the remaining runs.

(d) Calculated by Poiseuille's equation.

Five lubricating oils of different viscosities were used, the oil being pumped into a constant head tank by means of a Gould rotary pump and thence into the pipe line. After passing through the line, the oil was discharged into a tank supported by platform

<sup>1</sup> The work in this series of runs was carried out by Messrs. Greenough and Dinsmore in 1914 and submitted as a thesis in partial fulfillment of the requirements for the S.B. degree at the Massachusetts Institute of Technology.

scales, where the time and quantity of discharge were recorded. The density of the oil was determined by a Westphal balance and the viscosity by a modified Gurney Viscosimeter.<sup>1</sup>

In Table I are given representative laboratory data. It is remarkable that Poiseuille's equation, which was derived for capillary tubes, should hold (within the limits of experimental error) for fluids flowing through 136 ft. of 1 in. pipe with a pressure drop of 22.8 lbs./sq. in. and a velocity of 1.1 cu. ft./min.

The runs above the critical point were necessarily made at very high velocities and the pump, rated at only 10 gals. per minute, was consequently running at approximately its theoretical capacity. Moreover, the driving motor was running at from 50 to 60 per cent overload, thus causing great difficulty in properly regulating the pressure. At the highest velocities attained, if constant conditions were to be maintained in the pipe line, no oil could pass through the by-pass, used in previous runs to shunt part of the oil back to the reservoir. With this apparatus

Fig. I shows a Gurney viscosimeter as described in *J. Am. Chem. Soc.*, **34** (1912), 24. The apparatus consists simply of an upright capillary tube, provided with a jacket, through which may be passed water, or the vapor of some constant boiling liquid, in order that a constant temperature may be maintained. There is also an arrangement for applying a vacuum to draw the liquid into the tube.

The formula which Gurney published is useless, mainly because he did not take into account the non-uniformity of the cross-section of glass tubes. No capillary tube is of constant cross-section; the effect of the irregularity is a complicated function of the distance from the bottom of the tube, and to correct Gurney's formula for this point would be out of the question. If a tube is smaller at one end than at the other, as from the method of manufacture is usually the case, the liquid will flow much more rapidly when the large end is at the bottom than when the tube is reversed. Furthermore, Gurney's correction terms, although small and perhaps

negligible, are of doubtful validity. For example, the term  $\frac{0.005 \mu V^2}{r^2}$ , which is used for frictional resistance, holds for non-viscous fluids flowing in turbulent motion and is incorrect for parallel flow.

We propose a new method of calculation suggested by Lang (Thesis, Mass. Inst. Tech., 1914), which can be obtained directly from the fundamental equation of Poiseuille. Let the tube (Fig. II) be so adjusted that the capillary head,  $D_0$ , is maintained constant. Let the fluid be raised to A and allowed to flow by gravity from A to C. For capillary tubes, as

previously stated, Poiseuille's formula,  $P = \frac{8 \mu V}{r^2}$ , holds quantitatively.

Therefore, as pressure is proportional to the density of the fluid,  $h_p = \frac{8 \mu V}{r^2}$ .

For two different fluids, 1 and 2,

$$h_{p1} = \frac{8 \mu_1 V_1}{r^2} \quad (1), \quad \text{and} \quad h_{p2} = \frac{8 \mu_2 V_2}{r^2} \quad (2).$$

$$\text{Dividing (1) by (2),} \quad \frac{\rho_1}{\rho_2} = \frac{\mu_1 V_1}{\mu_2 V_2}$$

$$\text{Solving,} \quad \mu_1 = \frac{\rho_1 \mu_2 V_2}{\rho_2 V_1}, \quad \text{or} \quad \mu_1 = \frac{\rho_1 T_1 \mu_2}{\rho_2 T_2}$$

Therefore, if the tube be standardized by measuring the time of efflux of a liquid between two fixed points, B and C, the viscosity of any other fluid may be obtained by simply measuring its density and time of flow between the same points, providing  $\rho$  and  $\mu$  are known for the first liquid. This automatically corrects for unevenness of bore. We would suggest, as did Gurney, that the fluid be raised each time to A as described above, but that the time be taken between B and C for greater accuracy in time of starting.

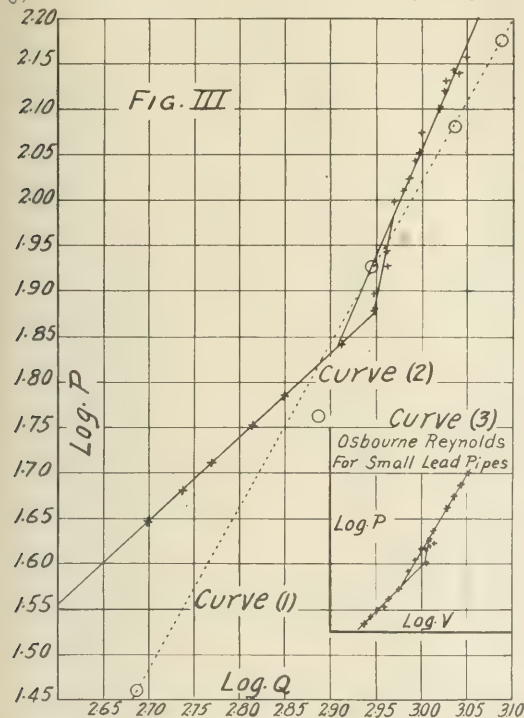
For high precision over wide ranges of temperature, the standardization and the viscosity determination should be carried out at nearly the same temperature, or the following correction may be made for expansion of the glass:

$$T_2 = \frac{T_1(1 + a_1 t)}{(1 + 2a_1 t)}$$

where  $a$  = linear coefficient of expansion of glass, and  $t$  = temperature difference between that employed and the temperature of standardization.

the experimental error for runs at high velocities was therefore large.

In order to determine the critical velocity of the oils and also to ascertain whether the equation  $P = (f)V^n$  would hold above the critical velocity, we plotted



the logarithm of the pressure drop against the logarithm of the velocity.<sup>1</sup>

In Fig. III, Curve 1 represents the least viscous oil ( $\mu = 0.089$ ) flowing above the critical velocity. Curve 2 represents the oil ( $\mu = 0.23$ ) flowing above and below the critical velocity. Curve 3, plotted from data collected by Osbourne Reynolds on the critical velocity of water, gives a means of comparison between water and a fluid twenty times as viscous.

Even a casual glance at the two latter curves will reveal their extraordinary similarity. Each liquid has two critical velocities: the first represents the higher one, where nonsinusuous motion becomes sinuous; the other shows the point where turbulent flow changes to direct motion. Usually, in industrial practice, a fluid enters a pipe with a turbulent motion produced by a rotary or centrifugal pump, compressed air or by some other means whereby violent eddies are set up in the field. We, however, were able to realize both conditions because of the introduction of a constant-head tank between our pump and the pipe line. This tank was provided with an air dome and insured fairly uniform and quiet conditions at the mouth of the pipe line. Nevertheless, this higher

<sup>1</sup> For if  $P = kV^n$ ,  $\log P = \log k + n \log V$ , the equation of a straight line having the form  $y = a + ny$ , the slope being  $\frac{\log P}{\log V}$  which is unaffected by  $\log k$  and is equal to  $n$ .

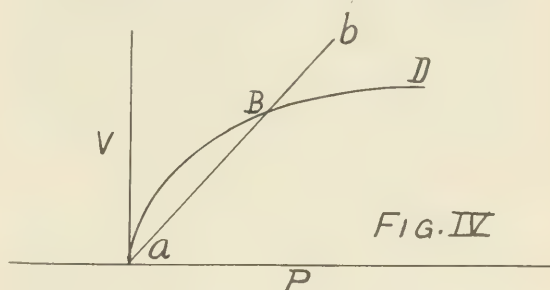
critical velocity is a point of unstable equilibrium and seldom reached in practice; hence when critical velocity<sup>1</sup> is referred to in this article, the lower point—the change from turbulent to nonsinusuous motion—will be understood. It is to be noticed that the curves do not deviate from straight lines up to the point of intersection, or, in other words, there is no intermediate flow between straight and turbulent motion.

The average value of  $n$  from the two curves is approximately 2 and we therefore make the same assumption made in hydraulics, namely that  $P = \frac{\rho f l v^2}{gr}$ ,

realizing that neither oil nor water follows this law without a varying constant. The frictional coefficients for those runs above the critical velocity were found to be nearly the same as those for water under the same conditions of flow. All exact work on flow above the critical velocity is, however, taken from Series B.

In this first series of runs it was impossible to carry the velocities of flow far above the critical point and in all runs at these high velocities, the experimental error was great, owing to inadequate equipment. In order to study the flow of liquids at varying velocities at rates well above the critical point, a second entirely separate series of runs was undertaken, using

<sup>1</sup> In order to derive an equation for the critical velocity of any fluid, let us consider the pressure-velocity plots for Poiseuille's and the sinuous formula. If a fluid is moving through a pipe below the critical velocity Poiseuille's formula, as above stated, holds quantitatively or, in other words,  $P = kV$ . The pressure-velocity plot is therefore a straight line (Fig. IV) passing through the origin and determined experimentally by



locating points between  $a$  and  $b$ . Let the same liquid flow above the critical velocity and accordingly follow the sinuous formula  $P = kV^2$ . This curve is a parabola passing through the origin with all experimentally determined points lying between  $B$  and  $D$ . If  $P = kV^{(2+n)}$ , where  $n$  was plus or minus a small decimal, the curve  $BD$  would cease to be a parabola but would remain a curve which nevertheless has the same general shape and in the following discussion would make no difference.

Between points  $a$  and  $B$ , the velocity is greater for a given pressure drop in turbulent motion than in straight line flow, while above  $B$  the reverse is true. It is clear that for a liquid moving with a greater velocity per unit pressure, less power is necessary to transmit a given amount of this fluid through a pipe. Below the point  $B$  therefore more energy is consumed by viscous than by sinuous flow. Above point  $B$  the reverse is true. This experimental work has, however, proven that below  $B$  the flow is viscous and sinuous above. In both cases the flow takes place in that way involving the greater energy consumption. This may be looked upon as a specific instance of the general rule that if a change can take place in a variety of ways the change tends to follow that path which corresponds to the greatest decrease in free energy.

At the critical velocity the two types of motion give identical pressure drops, i. e.,

$$P_c = \frac{f \rho l v_c}{gr} = \frac{8 \mu l V_c}{gr}$$

If the value of 2 be assigned to  $n$ ,  $V_c = \frac{8 \mu}{f \rho r}$ .

The value to use for  $f$  will be developed under Series B.



not only higher velocities, but also a 2-in. pipe in addition to the smaller pipes of the previous series.

#### SERIES B<sup>1</sup>

From a supply tank of 400 gals. capacity liquids were pumped by a Duplex Steam Pump into an air dome and thence through four pipe lines one of 2-in. wrought iron, one of 1-in. wrought iron, one of 1/2-in. wrought iron, and one of 1/2-in. steel pipe. In each case the liquid passed through a length of straight pipe around a return bend and back to the starting point, where it flowed into a slightly larger pipe which delivered it through two quick opening valves to two tanks set on platform scales.

A by-pass was used to shunt part of the liquid from the pump directly back to the supply tank in order to regulate the pressure as desired. The initial pressure was taken by calibrated gauges, the drop in pressure around the bend by a differential manometer and the back pressure by a U-tube manometer. As in all hydraulic experimentation, this work was subject to more or less error. The reciprocating pump would not give absolutely constant pressure even with the help of an air dome with 10 cu. ft. capacity. The best average values were obtained by throttling the gauge and the readings were again averaged by the graphical consideration of the data, but the values of  $p$  cannot be relied up to better than 5 per cent. The 1/2-in. wrought iron pipe, although new, was very rough and gave in all runs about 25 per cent greater friction loss than the steel. In small pipes the condition of the surface plays such an important part in the friction loss and the roughness varies so greatly with different pipes that we have assumed the 1/2-in. steel pipe as a standard for this size. The liquids used were water and gas oil. The viscosity of the former was obtained from the data of Thorpe and Rodger as found in Landolt-Börnstein. The viscosity of the latter was determined as in the previous series. The temperature and therefore the viscosity of the oil and water was changed by means of a steam coil in the supply tank. Series of runs were made with hot and cold water and with hot, warm and cold oil, the viscosity being determined in each case from the average temperature of the series. The viscosities are as follows:

	Temp.	Dynes/cm <sup>2</sup> .	Poundals/In. <sup>2</sup>
Cold oil.....	24.5° C.	0.169	0.0000789
Warm oil.....	40.0° C.	0.1045	0.0000488
Hot oil.....	60.0° C.	0.0596	0.0000278
Cold water.....	20.0° C.	0.0100	0.00000466
Hot water.....	48.5° C.	0.0056	0.00000261

It is to be noted that a wide viscosity range was covered as the cold oil was over 30 times as viscous as the hot water.

Runs were made at velocities up to 20 ft. per sec. in the 1/2- and 1-in. pipes and as high as 12 ft. per sec. in the 2-in pipe. The gauge pressure of each run was kept constant by the regulation of the by-pass valve. The results appear in Table II.

<sup>1</sup> The work in this series of runs was carried out by Messrs. Haylett and Lucey and submitted as a thesis in partial fulfillment of the requirements for the S.B. degree at the Massachusetts Institute of Technology in 1915.

Friction velocity curves were constructed from the experimental data by plotting the pressure drop against the velocity. It was found that for each pipe the pressure drop  $p$  varied with a power of the velocity  $v$ , or,  $p = av^n$ .

The value of  $n$  was determined by plotting  $\log p$  against  $\log v$  and determining the average slope of the curves of the four pipes. The lines were nearly parallel with an average slope of 1.85. To determine the variation of the pressure drop with the diameter, values of  $\log (p/v^{1.85})$  were plotted against the logarithm of the diameter for oils of the same

TABLE II—PRESSURE DROP: LBS. PER SQ. IN. PER 100-FT. LENGTH OF PIPE (SERIES B)

SIZE OF PIPE	Velocity in feet per second—							
	4	6	8	10	12	14	16	18
<b>1/2-in. Steel</b>								
COLD OIL:								
Observed	..	20.8	32.5	49.0	71.2	98.8	..	..
Calculated	..	20.1	34.0	51.5	71.8	71.8	..	..
Deviation	..	3.3	+4.6	+5.1	+0.8	-2.8	..	..
WARM OIL:								
Observed	..	21.5	33.6	47.7	64.1	83.0	104.2	..
Calculated	..	17.8	30.2	45.7	64.8	85.2	109.0	..
Deviation	..	..	10	-4.2	+1.1	+2.6	+4.6	..
HOT OIL:								
Observed	..	19.3	29.9	43.3	59.9	79.2	101.0	..
Calculated	..	16.3	27.6	41.8	58.4	78.0	99.8	..
Deviation	..	..	-7.2	-5.8	-2.5	-1.5	-1.2	..
COLD WATER:								
Observed	..	13.2	22.2	33.1	46.3	79.2	61.3	99.8
Calculated	..	14.3	24.2	36.6	51.2	73.2	93.7	109.0
Deviation	..	-8.3	+9.0	+9.5	+10	+16	+16	+19
HOT WATER:								
Observed	..	12.0	20.0	30.5	43.0	58.2	76.5	97.3
Calculated	..	14.2	24.1	36.5	51.0	73.0	93.5	108.0
Deviation	..	+18	+20	+20	+18	+25	+22	+11
<b>1-in. Wrought Iron</b>								
COLD OIL:								
Observed	4.5	10.3	19.0	29.3	41.5	55.0	68.8	..
Calculated	5.5	11.7	19.8	30.0	41.9	56.0	71.7	..
Deviation	+22	+11	+4.2	+2.4	+0.9	+1.8	+4.2	..
WARM OIL:								
Observed	5.1	10.7	17.8	26.7	36.7	48.0	60.4	..
Calculated	4.8	10.3	17.4	26.3	36.7	49.0	62.8	..
Deviation	-5.9	-3.7	-2.2	-1.5	0.0	+2.1	+3.8	..
HOT OIL:								
Observed	5.8	10.4	16.2	23.7	32.6	43.2	55.2	68.0
Calculated	4.4	9.2	15.7	23.7	33.0	44.2	56.6	70.2
Deviation	-2.70	-10	-3.1	0.0	+1.2	+2.3	+2.5	+2.9
<b>2-in. Wrought Iron</b>								
COLD OIL:								
Observed	2.64	5.50	9.08	13.67	..	..	..	..
Calculated	2.46	5.22	8.85	13.40	..	..	..	..
Deviation	-6.8	-5.1	-2.5	-1.5	..	..	..	..
WARM OIL:								
Observed	1.64	4.29	8.05	12.79	..	..	..	..
Calculated	2.15	4.56	7.78	11.70	..	..	..	..
Deviation	31.0	+6.3	-3.8	-8.3	..	..	..	..
HOT OIL:								
Observed	1.41	3.82	6.90	10.37	14.19	..	..	..
Calculated	1.92	4.09	6.92	10.50	14.60	..	..	..
Deviation	26.7	+7.0	+0.3	+0.9	+2.6	..	..	..

viscosity and again nearly parallel lines were obtained. The average slope of these was  $-1.22$ , i. e.,  $p$  varies inversely as  $d^{1.22}$ , or  $P = \frac{fv^{1.85}}{d^{1.22}}$

is the equation obtained where  $f$  varies with the viscosity of the liquid. This last relation was determined by plotting  $f$  against the viscosity, by which a straight line was obtained for the 1- and 2-in. pipes and another parallel to it for the 1/2-in. steel pipe. The equation of these lines was of the form  $f = k\mu + c$ . The slope  $k$  was found to be 115 and the intercept  $c$ , 0.0114—for the 1- and 2-in. pipes (0.0140 for the 1/2 in.). Thus, the completed equation becomes  $p = (115\mu + 0.0114) \frac{v^{1.85}}{d^{1.22}}$ , where  $p$  is the pressure drop due to friction expressed in lbs. per sq. in. per 100 ft. of pipe,  $\mu$  the absolute viscosity in poundals per sq. in.,  $v$  the velocity in ft. per sec. and  $d$  the diameter of the pipe in sq. ft.

Table II contains illustrations of the results of these runs giving the velocity in ft. per sec., the observed pressure drop in lbs. per sq. in. per 100 ft. of pipe, the pressure drop calculated by the use of the above formula, and the percentage deviation between the two. The equation

$$P = \frac{(115\mu + 0.0114)v^{1.85}}{d^{1.22}}$$

may be the form of a general law,

$$P = \frac{(k\mu + c)y^n}{d^m},$$

for all sizes of pipes, with varying velocities and different degrees of internal roughness. The constants, however, doubtless vary, as do all hydraulic constants, and only experimental data can possibly give the ones to use for any particular case. However, until further research has been carried out in this field, these laws, with the derived constants, will serve as a first approximation.

#### FRICTIONAL COEFFICIENTS FOR VISCOUS LIQUIDS

We have shown that flowing liquids of all viscosities when in sinuous motion follow substantially the same equation, differing only in the coefficient of that equation: *i. e.*, the flow of any liquid in sinuous motion may be expressed as a constant times some function of velocity, length, and radius. The constant  $f$  depends upon the viscosity of the liquid flowing, but the function of the velocity, length and radius is independent of the viscosity. In all ordinary hydraulic calculations it is assumed that this function of velocity,

length, and radius is  $\frac{v^2 l \rho}{gr}$ , and the fact that the flow

does not exactly follow this formula is provided for by the use of tables for the coefficient  $f$ , these tables showing the value of  $f$  as determined by radius and velocity, the two factors which influence it. Inasmuch as we have shown that the flow of viscous liquids has the same function of velocity, length and radius as the flow of water, it follows that the ratio of the constant to be employed for the flow of viscous liquids to that of water itself is the same as the ratio of the constant employed in the more exact exponential formula which we have derived above. If  $f_w$  be the hydraulic coefficient for the flow of water through a pipe and  $f$  that of any liquid, both to be employed on the assumption that the lost head or pressure drop is directly proportional to the length, to the square of the velocity and inversely to the radius, it follows that

$$\frac{f}{f_w} = \frac{0.0114 + 115\mu}{0.0114 + 115(0.00000467)^*} = 0.955 + 0.045\mu$$

or,  $f = f_w(0.955 + 0.045z)$ , where  $z$  is the *relative viscosity* of the liquid in question to water. The best way to determine  $z$  is to measure the relative time of efflux of the liquid and water through the same capillary tube. The tube should not be constricted at the ends and the use of the Gurney

viscosimeter as outlined above for this purpose is recommended.

We believe that the use of this formula

$$f = f_w(0.955 + 0.045z)$$

is at present the best means of estimating the carrying capacity of a pipe for viscous liquids. From the formula it is evident that for liquids of low viscosity the capacity is exactly the same as that for water, but for high viscosities the capacity rapidly decreases. We have experimentally confirmed the accuracy of this formula by the data given above up to viscosities of 20-fold that of water. Up to this point, the correction term for viscosity in the formula above is small, but for very high viscosities, such as are encountered in heavy mineral oils, glycerin, etc., this term becomes very great. We personally doubt the validity of this formula for high viscosities, believing that the pressure drops will be decidedly less than this formula indicates. On the other hand, the use of this formula should be safe, inasmuch as the actual carrying capacity of a pipe designed by its use will exceed the calculated rather than otherwise. We have hitherto not been in a position to confirm the use of this formula for more viscous liquids.

#### CALCULATION OF CARRYING CAPACITY

To estimate the carrying capacity of a pipe line for any liquid, proceed as follows: Determine the density of the liquid and its viscosity relative to water, doing the latter either with the Gurney viscosimeter or by measuring the time of efflux through a capillary tube for which the time of efflux of water or of any other liquid of known absolute viscosity has been measured. The relative viscosity times 0.0671<sup>1</sup> gives the absolute viscosity in pounds/sec./sq. ft. Now employ the two formulae,

$$p = \frac{8\mu l v}{gr^2}, \text{ and } p = \frac{f l \rho v^2}{gr},$$

where  $f = f_w(0.955 + 0.045z)$ . Choose that result which indicates the greatest resistance to flow.

A single illustration will make the procedure clear.

It is required to find the velocity of an oil of sp. gr. 0.91 through 600 ft. of standard 1-in. pipe (inside diameter, 1.07 in.) under a head of 30 ft. The time of efflux of the oil at 20° C. from a pipette which is not constricted at the tip is 108 sec., water flowing from the same pipette in 4.90 sec.

$$p = h\rho = 30(0.91)(62.3) = 1701 \text{ lbs./sq. ft.}$$

$$z = \frac{108}{4.90} = 22.05 \quad \mu = 0.0671z = 1.478$$

$$r = \frac{1.07}{(12)(2)} = 0.0446 \quad g = 32.2$$

Assume that  $f_w$ , from hydraulic tables for the pipe in question, is 0.0075.

$$\text{For viscous flow, } v = \frac{(1701)(32.2)(0.0446)^2}{(8)(1.478)(600)} = 0.0153 \text{ ft./sec.}$$

For sinuous flow,

$$v = \sqrt{\frac{(30)(32.2)(0.0446)}{(600)[0.995 + 0.045(22.05)](0.0075)}} = 2.22 \text{ ft./sec.}$$

The flows in viscous motion being but a small fraction of that required for sinuous flow, viscous motion

\* Viscosity of water at ordinary temperature (20° C.).

<sup>1</sup> The viscosity of water at 20° C.



will result and the low discharge is the one which must be expected. Had the sinuous formula given the lower value of  $v$ , the result by the formula for viscous flow would have been rejected.

#### SIZE OF PIPE FOR VISCOUS LIQUIDS

Liquids of even moderate viscosity flowing under low heads follow viscous motion unless the pipes be very large. It is very important to keep in mind the fact that, so long as the motion is viscous, doubling the size of the pipe increases the velocity 4-fold and the discharge 16-fold for the same pressure drop. For the same discharge a pipe twice the size requires only one-sixteenth the pressure drop and therefore but one-sixteenth the power. If a pipe is carrying liquid in viscous motion, increase in size of the pipe is always well worth consideration, owing to this very great effect on carrying capacity and power consumption. Decrease in size will ultimately result in converting the flow into sinuous motion, after which the effect of size is greatly lessened, being inversely proportional to only the first power of the diameter.

#### SUMMARY

Liquids flowing through pipes flow either in straight line motion in which case they follow Poiseuille's

formula,  $\phi = \frac{8\mu lv}{gr^2}$ , or in sinuous motion, the pressure

drop being represented by  $\phi = \frac{f\rho v^2}{gr}$ . The flow will

follow that formula which requires the higher pressure drop, the higher radius, or gives the lower velocity, as the case may be. Both formulae must therefore be employed and the result chosen according to the above rule. To obtain the coefficient  $f$  of the formula for sinuous motion: look up, in suitable hydraulic tables, the value of the coefficient for water flowing in the same size pipe at the same velocity and multiply this coefficient by the expression  $(0.955 + 0.045z)$  wherein  $z$  is the viscosity relative to water of the liquid flowing.

These formulae have been experimentally substantiated only for use in pipes up to 2 in. in diameter and for the flow of liquids of viscosity (relative to water at 20°) of 20. They are probably safe for use in larger pipes and at higher viscosities, but more exact expressions for these conditions must be determined by further experimentation.

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### THE DESIGN AND OPERATION OF OZONE WATER PURIFICATION SYSTEMS

By SHEPPARD T. POWELL<sup>1</sup>

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Although the first attempt to purify water on a practical scale by means of ozone was made less than thirty years ago, still this gas was generated and its chemical and physical properties have been studied by many investigators for more than a century. In all probability ozone has been recognized by scientists

since the earliest ages, if not by name at least by its characteristic properties. The first authentic record that we possess of the manufacture of this gas was in 1783 when Van Marum, a Dutch scientist, termed it "a smell of electricity," as a result of its production by this means.

It was not, however, until the exhaustive studies of Schoenbein in 1840 that the active properties of ozone were well understood or any analytical methods were devised for measuring this gas. Schoenbein recognized this active oxidizing agent as a distinct gas to which he gave the name of ozone.

For more than fifty years after Schoenbein's researches nothing was accomplished in placing ozone within the scope of a commercial possibility, although its active and oxidizing power was well known. With the development of the alternating current generators and transformers, which so materially reduced the cost of production, and the increasing knowledge of the bacteriology and chemistry of water, ozone was recognized as a water purification agent of great value. Berthelot, a French chemist, in 1890 undertook, with some degree of success, to apply this method of water purification, and from then on Europe, as well as America, has been practically flooded with numerous designs of generators and patented appliances for water treatment.

All the ozonizers that have been devised are based upon the same general principle, *viz.*, the production of the allotropic form of oxygen,  $O_3$ , from the oxygen of the atmosphere. This is accomplished by passing a current of air over a brush discharge which takes place between electrodes connected to a high voltage alternating current circuit; these usually have a solid dielectric interposed between them. There are, of course, many other ways of generating this gas, but none of these processes other than the one described has proven a commercial success.

Numerous theories have been advanced to account for the production of ozone in this manner but the one generally accepted is based on the theory of molecular motion.<sup>1</sup> This theory, as stated by Dr. C. P. Steinmetz, regards the chemical effect of all ether radiations recognized by light, heat and electrical waves as more or less specific for various compounds to definite frequencies of their movement setting up resonance effects upon the natural molecular or atomic motion.

Pure ozone is colorless, has a distinct and peculiar odor and instantly decomposes at 260° C. It can be liquefied by a pressure of 1840 lbs. per sq. in. and at a temperature of -103° C. In this condition it is highly magnetic but is not so powerful an oxidizing agent as the gas.

The great affinity of ozone for organic matter renders it peculiarly suited for water purification, in that it not only removes the bacteria by direct oxidation but will eliminate to a considerable degree other organic substances contained therein.

All ozonation plants for the purification of water consist of two distinct parts—the ozone generator and

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<sup>1</sup> *Engineering News*, 63 (1910), 488.

the mixing chamber or emulsifier. If the design or operation of either appliance is a failure then the failure of the system as a whole is a certainty, as the success of the plant depends equally upon both parts.

It would be impossible at this time to give descriptions of the numerous designs of all ozonizers that have been introduced within the past few years, but brief mention of a few of the more important types may be of interest.

#### THE SIEMAN-DEFRISE SYSTEM

The Sieman-DeFrise ozone generator, which has proved a commercial success at the St. Maur plant for the purification of the water supply of Paris, is shown in Fig. 1. The generator consists of an iron box divided into three sections by horizontal metal plates having the center compartment pierced by glass tubes which are made water-tight, so that there is a water jacket above these tubes. Within these glass cylinders are placed aluminum tubes of smaller diameter so that there is an annular space of about  $\frac{1}{16}$  in. between the surface of the electrodes and the dielectric. The aluminum tubes are thoroughly insulated in a metal case, and are connected to a high

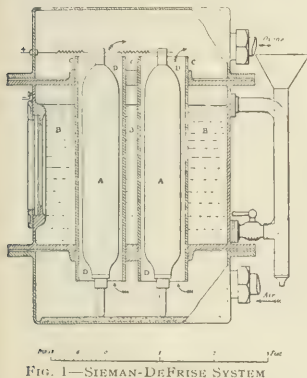


FIG. 1—SIEMAN-DEFRISE SYSTEM

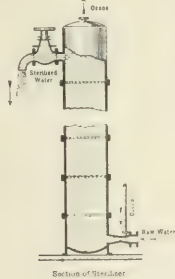


FIG. 2

tension circuit, and as the case is grounded the brush discharge is given off from the aluminum electrode. Under these conditions the oxygen of the air drawn through the tubes is converted into ozone, which is drawn off from the top of the generator by means of a pump and is then forced into and mixed with the water to be treated in a tower designed for this purpose. Each generator contains eight tubes, and the voltage used is said to be between 36,000 and 40,000 volts.

The mixing or sterilizing tower is cast iron lined with enamel, and is 25 ft. high and 1 ft. in diameter. Within this tower is a set of perforated celluloid discs for the purpose of thoroughly mixing the gas and water.

Dr. Samuel Rideal in 1908 approved of this system and pronounced it a thorough success, not only from a bacteriological standpoint but on account of the high reduction of organic matter, which was over 40 per cent as measured by the required oxygen tests. The general arrangement of the generators and mixing tower of the Sieman-DeFrise system is shown in Fig. 2.

#### THE VOSMAER SYSTEM

The Vosmaer system as originally designed was unique in that no solid dielectric was used. This type of generator, although a failure from the standpoint of efficiency, is of value to the engineer in designing

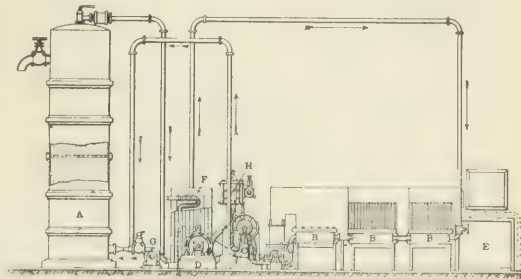


FIG. 3—VOSMAER SYSTEM FOR OZONIZING WATER

the generator in that it has proved, even to the mind of the originator, the futility of building an ozonizer without the use of a solid dielectric medium interposed between the electrodes.

This generator (Fig. 3), as described by Don and Chisholm,<sup>1</sup> consists of iron tubes provided with strips of metal fused along their length inside and insulated on porcelain supports. The width of the strips was such that the free edges did not reach the central line towards which they were directed. These edges were cut saw-shaped and each strip was connected to one pole of the high tension transformer while the tubes were connected to the other pole.

#### THE OTTO SYSTEM

The Otto system, which was used in ozonizing the water supply at Nice, France, differs quite materially from the other systems that have been described. This generator is composed of a series of metallic plates upon which is coated a metallic foil. In each pair of plates a different potential is maintained and the plates are so spaced as to generate a maximum con-

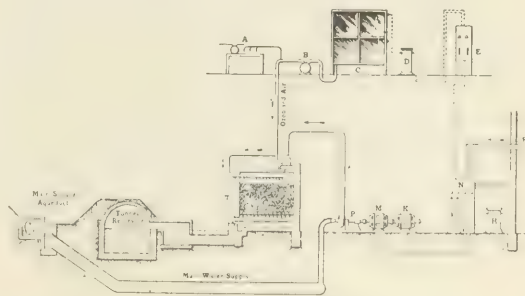


FIG. 4—OTTO SYSTEM

centration of ozone by the electrical discharges as the air is drawn through the space between each pair of plates (Fig. 4). A feature of this system is a sterilizing chamber where the ozone is thoroughly and efficiently mixed with water.

#### THE GERARD OZONIZER

The Gerard ozonizer, although based upon the same general principle as the other types, has an additional

<sup>1</sup> Don and Chisholm 1913, p. 119



feature in that the stream of air during the process of ozonization is subjected to the electrical discharge twice instead of once. This is accomplished (Fig. 5) by drawing the air down the inside of the tubes and back again through the annular space between the inner and outer set of electrodes. These tubes are of glass with tinfoil coated upon them, and are housed in a

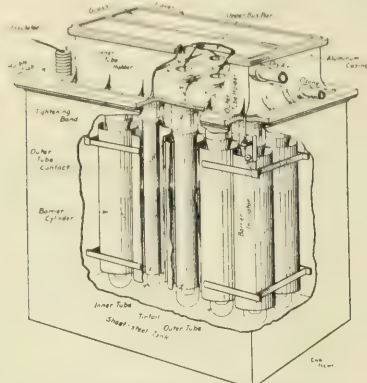


FIG. 5—GERARD OZONE GENERATOR

sheet iron box on top of which is a marble slab; over the slab is an aluminum case having a glass top so that the discharge can be seen at all times. The ozonized air is mixed with water by a spraying system (Fig. 6) permitting three separate applications by means of chambers in the mixing device. The air used in these generators is treated by refrigeration and the generators are cooled by oil.

#### THE HOWARD BRIDGE SYSTEM

In the Howard bridge system aluminum electrodes and micanite dielectrics are used, and are of either the cylindrical or flat plate design. The plant built at Lindsay, Canada, was constructed of flat plates, while the Ann Arbor, Michigan, and the Herring Run, Maryland, plants made use of the tubular design. A feature of this original patent consisted in perforated electrodes, the object of which was to increase the output by bringing the air into more intimate contact with the brush discharge: theoretically to have each jet of air as it was drawn through the perforations completely surrounded by the discharge. Also the air is not forced into the ozonizers, as is the procedure at the majority of plants of this character, but is aspirated through the generators by means of the raw water flowing through specially designed nozzles; the object of this is to reduce the cost of pumping the ozone into the water and to obtain a more intimate mixture as the ozone is drawn into the aspirator tubes.

The Herring Run plant was originally constructed under the Bridge patents, and similar in design to the plant at Ann Arbor. Owing to certain minor defects and to local conditions this plant was not a success, so it became necessary to redesign the system. The plant at Herring Run as it exists to-day, although it embodies the general features of the Bridge design, has many additional features as a result of the experimental work carried on by the Water Company under the supervision of Mr. A. E. Walden.

The generators proper are cylindrical iron drums 3.3 in. high by 36 in. in diameter, within which are 109 aluminum tubes (Fig. 7). These tubes are rolled into the head of the drum in much the same manner as the tubes in a tubular boiler, so as to be water tight. Within these tubes are micanite dielectrics, and within the dielectrics are another set of aluminum electrodes. The case of each generator is connected to one pole of the transformer and is grounded, while the inner electrodes are connected to the other pole. Discharge takes place between the electrodes and ozonizes the air as it is drawn through the annular spaces on either side of the dielectrics. The air is refrigerated and the drums are cooled by artesian well water. The ozonized air is sucked through the generators by means of the aspirators and delivered to the bottom of the mixing well.

The Herring Run plant is quite flexible in operation and has demonstrated the fact that ozone generators can be so constructed as to be capable of continuous operation under varying atmospheric conditions for long periods without serious breakdowns.

It might be of interest to state briefly the reason for the particular character of dielectrics and electrodes that have been used in the construction of these generators. It is well known that many other metallic electrodes could be used in place of aluminum,

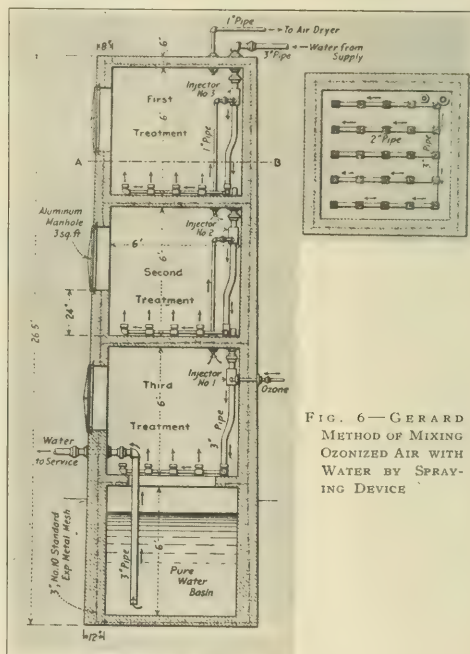


FIG. 6—GERARD METHOD OF MIXING OZONIZED AIR WITH WATER BY SPRAYING DEVICE

at a much less first cost. Aluminum, however, is the only metal of which we are aware, other than gold or platinum, that will withstand the corrosive action of the ozone. Vosmaer and others have claimed that the choice of material for electrodes is immaterial, but this is contrary to our experience during the past six years. The main objection to the use of aluminum

for this purpose is that sooner or later aluminum nitrate is formed upon the surface of the tubes, and as this compound is deliquescent it creates disastrous arcs. This condition, however, can be overcome by removing the electrode and cleaning the surface. The production of nitrate on the electrodes would indicate that some nitrous compounds are formed, and undoubtedly this is so but from careful tests we have not been able to determine this, so the quantities formed must be infinitesimal.

A number of dielectrics of various materials were tried but up to the present time none of them have, under actual tests in this particular generator, proven

imported, they would probably be prohibitory on account of breakage.

The aspirators in use to-day are not the result of a chance design but the logical result of several months of experiments with various types of nozzles designed by Mr. Walden. They are of cast iron lined with porcelain and so constructed as to furnish the maximum velocity of air with comparatively low head of water over the throats.

In the operation of ozonizers for water purification many factors must be taken into consideration, and it is due to a lack of comprehension of this fact that so many failures, in this country at least, have been

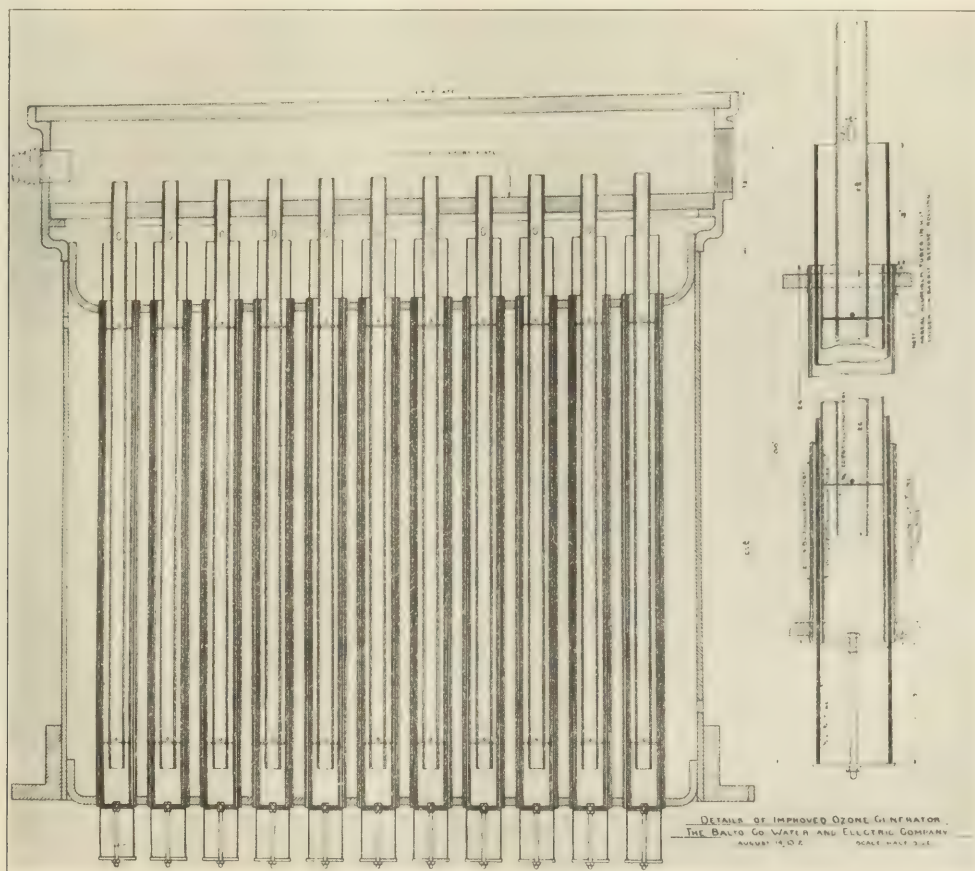


FIG. 7—DETAILS OF IMPROVED OZONE GENERATOR

as satisfactory as the micanite tubes in use. The objection that has been raised against the use of micanite is that under continuous use the mica sheets separate, causing unevenness in thickness. It has been demonstrated in our experience that this can be overcome by careful manufacture of the micanite. At the present time we have in the generators at Herring Run dielectrics of this material that have been in constant use for six years without failure.

Glass dielectrics have been tried in an experimental way at this plant and are quite satisfactory, but our results tend to show that, as these tubes have to be

experienced. The operator must keep a record of atmospheric conditions, as temperature and humidity have a considerable bearing not only on the purity of the gas but the amount generated. Generally speaking, the concentration under uniform operating conditions is, up to a certain limit, in proportion to the electrical energy expended. This yield, as has been demonstrated (Fig. 8), could be increased by the use of oxygen, but such a procedure is without the sphere of practical application. Experience at the Herring Run plant has shown that high concentrations, at least above a certain point, are not essential to efficient



sterilization, as such concentrations caused a waste of ozone as the gas passes through the mixing chambers unconsumed. We have experimented with concentrations ranging from 0.3 to 3.2 g. per cubic meter and have found that under ordinary conditions a concentration of 1 to 2 g. is enough for efficient operation.

The amount of ozone required would vary in different places, as the organic matter present in the water is to a great extent a guide as to the treatment required.

Since the operation of this plant was started, many interesting and instructive facts have been learned with reference to the effect of ozone upon the organic contents of water. Space does not permit us to go into the details concerning these experiments here, but it may be of interest to recite our experience with the action of ozone upon algae.

It was noted that at certain times the ozonized water instead of being bleached was more highly colored. This, as was found out later, was due to the breaking up of certain types of algae and similar organisms by direct oxidation of the ozone and disseminating the chlorophyll matter through the water, the ozone having, as it was later proved, no bleaching

this character before attempting ozonization, although the failure of one plant at least was caused to some extent by disregard of this condition.

From the results that have been mentioned above it is readily seen that the use of ozone as a sterilization agent is considerably more efficient than many of the other sterilizing agents used for water purification at the present time, owing to the fact that it can be used efficiently with water containing turbidities and colors comparatively high, while the other sterilizing agents cannot be guaranteed to maintain their efficiencies under these conditions.

As is well understood, the principal object of ozone treatment is sterilization, particularly the elimination of pathogenic organisms. To accomplish this two conditions must be fulfilled. Ozone must be generated in quantities sufficiently great to oxidize these growths and the gas when so generated must be thoroughly and intimately mixed with the water under treatment. Without attempting to dogmatize, it might be well to review briefly the use of ozone as a water purification agent and its application to this purpose.

If a water contains so excessive a turbidity, or a turbidity in such a state of fineness that it will require filtration at low rates with chemical coagulation, then such a water is not well suited to ozone sterilization, owing to the cost of double treatment.

There are on the other hand many types of surface waters in which the turbidity is never excessive nor do they contain suspended matter in such condition that plain sedimentation or filtration at very high rates will readily remove it. Such waters lend themselves readily to ozone treatment. To this class might also be added highly colored waters, provided the coloring matter is such that it can be bleached by ozone.

There is no doubt but that the public generally leans towards a method of water sterilization which will efficiently sterilize the supply by means other than the use of chemical compounds. This, of course, is from an aesthetic standpoint, and from the after-effects that have been experienced in chemically treated waters it is not surprising that the layman should take such a stand. A more careful study, on the part of the engineering profession, of this method along these lines might indeed prove fruitful of gratifying results.

BALTIMORE COUNTY WATER AND ELECTRIC COMPANY  
BALTIMORE, MARYLAND

effect upon this substance. These studies have also shown that the bacterial efficiency of the plant was reduced in proportion to the algae content of the raw water supply.

TABLE I—SHOWING THE EFFECT OF ALGAE GROWTH UPON THE EFFICIENCY OF OZONE STERILIZATION

BACTERIA PER CC			ALGAE PER CC			Concentration %, O <sub>3</sub>
Raw	Ozonized	Removal %	Raw	Ozonized	Removal	
1040	390	62.5	210	95	54.7	0.84
950	250	73.6	150	135	10.0	0.84
1500	210	86.0	90	30	66.6	0.92
400	40	90.0	No Algae	No Algae	....	0.84
2720	25	99.1	No Algae	No Algae	....	1.05
1400	14	99.0	No Algae	No Algae	....	0.84

Waters containing excessive turbidity cannot be efficiently treated by this method, unless the turbidity is first removed by filters, owing to the fact that the bacteria may be to some extent mechanically protected from the oxidizing effect of the gas. We can, however, and have for long periods of time, operated the ozone plant at Herring Run with a turbidity of about 40 parts per million, and by proper concentration and mixture have efficiently sterilized such waters. In one particular instance we operated upon a water with a turbidity in excess of 100 parts per million and even under such conditions the bacterial efficiency was about 90 per cent reduction over the raw water count. It is, however, customary to filter waters of

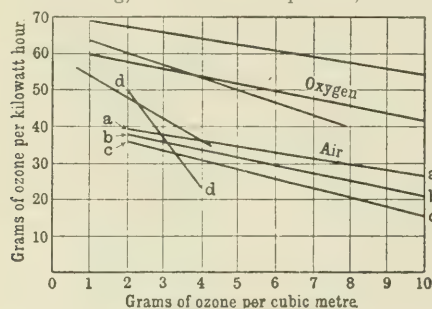
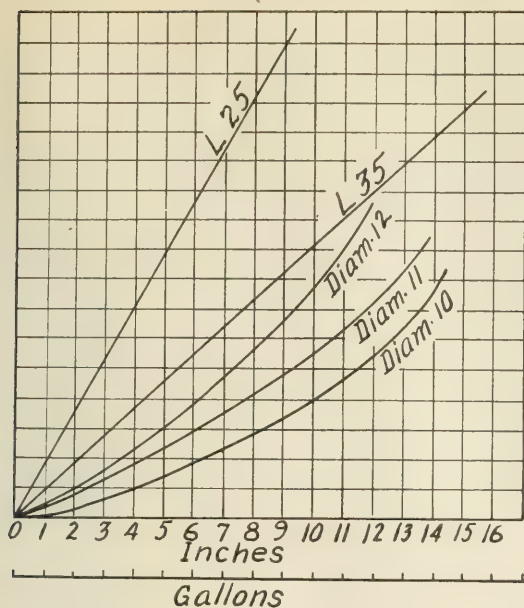


FIG. 8

## A CONVENIENT METHOD FOR RECORDING CONTENTS OF CYLINDRICAL, HORIZONTAL TANKS

By STUART W. MAHER  
Received January 13, 1916

The volume of liquid in a cylindrical tank lying on its side depends on the length and diameter of the tank, and the depth of liquid in the tank. A table giving the volumes corresponding to various values of these variables is apt to be involved and liable to errors in use. The following graphical method of tabulating these values is simple, may be put on a single sheet, and is easily used, with slight danger of error.



The chart is constructed as follows: For a tank of a certain diameter, the areas of the cross sectional segments are calculated for each inch in depth. A curve is then plotted with the inches as abscissas, and the areas as ordinates. Next, for a tank of definite length, a curve is plotted with areas of cross sectional segments as ordinates and volumes in gallons as abscissas. (It may be noted that the curves of "constant length" are straight lines passing through the origin. Hence it is sufficient to determine one point for each of these curves.) It is convenient to give the gallons on a line below that on which the inches rise are given, in order to avoid confusion.

The method of using the chart may be best shown by a specific problem on the diagrammatic curves shown in the figure. Let it be required to find the contents of a tank 25 ft. long, 10 ft. in diameter, and contents 12 in. deep. Referring to the figure, follow the ordinate rising from 12 in. to its intersection with the curve marked diam. 10. Then proceed horizontally to the line L 25, and vertically below is the required number of gallons.

ROAN MOUNTAIN, TENNESSEE

## A TABLE FOR VALUES OF CARBON IN CARBON DIOXIDE

By HOWARD LOOMIS

Received March 24, 1916

In the *J. Am. Chem. Soc.*, **31** (1909), 237, in an article entitled "The Weight of Carbon Dioxide with a Table of Calculated Results," by S. W. Parr, there is given a table of values for carbon in carbon dioxide for barometric pressures of 720–770 mm. and temperatures of 10–30° C., calculated in accordance with the formula given and discussed in that article. In making determinations of total carbon in soils in this laboratory recently, it was found that very many

of the barometric readings fell below 720 mm. Consequently, it became necessary to work out a table of values for these lower pressures. The same formula, as given in the article cited previously, was used with the additional factor for converting the results directly to milligrams of carbon, since it was in terms of the element that the final results were desired. The accompanying table is based upon the formula as used by Parr with the addition just mentioned. Values for pressures of 708–716 mm. and temperatures 20–26° C. were worked out entirely by the formula. The remaining values were interpolated from the table of values for carbon published in the pamphlet which

### WEIGHT OF CARBON IN MILLIGRAMS PER CUBIC CENTIMETER OF CO<sub>2</sub> For Bar. 700 to 718 mm. and 10 to 30° C.

Corrected for aqueous vapor and barometer readings, glass scale  
Calculated from 1.976 = wt. 1 liter CO<sub>2</sub> at 0° C. and 760 mm. at 41° Lat.

P	700	702	704	706	708	710	712	714	716	718
10° C.	0.4714	0.4728	0.4741	0.4754	0.4768	0.4782	0.4796	0.4809	0.4823	0.4837
11	0.4693	0.4707	0.4720	0.4734	0.4747	0.4761	0.4774	0.4788	0.4801	0.4815
12	0.4670	0.4684	0.4697	0.4711	0.4725	0.4738	0.4752	0.4765	0.4779	0.4792
13	0.4648	0.4662	0.4675	0.4689	0.4702	0.4716	0.4729	0.4743	0.4756	0.4770
14	0.4626	0.4639	0.4653	0.4667	0.4680	0.4693	0.4706	0.4720	0.4733	0.4747
15	0.4603	0.4616	0.4630	0.4643	0.4657	0.4670	0.4683	0.4697	0.4710	0.4724
16	0.4581	0.4594	0.4607	0.4621	0.4634	0.4647	0.4660	0.4674	0.4687	0.4701
17	0.4557	0.4570	0.4584	0.4597	0.4611	0.4624	0.4637	0.4651	0.4664	0.4678
18	0.4534	0.4547	0.4560	0.4574	0.4587	0.4601	0.4614	0.4627	0.4641	0.4654
19	0.4510	0.4523	0.4536	0.4550	0.4563	0.4577	0.4590	0.4603	0.4617	0.4630
20	0.4489	0.4502	0.4515	0.4529	0.4542	0.4555	0.4568	0.4581	0.4594	0.4607
21	0.4465	0.4478	0.4491	0.4505	0.4518	0.4531	0.4544	0.4557	0.4570	0.4583
22	0.4442	0.4455	0.4468	0.4481	0.4494	0.4507	0.4520	0.4533	0.4546	0.4559
23	0.4418	0.4431	0.4444	0.4457	0.4470	0.4483	0.4496	0.4509	0.4522	0.4535
24	0.4393	0.4406	0.4419	0.4432	0.4445	0.4458	0.4472	0.4485	0.4498	0.4511
25	0.4369	0.4382	0.4395	0.4409	0.4422	0.4434	0.4447	0.4460	0.4473	0.4486
26	0.4344	0.4357	0.4370	0.4383	0.4396	0.4409	0.4422	0.4435	0.4447	0.4460
27	0.4319	0.4332	0.4345	0.4357	0.4370	0.4383	0.4396	0.4409	0.4421	0.4434
28	0.4293	0.4306	0.4319	0.4331	0.4344	0.4357	0.4370	0.4383	0.4395	0.4408
29	0.4268	0.4281	0.4293	0.4306	0.4318	0.4331	0.4344	0.4357	0.4369	0.4382
30	0.4242	0.4255	0.4267	0.4280	0.4292	0.4305	0.4318	0.4330	0.4343	0.4355

usually accompanies the Parr Total Carbon apparatus and which is based on the table of values for carbon dioxide as published in the preceding Journal article. These interpolated values were in many cases checked by the formula for accuracy, as were many of the values in the table in the little pamphlet from which the interpolations were made. These values are worked out for Lat. 41°, the same as the original table of values.

AGRICULTURAL EXPERIMENT STATION  
BROOKINGS, SOUTH DAKOTA

## A RAPID METHOD FOR THE ACCURATE DETERMINATION OF TOTAL CARBON IN SOILS

By ROBERT M. SALTER

Received March 13, 1916

Most methods in common use for the determination of total carbon in soils are not sufficiently rapid to be well adapted to routine laboratory practice. This fact led the writer to attempt an adaptation of the direct combustion method, as now used in the rapid determination of carbon in steel, to the determination of total carbon in soils. The method evolved and successfully used in several hundred determinations is an adaptation with modifications of the method described by Fleming<sup>1</sup> for the rapid determination of carbon in iron and steel. It depends upon the direct combustion of soil in a current of oxygen, the gases being dried by phosphoric anhydride and the carbon

<sup>1</sup> *The Iron Age*, **93**, 64–66.



dioxide absorbed in soda-lime and determined by weight.

In the apparatus shown in Fig. I, the gas enters bottle *C*, through a Folin absorption tube. The KOH solution frees the oxygen from any traces of carbon dioxide. *D* dries the gas and insures freedom from carbon dioxide. The mercury valve bottle prevents gas from backing into bottles *C* and *D*. The furnace *F* is an Eimer and Amend, having replaceable heating units, but is modified by installing 4 platinum-nichrome thermocouples connected in series of galvanometer *G*, so as to show the furnace temperature at all times; the scale on the galvanometer is calibrated by comparison with a standard pyrometer. The tube *I* contains, just within the exit end of the furnace, 5 in. of coarsely granular cupric oxide, held in position by 2 plugs of asbestos fiber. *J*, containing granular zinc, serves to stop sulfur, chlorine or acid fumes; it also acts as a filter. *K* removes moisture from the gases, and as the  $P_2O_5$  liquefies it is absorbed by the glass wool, more anhy-

drous allowing it to pass through the absorption end of the train. The whole apparatus is permanently set up in an electrically lighted case with sliding glass doors.

#### METHOD OF PROCEDURE

A 2-g. sample of soil<sup>1</sup> is weighed, mixed with 2-3 g. of 40-mesh alundum and transferred to an alundum boat.<sup>2</sup> Before introducing the sample into the combustion tube<sup>3</sup> it is necessary to see that the exit tube of the absorption bulb is disconnected from the suction bottle at the point *a*, that the two-way cock *S* stands in a position to permit gas entering the absorption end of train, and that the screw clamps *b* and *c* and stop-cock *d* are closed. The furnace<sup>4</sup> should stand at a temperature of 925-950° C. The boat is introduced into the end of the combustion tube, followed by asbestos plug *R*. Both are then pushed to the center of the furnace by means of a stiff nichrome wire and connection *e* quickly made. After a few seconds to allow the gas immediately produced to escape,

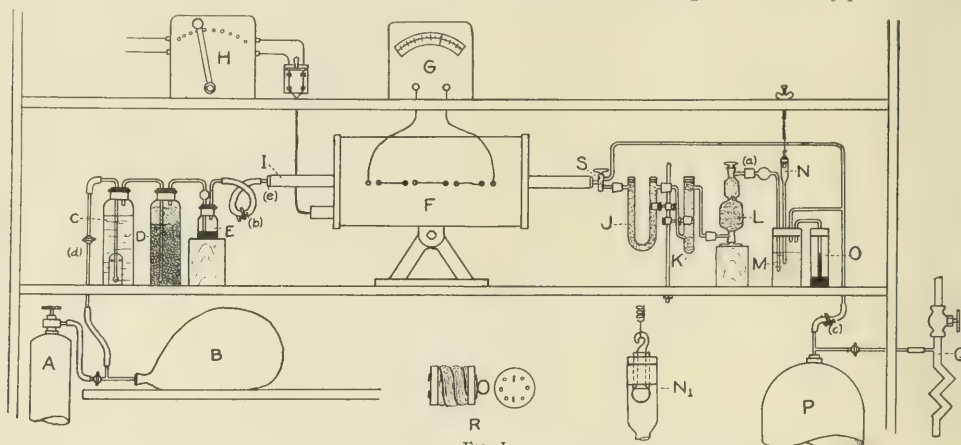


FIG. I

A—High Pressure Oxygen Tank, 150 gal., 1800 lbs. pressure. (S. S. White Dental Co., C. P. oxygen)  
B—Rubber Bag, 1 gal. capacity C—30 per cent KOH Solution  
D—Granular, Anhydrous CaCl<sub>2</sub> (below), Separated by Layer of Asbestos Fiber from 20 mesh Soda-Lime (above)  
E—Mercury Valve Bottle F—Electric Combustion Furnace H—Rheostat  
I—Silica Combustion Tube, Glazed, 24 in. long by 7/8 in. inside diameter

J—U-tube Containing 2 mm. Granulated Zinc  
K—P<sub>2</sub>O<sub>5</sub> Supported on Glass Wool  
L—Fleming Soda-Lime Absorption Bulb M—Suction Bottle  
N—Safety Valve, Ground Glass (shown below at N<sub>1</sub>)  
O—Mercury Suction Gauge P—10 gal. Suction Tank  
Q—Water Suction Pump R—Asbestos Plug  
S—2-way Stopcock

dride being added from above. The lower portion of the absorption bulb *L* is filled with alternate layers of Baker's 20- and 40-mesh soda-lime, the quantity used being sufficient for 60 or more determinations of total carbon on average soils. The upper portion contains  $P_2O_5$ , which insures the gases leaving the bulb with the same moisture content as on entering. The valve *N* prevents accidental drawing of mercury from *O* into *M* and facilitates regulation of suction. The suction tank *P* gives more uniform suction than the pump alone, and one exhaustion serves for 15 or more determinations. *R* is made by joining 2 perforated discs of asbestos board by means of a stiff nichrome wire (B. & S. gauge 20) so as to leave a loop at one end by which the plug may be withdrawn from the combustion tube. Between the 2 asbestos discs is some loose asbestos fiber, held in place by a spiral of nichrome wire. The stop-cock *S* permits drawing oxygen through the combustion tube with-

screw clamp *b* is opened and connection *a* closed. Sufficient suction, measured by mercury gauge *O*, to produce somewhat more than the desired rate of gas flow (previously determined) is then applied. The gas flow is regulated by adjusting stop-cock *d* so that 750 cc. to 1000 cc. of oxygen pass through the apparatus in 20 min., which is sufficient time

<sup>1</sup> With soils containing over 5 per cent total carbon, a 1-g. sample is sufficient.

<sup>2</sup> Convenient size of the boat for 2-gram sample is 3 3/4 in. X 5/8 in. outside dimensions. Alundum mixed with soil increases porosity and insures access of oxygen to all parts. "R. R. Alundum, alkali-free, especially prepared for carbon determinations," is used.

<sup>3</sup> Before starting a single determination, or a series of determinations, the apparatus should be connected up and sufficient oxygen passed through to burn out any carbon contained in the asbestos plugs and to sweep out the air originally in the train. The further passage of oxygen should produce no increase in the weight of absorption bulb.

<sup>4</sup> Caution must be observed to prevent the furnace attaining a temperature of much over 1000° C., as cupric oxide fuses at 1064° C. and when this occurs the silica tube slugs with the fused oxide and invariably cracks on cooling. A temperature of over 825° C. is necessary to insure decomposition of carbonates.

for complete combustion.<sup>1</sup> The temperature is maintained at 925–950° C. throughout the combustion. The absorption tube<sup>2</sup> is finally disconnected, both inlet and exit closed, allowed to stand on the balance pan 15 min., and weighed.<sup>3</sup>

Little difficulty is experienced in getting duplicate determinations to check within 0.01 per cent total carbon, equivalent to about 0.0007 g. CO<sub>2</sub> on a 2-g. sample. A sample of acetanilide (Merck, U. S. P.—no precaution taken to purify sample) gave in duplicate determinations 0.0409 and 0.0409 g. carbon instead of the theoretical quantity 0.0411 g. These determinations indicate that any oxides of nitrogen formed by the oxidation of organic N-compounds are sufficiently reduced, probably in the zinc tube, to prevent absorption in the soda-lime bulb. The combustion of a previously burned sample of soil to which was added 0.0060 g. N, as nitrate, also failed to show any increase in weight of the absorption bulb.

In routine work, using 2 absorption bulbs besides the one used as a tare in weighing, the time required for each determination is approximately 25 minutes.

DEPARTMENT OF SOILS  
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MORGANTOWN, WEST VIRGINIA

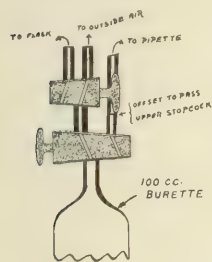
#### A MODIFICATION OF THE GAS BURETTE OF THE PARR TOTAL CARBON APPARATUS

By HOWARD LOOMIS

Received March 24, 1916

While determining total and inorganic carbon in soils in this laboratory, it was soon observed that many times after passing the mixture of air and carbon dioxide evolved into the absorption pipette the residual volume of air was less than 100 cc. and could not be measured directly in the burette. This necessitated the introduction of air into the burette in measured volume sufficient to allow the residual air in the pipette to be measured. As originally designed no way was offered for this but to introduce air into the burette through the tube leading from the generating flask, which,

even after removal of the flask, is always filled with the liquid forced over to the burette when the final portion of the air-carbon dioxide mixture is expelled from the flask and the tube. The introduction of



<sup>1</sup> Drawing the gas through by suction is found preferable to forcing it through by pressure, it being much easier to prevent leakage. Any error from this source would be comparatively insignificant as the leakage would be inward rather than outward. The content of CO<sub>2</sub> in ordinary air is such that it would require an inward leakage of approximately 160 cc. to cause an increase of 0.0001 g. in the weight of the absorption bulb. All connections, where possible, were made of rubber stoppers, these being less liable to develop leaks than connections of rubber tubing.

<sup>2</sup> The Fleming absorption bulb was found to be very efficient, it being possible to increase the rate of gas flow 5 to 8 times that actually used without danger of incomplete absorption of CO<sub>2</sub>.

<sup>3</sup> Due to the rather large size of the absorption bulb, some precaution is necessary in weighing to prevent errors due to differences in the amounts of moisture condensed on the surface of the bulb and to changes in temperature and atmospheric pressure. By using a second bulb or glass bottle of approximately the same weight, containing about the same quantity of soda-lime, as a tare in weighing, these errors are rendered insignificant.

this amount of liquid, containing as it does much sediment, leaves the burette in a badly soiled condition after a few determinations, as well as clouding the liquid in the leveling tube, thus making correct readings difficult. To eliminate these difficulties, a second three-way stop-cock was introduced into the line from the generating flask to the burette, as shown in the accompanying sketch. By turning this cock to open to the outside air, 100 cc. or more of air can be accurately measured into the burette, then the residual air from the absorption pipette can be forced back into the burette as usual and its volume measured by difference. Thus the only amount of liquid introduced into the burette is that included between the two stop-cocks, a very small amount which usually carries little sediment.

AGRICULTURAL EXPERIMENT STATION  
BROOKINGS, SOUTH DAKOTA

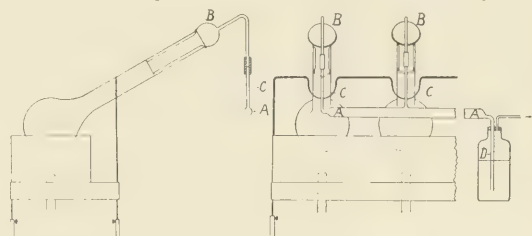
#### APPARATUS FOR KJELDAHL DETERMINATIONS

By WYATT W. RANDALL

Received June 13, 1916

In THIS JOURNAL 8 (1916), 521, there is described an apparatus whose object is to facilitate Kjeldahl determinations. The flasks are closed by means of rubber stoppers fitted with lead tubes through which the vapors given off are conducted to some form of absorption vessel. To the present writer any device which permits the products of the action of hot sulfuric acid fumes upon rubber to drip into a Kjeldahl digestion, appears on its face highly unsatisfactory, although it must be confessed that this is finding fault *a priori*.

The device indicated in the accompanying figure has for several years been used in this laboratory with



great satisfaction. It calls for a little glassblowing of a simple kind, and ought to be easy of construction in any laboratory. Calcium chloride drying tubes, *B, B*, of the common type are somewhat flared at the wider end, until they fit more or less closely in the necks of the Kjeldahl flasks, as shown in the figure. The narrow tube of each is lengthened by fusing on a piece of similar tubing, which in turn is bent as indicated. A glass tube, *A*, of about 10 mm. bore, and of the proper length for the rack used, is provided with side tubes, *C, C*, fused in at the proper intervals, and with an outlet, *D*, dipping below the water surface in a bottle which is, in turn, connected with a water pump. The bulb tubes are connected with the tubes *C, C* by means of short pieces of rubber tubing; these, of course, become corroded in time and may have to be replaced. As is evident, the ap-



paratus is only a modification of that of Sy, but it is probably easier to construct. The products of the digestion remaining in the flask at the end of the operation will thus have come in contact with nothing but glass. A slow stream of air drawn through the bottle serves to prevent the escape of any fumes from the digestion flasks into the air of the laboratory.

It may be that the slightly increased pressure under which Mr. Merkle conducted his determinations has-tens appreciably the completion of the digestion. I can only say that with the apparatus here described foaming has never been a source of inconvenience.

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## SIMPLIFICATION OF GAS ANALYSIS CALCULATION

By WILLIAM J. WALKER

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The following note is an attempt to simplify existing methods of estimating the various quantities involved in engineering gas analysis calculations. These are met with in flue gas analysis, gas engine supply and exhaust gas analysis and in dealing with gas producer reactions and tests.

In gas analyses all quantities are stated in terms of proportion by volume and the first operation generally necessary is to reduce these to proportion by weight. This is obtained by the use of the formula

$$\left. \begin{array}{l} \text{Proportion by weight of the} \\ \text{constituent A in the gas mixture} \end{array} \right\} = \frac{aA}{aA + bB + cC + dD + \text{etc.}}$$

where A, B, C, etc., = proportion by volume of each constituent in the gases and *a*, *b*, *c*, etc., = molecular weights. Thus if in a gas engine exhaust analysis the constituents CO<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub> only are present then

$$\left. \begin{array}{l} \text{Proportion by weight of carbonic} \\ \text{acid gas in the mixture} \end{array} \right\} = \frac{44\text{CO}_2}{44\text{CO}_2 + 28\text{N}_2 + 32\text{O}_2}$$

and so for the proportion of any constituent. Also, if it is desired to obtain the proportion by weight of any element it is only necessary to multiply each of the constituents containing that element by the total atomic weight of the element contributed by it towards the molecular weight of the constituent. Thus, if the constituent gases A, B and C contain a common element *x*, then

$$\left. \begin{array}{l} \text{Proportion by} \\ \text{weight of } x \end{array} \right\} = \frac{a'A + b'B + c'C}{aA + bB + cC + dD + \text{etc.}}$$

where *a'*, *b'* and *c'* = total atomic weights of the element contributed towards the molecular weight of the constituent containing it.

Thus, if a producer gas consists of a mixture of CO, C<sub>2</sub>H<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub> and CO<sub>2</sub>, then

$$\left. \begin{array}{l} \text{Proportion by weight} \\ \text{of carbon} \end{array} \right\} = \frac{12(\text{CO} + \text{CO}_2 + 2\text{C}_2\text{H}_4)}{44\text{CO}_2 + 28(\text{CO} + \text{C}_2\text{H}_4 + \text{N}_2) + 2\text{H}_2}$$

and

$$\left. \begin{array}{l} \text{Proportion by weight} \\ \text{of hydrogen} \end{array} \right\} = \frac{2(\text{H}_2 + 2\text{C}_2\text{H}_4)}{44\text{CO}_2 + 28(\text{CO} + \text{C}_2\text{H}_4 + \text{N}_2) + 2\text{H}_2}$$

Hereafter, the symbol X will stand for the summation of the series *aA* + *bB* + *cC* + *dD* + etc., for the gas mixture considered. This quantity X is required for many purposes in different calculations. To obtain it quickly and with the minimum of calculation the chart shown opposite has been constructed. For

the present, attention is called to the three series of lines drawn at angles whose tangents, according to the scale chosen, are 44, 32 and 28. Suppose that the gas analyzed consists of a mixture of CO<sub>2</sub>, O<sub>2</sub>, CO, N<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, and H<sub>2</sub>. Such a mixture includes the large majority of cases which come before the engineer.

The molecular weight of CO<sub>2</sub> is 44  
The molecular weight of CO, H or C<sub>2</sub>H<sub>4</sub> is 28  
The molecular weight of O<sub>2</sub> is 32  
The molecular weight of CH<sub>4</sub> is 16

To obtain X multiply the volumetric proportion of hydrogen by 2. Finding this value on the right-hand A scale, the approximate position between two of the lines sloping at an angle of tan<sup>-1</sup> 32 can be judged and maintained while these lines are followed until the value of (1/2 CH<sub>4</sub> + O<sub>2</sub>) is reached on the horizontal scale. Proceeding horizontally from there to the left-hand A scale thus gives the value, on that scale, of 2H<sub>2</sub> + 16CH<sub>4</sub> + 32O<sub>2</sub>. From this point following the lines at the angle tan<sup>-1</sup> 28 until the value of CO + N<sub>2</sub> + C<sub>2</sub>H<sub>4</sub> is reached on the horizontal scale gives the value of 2H<sub>2</sub> + 16CH<sub>4</sub> + 32O<sub>2</sub> + 28(CO + N<sub>2</sub> + C<sub>2</sub>H<sub>4</sub>) on the left-hand scale A. Lastly, from this point proceeding along the lines at the angle tan<sup>-1</sup> 44 until the value of CO<sub>2</sub> is reached on the horizontal scale, the value of X is obtained on the vertical scales A. The whole operation can, of course, be carried out much more quickly than it can be described. The accuracy obtainable with the diagram given is well within 1 per cent.

Thus, if the analysis of the supply and exhaust gases from a gas engine is obtained, the weight of air per pound of supply gas is given by

$$\left\{ \begin{array}{l} \text{Proportion by weight} \\ \text{of hydrogen} \end{array} \right\} + \frac{\text{Proportion by wt. of C in supply gases}}{\text{Proportion by wt. of C in exhaust gases}} - 1$$

All the quantities involved here can be obtained rapidly from the diagram. The method of procedure is evidently much better than the laborious compilation of quantities, each involving the weights per cubic foot of the constituent gases.

Another quantity, the compilation of which one often sees carried out by roundabout methods, is the volume of any constituent per pound of the gas mixture.

Thus,

$$\left. \begin{array}{l} \text{Volume of constituent A} \\ \text{per lb. of gas} \end{array} \right\} = \frac{A}{\text{Weight in lbs. of 1 cu. ft. of gas}} = \frac{A}{0.0028X}$$

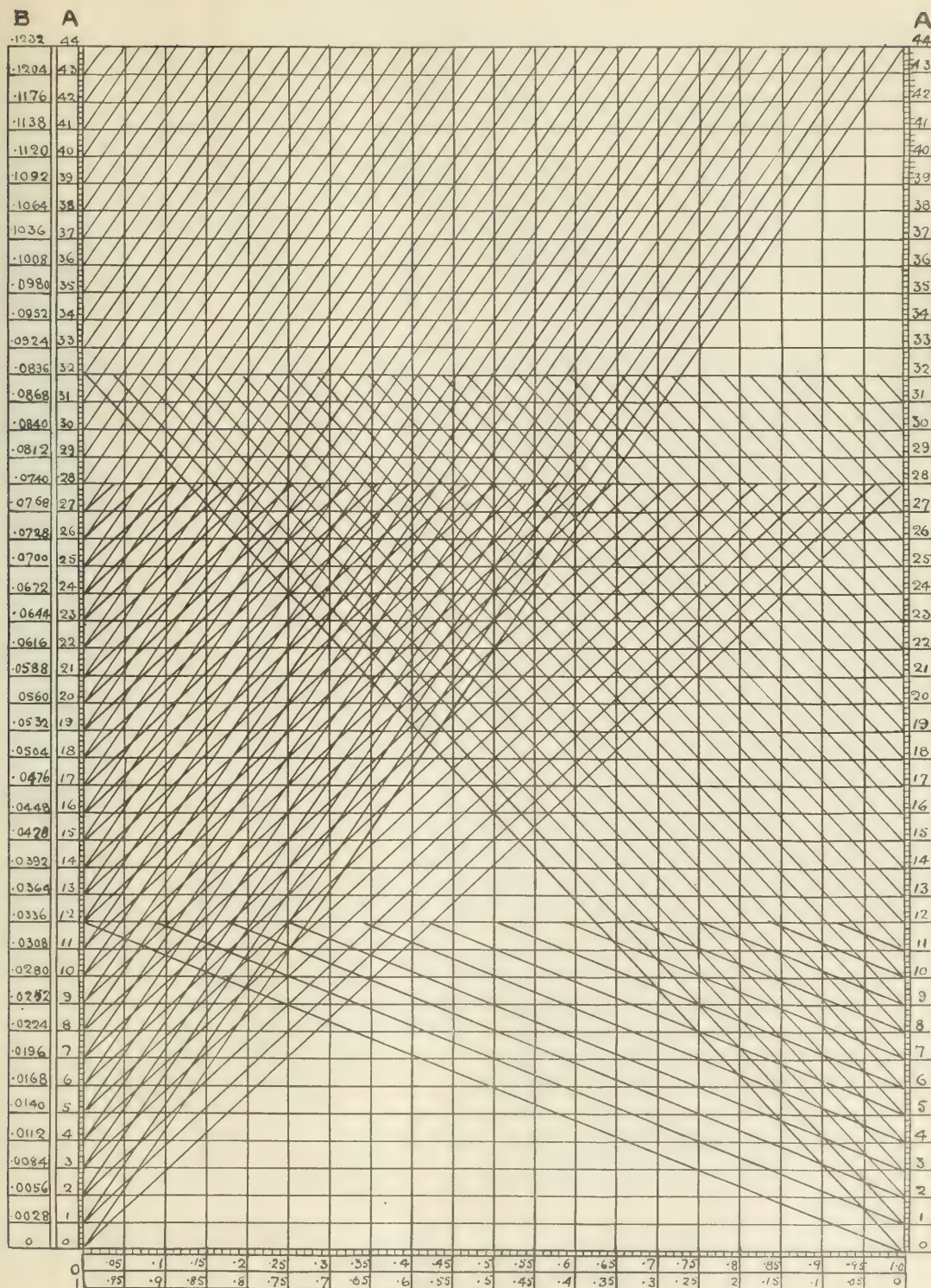
where 0.0028 = weight in lbs. of 1/2 cu. ft. of hydrogen and A and X have the same signification as before. This is evident since the weight per cu. ft. of any gas equals its molecular weight multiplied by the weight of half a cubic foot of hydrogen. Thus if a gas contains 0.25 part of CO and 0.13 part of H<sub>2</sub>, then

$$\left. \begin{array}{l} \text{The weight of CO + H}_2 \\ \text{per lb. of gas} \end{array} \right\} = \frac{0.25 + 0.13}{0.0028X} = \frac{0.38}{0.0028X}$$

Column B in the chart gives the values of 0.0028 X, or the weight of one cubic foot of the gases considered.

The lines drawn at an angle of tan<sup>-1</sup> 12 are, for the purpose of obtaining the value of 12(CO + CO<sub>2</sub> + CH<sub>4</sub> + 2C<sub>2</sub>H<sub>4</sub>) which is required in the computation of the proportion by weight of carbon in the gases.

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# THE ACTIVATED-SLUDGE METHOD OF SEWAGE PURIFICATION

Papers presented at the 52nd Meeting of the AMERICAN CHEMICAL SOCIETY, University of Illinois, Urbana-Champaign, April 18 to 21, 1916

## PURIFICATION OF SEWAGE BY ACTIVATED SLUDGE IN WINTER AT THE SEWAGE TESTING STATION, MILWAUKEE, WISCONSIN

By W. R. COPELAND

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In winter the temperature of the Milwaukee sewage averages about 51° F. with occasional drops to 40° F. or less when melted snow enters the sewers. These low temperatures, especially the latter, retard oxidation of organic matter and decrease the stability of the treated liquor. By applying 2 1/4 cu. ft. of air per gallon of sewage the continuous-flow plants removed 90 per cent of the bacteria in the sewage of Milwaukee and reduced the suspended matter to about 15 parts per million. The sludge contained about 5 per cent of nitrogen calculated as ammonia, 1 3/4 per cent of available phosphoric acid, and 0.4 per cent of potash. This sludge can be recovered by pressing without the use of lime.

The sewage testing station of Milwaukee, on the shore of Lake Michigan, is exposed to the full rigor of this northern climate. During January and February the thermometer registered below zero on nine days and dropped to -15° at the coldest period. The sewage temperature dropped with the approach of winter from 67° F. in September to 50° F. in January, but

sewage purification have maintained for years that quantities of material valuable for fertilizer were being wasted by dumping the sewage of Milwaukee into Lake Michigan. The great problem connected with the recovery of these products lies in separating the sludge from the water. The activated sludge contains 98 per cent of water and 2 per cent of suspended solids and some of the solids seem to be sticky. Centrifuges or presses of the usual patterns heretofore employed have proved unsatisfactory either because the cloths used as strainers became choked with the gluey matters or because considerable quantities of lime had to be added to give enough body to the liquor for the presses to work on. The lime added attacked the nitrogen compounds, driving off ammonia, and combined with the fats to form insoluble soaps. Such treatment decreased the value of the sludge and by building up the volume increased the cost of removal. The Henry R. Worthington Co. installed a new type of press at the Milwaukee sewage testing station that has treated the activated sludge with marked success. No lime is required, the bags do not get sticky, comparatively little power is used, and the sludge obtained can be converted into fertilizer. Typical analysis of activated sludge re-aerated and of pressed sludge cake are given in Table II.

Some characteristic samples of the sludge that were sent to

TABLE I AVERAGE DAILY ANALYSIS OF SEWAGE BEFORE AND AFTER PURIFICATION BY THE MILWAUKEE CONTINUOUS-FLOW ACTIVATED-SLUDGE PROCESS AT FALL AND WINTER TEMPERATURES: SOURCE OF SAMPLES—SEWAGE AND EFFLUENT

Month and Year	TEMPERATURE ° F.		Sewage Treated Gal.	AIR PER GAL. Cu. ft.	BACTERIA PER CC.		Stability Hours	Suspended		P. P. M. NITROGEN AS				P. P. M. OXYGEN	
	Air	Liquor			20° C.	37° C.		P. P. M.	Free NH <sub>3</sub>	Organic	Nitrite	Nitrate	Consumed	Dissolved	
Oct., 1915.	53	62	59,000	1.6	1,384,000	347,000	120	263	17.0	38	0.21	0.10	127	1.5	
		63			50,000	12,000		16	5.1	9	0.22	8.70	19	2.8	
Nov., 1915.	41	59	60,000	2.1	1,242,000	297,000	120	438	17.5	40	0.16	0.20	149	2.3	
		61			119,000	12,000		16	11.4	17	1.09	4.10	27	6.3	
Jan., 1916.	27	50	71,000	1.7	770,000	170,000	88	336	15.4	35	0.13	0.51	135	5.5	
		49			62,000	8,800		11	14.7	19	0.16	0.67	31	6.1	
Feb., 1916.	22	51	68,000	2.1	960,000	150,000	96	300	17.2	42	0.16	0.36	143	4.8	
		50			68,000	8,000		14	16.5	22	0.17	0.50	27	6.4	
Mar., 1916.	37	50	71,000	2.3	1,000,000	126,000	67	383	15.8	36	0.13	0.41	146	4.7	
		50			159,000	16,000		15	15.2	21	0.19	0.42	35	6.0	

the zero weather did not reduce it further. When melting snow water entered, however, the temperature of the sewage dropped for several hours at a time to 43° F. and on a few occasions registered only 34° F. As the oxidation of organic matter obtained with the activated sludge process depends upon the activity of living bacteria which do their best work at 68° F. to 70° F., we looked forward with some misgiving to the winter period because their vitality would be checked by the cold sewage. But by increasing the air supply the plants were enabled to remove the suspended matter, colloids, and bacteria in a satisfactory manner as indicated by the analyses given in Table I. The data show that as the temperature of the sewage dropped the oxidation of the organic matter decreased, as indicated by the fact that nitrate in the effluent fell from 8.7 in October to 0.67 part per million in January, and the oxygen consumed increased from 19 to 31. The decrease in oxidation was accompanied by a decrease in stability of the effluent from 5 to 3 days. The treated liquor contained 6 parts per million of dissolved oxygen in January, February, and March and only a trace of nitrate, whereas in summer nitrate is high and dissolved oxygen is low; therefore, the liquor seems to depend for its stability on nitrates in summer and dissolved oxygen in winter. Briefly, the data show that good bacterial removal and clarification can be maintained at winter temperatures without oxidizing the ammoniacal nitrogen into nitrate.

Bearing in mind that quantities of fat, nitrogen, and perhaps phosphoric acid are turned into the sewers daily by the houses, breweries, packing houses, tanneries, etc., men interested in

other laboratories for analysis contained about 0.43 per cent of potash.

From the data obtained at the Milwaukee sewage testing station it appears that the activated sludge process will yield about 3000 or 4000 gallons of sludge containing 98 per cent of water per 1,000,000 gallons of sewage treated. When reduced to 10 per cent of moisture this sludge will weigh about one-half ton. Assuming that the nitrogen is worth \$2.00 per unit, the value of the sludge should range between \$10.00 and \$12.00 a ton. We estimate that it will cost \$5.00 to \$6.00 to convert the sludge into fertilizer and pay freight to the consumer.

The data in Table I show that the suspended matter in the Milwaukee sewage received at the station is rather high, perhaps one-third to one-half greater than that of average American

TABLE II—AVERAGE ANALYSIS OF REAERATED ACTIVATED SLUDGE AND PRESS CAKE

SOURCE	Sp. gr.	Mois- ture	PER CENT BY WEIGHT			BASIS 10% MOISTURE			Ni- trate	Total P <sub>2</sub> O <sub>5</sub>
			Min- eral	Or- ganic	FAT	Free NH <sub>3</sub>	Alb- um.	NH <sub>4</sub>		
Sludge...	1.004	98.9	32.5	57.3	5.8	5.6	1.17	3.19	0.30	2.3
Cake...	1.113	74.6	30.2	59.9	4.3	6.3	0.59	2.82	0.12	1.88

(a) The figures are for nitrogen calculated as "Free Ammonia" and were obtained on sludge which had been stored with continuous aeration for several days, and they are about 1 per cent higher than those that would be obtained by pressing fresh sludge.

sewage. For that reason the volume of the sludge recovered here may be greater than would develop in cities where water is used more extravagantly.

Experiments on purification of sewage by the activated-sludge

process in winter have therefore shown that about 90 per cent of suspended matter and bacteria were removed, that the sludge can be dried by pressing from 98 to 75 per cent moisture, thereby converting the sludge into a small volume which can be easily handled, and that the sludge has sufficient value to ensure a constant market.

MILWAUKEE, WISCONSIN

## AERATION OF SEWAGE IN THE PRESENCE OF ACTIVATED SLUDGE

By E. J. FORT

Chief Engineer of Sewers, Borough of Brooklyn

The engineering profession for a number of years has been looking for a method of sewage treatment based on biological and biochemical principles and employing air under pressure applied directly to the sewage. The advantages that such a method promises of very intensive treatment with relatively small expense for land and elimination of extensive filter beds and the entire septic cycle, thus doing away with the offensive odors that evolve from the putrefaction of sewage and sludge, have rendered it a very attractive subject for investigation and experiment. Until recently the results of many investigations and studies have been little more than suggestive of unrealized possibilities.

The experiments of Black and Phelps at the Brooklyn Sewage Disposal Plant in 1910 were about the first that indicated the possibility that there had been discovered a method of treatment with compressed air, which might on further study and development prove to be the one sought so long. These experimenters found it possible to reduce the demand of sewage for oxygen 33 to 50 per cent in a retention period of about three hours by using about two volumes of air per volume of sewage. As the scale on which these experiments were made was small and the apparatus was rather crude a more thorough investigation obviously was necessary before their results and the principles could be utilized in designing and operating full-sized plants.

In 1912, sewage-treatment experiments were authorized by the City of New York on a rather liberal scale, and several units were provided in the design of the experimental plant to carry on studies of sewage aeration. A 16,000-gal. tank arranged for aeration experiments and named the tank aerator, the design of which met the approval of Professor Phelps, was put in service in the fall of 1913 as a continuously flowing sewage aerator. This tank was so connected to the system that it could be operated either by the continuous flow or by the fill-and-draw method and could be supplied either with crude sewage or with the effluent from Imhoff tanks. Sewage was introduced at the top and withdrawn from the bottom, though this method of operation could easily be reversed by a slight change of pipe. The crude sewage was supplied by gravity from the sewage supply, or quieting tank, that served the entire experimental work of the station. It was pumped from the sewer by a reciprocating pump and was detained less than five minutes in the quieting tank. Compressed air was supplied by a duplex air compressor of ample size, installed as part of the experimental plant.

The tank was 12 ft. in diameter and 25 ft. 8 in. in depth. A grid for supplying compressed air, which was placed at the bottom of the tank, was supported by  $7\frac{1}{2}$  in. of broken stone which passed a 2-in. but was retained by a 1-in. ring. An equal depth of broken stone of the same size was placed over the grid, so that the air first passed upward through the voids in the broken stone. The outlet of the tank, as originally installed for sewage-aeration experiments, was about one foot above the surface of the broken stone, so that one-twentieth to one-twelfth of the contents of the tank was retained at each emptying. A lower outlet was provided for draining the lowest level of the tank. The compressed-air grid consisted of two  $1\frac{1}{2}$ -in. pipes crossed at right angles in the center. The arms of the cross

were connected with quarter circles of  $\frac{3}{4}$ -in. pipe to form five concentric rings, each of which was perforated at 6-in. intervals with  $\frac{1}{16}$ -in. holes. The air, entering through  $1\frac{1}{2}$ -in. pipes, was thus distributed to the rings and discharged into the broken stone surrounding the grid.

Nine deflector discs, supported by a vertical 4-in. pipe in the center of the tank, formed a feature of the tank. The discs were in form not unlike wheels; the supporting pipe passed through their hubs. The surface of each disc was horizontal, and occupied the entire cross-section of the tank, which was thus divided into story-like compartments. They were designed to deflect the downward flow of sewage in order to prevent downward streaming and to equalize and give a sinuous motion to the upward flow of air; thus more even distribution of both air and sewage were secured. As stated above they were each made in the form of a wheel, supported on six arms, between which were slats, radiated from the iron hub of each disc. The slats were set in grooves in the arms with a dip of  $45^\circ$ . The slats in alternate discs were set sloping from and toward the center.

The first experiments, in 1913, on the continuous-flow plan with plain aeration of sewage in the tank aerator, were made with an air supply of 0.75 volume per volume of sewage and 2-hr. retention period. This it was considered would be the minimum treatment. It was insufficient to produce any marked result. The retention period was, therefore, doubled, but with little improvement. A greater volume of air was then applied but the result was not satisfactory, and the results secured were not even promising during the winter and early spring of 1914. As it was thought that the tank would work better after it had been thoroughly seeded with aerobic bacteria, the continuous-flow method was suspended, and the sewage was retained in the tank under aeration for 24-hr. periods, the fill-and-draw method of operation being followed. Some phenomena of activated sludge were observed at this stage of the experiment, but the principle was not then recognized as being important. This method of ripening was carried on until June 14, when apparently the tank had ripened, and a fine clear effluent could be obtained with certainty from crude sewage or Imhoff tank effluent on the fill-and-draw plan with 24 hrs. aeration.

Return was then made to the continuous-flow method, and operation was commenced with 3.25 volumes of air per volume of sewage with 5-hr. tank retention. This did not produce an effluent of satisfactory stability. The retention period was increased to 24 hrs., with the same rate of air flow per minute, the air supply being thus increased to 18 volumes per volume of sewage. The effluent after passing a settling tank with 3-hr. retention then showed a quality comparable with that from a sprinkling filter. Its average relative stability was 84 per cent. The quantity of air was later reduced one-half, or to 9 volumes per volume of sewage treated, the continuous-flow plan being retained. Under these conditions the relative stability of the settled effluent fell to 59 per cent. This work was continued until it seemed to be demonstrated completely that though a fairly satisfactory effluent could be obtained the cost of air made the treatment considerably more expensive than treatment by the sprinkling filter.

Table I shows the average of results of operating the tank aerator to October 1, 1914, on the continuous-flow plan without the employment of activated sludge. Of course, some activated sludge may have been present, but if so it was not recognized as such, and we had then no knowledge of that method, which was not announced until this series of experiments was about completed.

As experiments in sewage aeration with activated sludge characterized our work during 1915, the aerator tank was rearranged in March for use as an activated-sludge tank. The accumulation of activated sludge, which had been commenced about the middle of March, was sufficient to permit regular



operation of the experimental unit by the middle of May, but it was thought best to continue until June 1st, on which date the tank was put into service on a regular cycle of operation. The cycle began with a period of sedimentation, during which the air was shut off, followed by a period of discharge, which con-

TABLE I—RESULTS OF OPERATING TANK AERATOR ON CONTINUOUS FLOW PLAN WITHOUT ACTIVATED SLUDGE

[Parts per Million Except as Otherwise Designated]			
Period of retention in tank aerator, 24 hours. Amount of crude sewage treated in 24 hours, 16,000 gallons. Air applied, 2.3 cu. ft. per gallon.			
Settling period of effluent in settling tank No. 1, 3 hrs., 12 min.			
	Crude sewage	Tank aerator	Settling Tank No. 1
Settling matter (cc. per liter).....	2.3	5.4	0.2
Total suspended solids.....	161	103	40
Volatile suspended solids.....	130	79	30
Total oxygen consumed.....	58	39	26
Dissolved oxygen consumed.....	37	27	22
Total dissolved oxygen.....	1.4	3.1	1.1
Dissolved oxygen demand.....	191	55	31
Relative stability (percentage).....	.....	.....	.....
Undiluted.....	.....	43	84
Diluted 1:10 with distd. water.....	45	94	100

tinued 1½ hrs., when refilling began and the air was turned on. Refilling continued for 1½ hrs., and aeration was continued for a period of 20 hrs., when the cycle began again. The air was measured by a Venturi meter devised for the purpose. Both influent and effluent sewage were measured. The results in averages for June, July and August, 1915, are shown in Table II.

TABLE II—RESULTS OF SEWAGE AERATION IN PRESENCE OF ACTIVATED SLUDGE ON FILL-DRAW PLAN

		[Parts per Million]				
		Crude sewage	HOURS AFTER REFILL			
DETERMINATION		0	2	5	20	
Suspended solids.....	June	180	35	24	20	14
	July	147	21	12	9	8
	August	154	24	12	8	6
Dissolved oxygen.....	June	1.0	0.0	0.1	0.4	2.5
	July	0.7	0.0	0.0	0.2	1.7
	August	0.5	0.0	0.0	0.1	0.9
Relative stability.....	June	.....	14	31	76	100
	July	.....	11	34	84	100
	August	.....	12	28	63	88
Oxygen demand.....	June	230	53	38	.....	7
	July	173	63	38	.....	4
	August	211	53	34	.....	11
Nitrite.....	June	.....	0.08	0.11	0.49	1.50
	July	.....	0.01	0.07	0.25	0.53
	August	.....	0.00	0.07	0.12	0.66
Nitrate.....	June	.....	0.10	0.60	1.20	7.30
	July	.....	0.00	0.25	1.57	7.80
	August	.....	0.00	0.10	0.55	2.80
Volumes of air per volume of sewage.....		1.17	3.50	7.00	24.55	

It will be observed that a very good effluent was obtained on the fill-and-draw method of operation after 5 hrs.' aeration with 7 volumes of air per volume of sewage. This may be compared with the work of the tank aerator in 1914 under the continuous-flow method without activated sludge, with 9 volumes of air and 24 hrs.' retention; and also with 18 volumes of air in the same period.

The following extract from our laboratory record is of interest:

"The rapidity with which the organisms present reduce the demand for oxygen is noteworthy. During the process of refilling, the demand falls from about 200 parts per million on the average to about 60 parts per million. Part of this drop is, of course, due to dilution with purified liquid from the previous run which remains with the sludge in the part of the tank below the draw-off pipe. Dilution, however, would reduce the demand only to 10/16 of its original value, or to 123 parts per million. This demand of 63 parts (123—60) is satisfied by the nitrite and nitrate oxygen, which is also reduced much more than the dilution would account for, in addition to the atmospheric oxygen dissolved from the air blown through the tank. This 63 parts is seen to be about seven complete saturations at summer temperatures. Bartow and Mohlman<sup>1</sup> call attention to the effect of nitrite and nitrate oxygen from the previous cycle in aiding the stability of sewage in the early stages of treatment.

"The rate of fall of demand constantly diminishes throughout the cycle, thus conforming to what seems to be a general law of all purification processes, namely, that the action proceeds most rapidly at the start. This seems to indicate that there is proportionally a large volume of the less resistant matter present, which having high avidity for oxygen is attacked promptly, and that as the process continues the more resistant matter becomes a large proportion of the whole. It may indicate that a given amount of air would be most advantageously utilized

by blowing it very rapidly at the beginning and less rapidly as the treatment proceeds.

"A drop in efficiency is noticeable during August in all points under observation. This is very possibly due to accumulations of sludge in the bottom of the tank which are not lifted by the air and consequently interfere with nitrification. The presence of the deflectors makes direct observation of this point impossible without interruption of the experiment, but indirect evidence supports this theory.

"The phenomena attending the sedimentation of well-activated sludge are very interesting. When the quantity is considerable (about 20 per cent at complete subsidence) the behavior in a settling cylinder is much the same as that of the precipitate resulting from the addition of manganous sulfate and alkaline iodide to water in the determination of dissolved oxygen. The material subsides as if it were a mass of loose cotton undergoing compression, with a sharp line of demarcation between the suspensa and the supernatant, and not like an aggregation of free falling particles with widely varying rates of subsidence, giving rise to a shading off into clear supernatant. The initial rate of settling in a test recently made was a trifle over an inch per minute, which rate rapidly diminished as the process of compacting went forward."

Experiments were also successfully made with a continuous-flow activated-sludge aerator tank, but these have not yet been fully completed, and further work will be done this summer. In economy of operation the results so far obtained are fully equal to those obtained by the fill-and-draw method. One of the main drawbacks of the process seems to be its unreliability or the tendency toward deterioration of the effluent as treatment continues unless constant vigilance is exercised.

The problems met in the operation of a full-sized sewage-treatment plant are not identical with those in an experimental laboratory. The vast mass of sewage to be treated cannot be handled in a full-sized plant with the exactness and facility afforded in experimental work. Our main object in designing sewage treatment works (from an engineering standpoint) is to provide methods of treatment that shall at all times afford satisfactory effluents for discharge into local waters. An effluent need not necessarily be clear and sparkling, nor need it be of a higher degree of stability than is locally required, but it must always be satisfactory and never subject to such deterioration that the plant provided may for a time fail from any cause against which provision can be made.

The plant that will give the most certain result under all local and general conditions of practical care with the ordinary risk of carelessness considered must, of course, commend itself to the engineer responsible for the work. Explanations and excuses do not produce results or absolve the designer for taking chances with methods that have not proved entirely reliable. The attitude of the designer must necessarily differ from that of the experimenter. At the same time, though these considerations in all their force may be admitted, the attitude of the engineer ought not to be so conservative that his employer may lose the advantage of any real advance.

We must not lose sight of the facts that a sewage-disposal plant when it is put into service is intended to be operated continuously at the efficiency for which it was designed, and that a constantly increasing burden will probably be put on it in consequence of rapidly increasing service and inefficient management. The scientist may design a plant to meet the requirements of a certain standard of service and up-keep, but the politician at once comes on the scene and dictates by whom the plant operation shall be directed and what supplies and repairs shall be provided for it in the annual budget. If the plant as designed and installed requires the watchful care of a scientist and daily supervision by a sewage expert to make it give satisfactory service with reasonable certainty it will have no place in the ordinary American city while our governmental institutions are what they generally are; moreover, if the plant is small, the cost of operation will be greatly increased by the expense of providing scientific management. Everything considered, therefore, the con-

<sup>1</sup> THIS JOURNAL, 7 (1915), 318.

clusion seems to me to be justified that, so far as we have gone and, as far as I can learn, so far as others have gone with this process, its excessive cost and sensitiveness or lack of reliability are such that the engineer is not warranted in recommending it for general adoption except where special conditions control.

1013 MECHANICS BANK BUILDING  
BROOKLYN, NEW YORK

## ACTIVATED-SLUDGE EXPERIMENTS AT THE SEWAGE DISPOSAL PLANT, BALTIMORE

By CALVIN W. HENDRICK

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Work on activated-sludge experiments began during late winter. After developing ideas for general operation of a converted Imhoff tank along the continuous-flow activated-sludge method the first question to decide was the selection of suitable porous material, through which air in small bubbles was to be admitted to the mixture of sewage and sludge. Experiments were conducted in an iron cylinder to determine the necessary pressure and the volume of air passed through various types of porous material. Carborundum, alundum, sand and cement, filtros, and unglazed tile were the materials tested, specimen samples having been furnished by the various manufacturers. The apparatus consisted of an iron cylinder, flanged at each end, with plate glass to allow easy inspection. Inside the cylinder a disc of the material, 3 in.  $\times$  1 in., was clamped to a recessed flange, which in turn was attached to a compressed-air container. Mercury tubes and valves were arranged to measure the pressure and to regulate the volume of air. Water was put into the iron cylinder to cover the disc in order that some idea could be obtained regarding the size of air bubbles. When air was admitted to the flange it escaped by passing through the porous disc in small bubbles. Pressures, both pre-disc and post-disc, were maintained, equaling those in the bottom of the converted Imhoff tank. A record was kept of the pressures necessary and the volumes of air passing through the disc, and curves were drawn.

The cement and unglazed tile discs broke on being clamped to the flange and were eliminated because of their unreliable strength. The filtros tile needed but a few inches of head to force air through it but was discarded because the bubbles emitted were too large. Both carborundum and alundum were acceptable because of the smallness of the bubbles, but carborundum discs are less expensive. It was necessary to exert greater pressure on carborundum than on filtros, but the great advantage of having very small bubbles, thereby giving a larger contact per unit volume, is more important.

Five 4-liter bottles nearly filled with various mixtures of sewage and sludge were aerated from March 3 to about June 10. The information sought was to determine the mixture that produced most quickly an activated sludge, the rate at which the sewage could be purified, and the composition and other features of the sludge itself.

The tests made May 17, 1915, give an idea of the purification obtained under this laboratory method of aeration: the results are expressed in parts per million.

No.	CONTENTS OF BOTTLES		AMMONIA NITROGEN	NITRATE NITROGEN	DISSOLVED OXYGEN CONSUMED
	Per cent sludge	Balance			
1	20 (settling basin)	Raw sewage	0.9	6.2	0.6
2	None	Raw sewage	0.2	3.0	...
3	20 (settling basin)	Filter effluent	0.8	2.6	0.8
4	20 (settling basin)	Very fresh sewage	0.5	9.8	0.5
5	20 (hydro tank)	Raw sewage	0.3	7.2	2.0

The supernatant liquid was drawn from Bottles 1, 3 and 4 four times a day, and from 2 and 5 twice a week. Samples 1, 3 and 4 produced activated sludge within 3 wks., but the fresh sludge from the hydro tank needed about 6 wks. to become activated. This tended to prove that the sludge or humus from the sprinkling filters has characteristics somewhat similar to activated sludge.

Bottle 3 was covered, May 14, with a cloth to exclude light absolutely in order to render conditions similar to those at the bottom of a large tank. Subsequent analysis showed that the absence of light had no noticeable effect on the activated-sludge organisms.

A sample of sludge taken from Bottle 1, May 13, had a total nitrogen content on a dry basis of 4.39 per cent, which is a higher figure than any determined on our ordinary sludge and more than twice as high as the average nitrogen content of ordinary digestion-tank sludge. The low average figures for nitrate nitrogen in the effluent apparently show that most of the nitrogen in all forms stays in the sludge. This, of course, makes it more valuable as a fertilizer. The first English experiments last year showed that sludge produced by this method contained about three times as much nitrogen as did ordinary sludge.

During the spring, work was done in arranging Imhoff Tank 3 for operation on a continuous-flow activated-sludge basis. A series of pipes leading to 79 discs of No. 120 grit carborundum 6 in.  $\times$  1 in. were laid on the hopper bottom of the tank and connection was made by a 2-in. down pipe to a Hollingsworth blower, belt-driven by a motor. The tops of all the discs were brought as near as possible into the same horizontal plane. Sludge from the settling basins was dumped into the tank and air was pumped continuously into the mixture of sludge and raw sewage after August 5. A 12-in. iron pipe set upright and filled with graded gravel, over which clean water was sprayed, was placed in the air line between the blower and the porous discs. The air passed upward through the gravel, and the apparatus was designed to clean the air of any particles of dust or oil vapor from the blower.

Aeration was continued with the original loading of sludge and sewage till August 17, when raw sewage was allowed to flow for two days continuously through the tank. About 0.25 second-foot of sewage probably passed through. In this short time the effluent went back to its raw state showing that the sludge had lost its ability to purify. The flow of sewage was stopped and more sludge was at once dumped into the tank till a sludge ratio of about 30 per cent was attained. No more raw sewage was allowed to enter the tank till September 20, when a small stream was continuously passed through with a stream of purified sewage. The air has been roughly measured at about 5 volumes per volume of raw sewage. The operation has remained the same to date.

It was found necessary to agitate the sludge which settled underneath the grid of porous discs. This was done by putting a 1-in. pipe down the sludge pipe and attaching it to the flushingwater system. The purified sewage, from this system traveling at high velocity, tends to stir up the settled sludge, which otherwise would become septic and create conditions unfavorable to the life and increase of activated-sludge organisms. It is hoped that this agitation may be discontinued when the inflowing raw sewage has been increased to such volume that it is itself capable of performing the necessary agitation. Whether this purified sewage has a good or a bad effect on the effluent is uncertain. The effluent from the tank is now clear and sparkling. A sample taken October 4 has the following constituents:

Sludge ratio.....	27 per cent
Nitrate nitrogen.....	Trace
Ammonia nitrogen.....	12 parts per million
Dissolved oxygen consumed.....	2.6 parts per million
Dissolved oxygen.....	1.1 parts per million

The low figure of dissolved oxygen consumed indicates that no nuisance would occur by running an effluent of this character into a small stream. At the present slow rate of flow the raw sewage has an oxidation and sedimentation period of about 24 hrs., equivalent to a total tank replacement once a day. It is intended to increase gradually the rate of flow till a maximum is obtained.



Much trouble has been experienced with the present method of introducing air into the sewage. It seems impossible to prevent oil from passing over with the air to the lower side of the porous discs where it forms a film which increases greatly the resistance to the passage of air through the material. The carborundum is very finely divided and is easily choked up, which detracts greatly from its other advantages as part of a permanent installation. As the oil collects the air pressure increases and less air escapes through the discs because of greater slippage in the blower. The increasing resistance to passage through the discs acts in the same manner as the closing of a valve does on a stream of water. This serious difficulty is being considered with care. A limit to the air supply limits the amount of raw sewage that may be passed through the tank, and, until the proper flow is determined, an elastic air system covering wide variation of volume is necessary.

The air washer has been rearranged several times with negligible improvement. It may become necessary to replace the carborundum discs with more porous ones like filtros. This, of course, loses to the equipment the advantage of producing very small air particles, but the first and most important consideration is to put the operation on a sound working basis, which cannot be done, seemingly, with the present discs.

It was originally decided to conduct experiments in another tank aerated by a propeller enclosed in a draft tube, but it was found impracticable to run both experiments at the same time.

Laboratory analyses and physical observations on the action of the experiments have developed to a great extent our knowledge of this form of sewage purification, but we feel, in order that the final conclusions may have value, that no pains should be spared to know exactly and make a record of each step and change in everything pertaining to the experiment. The temperature of inflowing and outflowing raw sewage, the temperature of the atmosphere and the compressed air, and rate of sewage flow are recorded every hour. The rate of air supply will be recorded after the air meter has been installed.

We have already proved that it is possible to purify sewage by an activated-sludge method and that operation may be made continuous. It remains to determine the rate at which sewage can be purified and the total cost of operation.

DEPARTMENT OF PUBLIC IMPROVEMENTS  
BALTIMORE

## COMPOSITION OF THE EFFLUENT AIR FROM AN ACTIVATED-SLUDGE TANK

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The remarkable purification effected by aeration in the presence of activated sludge indicates that air plays an important rôle in the process. As an increase in the content of carbon dioxide and a decrease in the content of oxygen of the effluent air were expected, determinations of those two constituents of the effluent air from tanks at an experimental plant treating domestic sewage at the University of Illinois were made from January to April, 1916. Carbon dioxide was determined according to the method of Hesse with an accuracy between one and two parts per 10,000. The air was measured over water in an unjacketed Winkler burette, and its content of oxygen was determined by absorption in alkaline pyrogallol in a Hempel double absorption pipette for liquid reagents with an accuracy between 0.2 and 0.3 per cent; no corrections were made for temperature or pressure.

The influent air, obtained from the compressed-air supply of the University, was measured by a common gas meter at about 5 lbs. more than atmospheric pressure. The effluent air was collected in Erlenmeyer flasks of 500- to 800-cc. capacity by displacement of the medium through which the air passed, no

chance for outside contamination thus being afforded. The carbon dioxide was determined in the flask in which it was collected. The compressed air, according to numerous analyses, has substantially the same composition as the atmosphere, containing 4.3 parts per 10,000 of carbon dioxide and 20.5 per cent of oxygen.

Aeration was carried on according to a regular schedule, each aeration period occupying 5 hrs. Hourly samples were generally taken, or 6 samples for each aeration period. An initial decline in the amount of carbon dioxide blown out usually occurs at the beginning of the aeration period. A marked increase usually follows this decline though the final amounts are not always the highest. These variations are illustrated by the results of the first five series of tests in the accompanying table of representative data. Some analyses showed an increase from beginning as indicated in the sixth series. The average flow of air into 400 gal. of sewage was 187 cu. ft. an hour at atmospheric pressure.

CARBON DIOXIDE IN EFFLUENT AIR EXPRESSED IN PARTS PER 10,000 BY VOLUME

Date (1916)	Start	After Aeration of—				
		1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.
Jan. 10.....	.....	32.4	30.8	38.4	40.0	45.6
Jan. 12.....	41.2	33.0	37.7	44.2	36.8	50.6
Jan. 13.....	32.2	29.2	37.2	38.0	.....	.....
Feb. 4.....	37.1	36.6	33.9	37.1	38.8	37.6
Feb. 18.....	41.3	38.3	37.0	38.3	43.5	42.2
.....	19.1	26.8	37.6	31.0	42.0	66.8
Average.....	39.67	37.5	36.41	38.02	38.94	39.42

The rate of flow of air has little relation to the amount of carbon dioxide in the effluent air; with an average flow of 240 cu. ft. an hour the content of carbon dioxide was 45.6 and 66.8 parts per 10,000, whereas at another time, with an inflow of only 89 cu. ft. an hour, the content was as much as 50.6 parts per 10,000. During an aeration period, while the tank was filled with sewage and no sludge, the content of carbon dioxide was highest at the beginning, dropping from 14.2 to 8.6 parts per 10,000. During another, on the second day after sludge had begun to accumulate the contents of carbon dioxide at the beginning and the end were substantially alike, 19.7 and 20.8 parts per 10,000.

When the content of carbon dioxide increased, the content of oxygen of the effluent air was 1.0 to 1.2 per cent less than that of the influent air. The effluent air contained 19.3 to 19.5 per cent of oxygen; that is, about 5 per cent of the oxygen in the air was used in the process. The increase of carbon dioxide probably could not take place by simple oxidation of carbonaceous matter without bacterial action. It was believed that some of the carbon dioxide might be dissolved in the sewage; that the initial decrease in content of carbon dioxide of the effluent air was due to loss of dissolved carbon dioxide was proved by aerating tap water under conditions similar to those under which sewage was aerated.

When tap water in a tank was aerated the temperature remained constant throughout the aeration period, but the content of dissolved carbon dioxide rapidly decreased as shown by tests of half-hour samples. The general average content at the start in three experiments was 22.8, at the end of 1 hr. 14.1, at the end of 2 hrs. 6.5, and at the end of  $2\frac{1}{2}$  to 3 hrs it became 0.0. The disappearance of dissolved carbon dioxide was quickly followed by an alkalinity in presence of phenolphthalein, which slowly increased to 26 to 32 parts per million at the end of the aeration periods. The total alkalinity, about 350 parts per million, remained practically constant in the experiments. The average content of carbon dioxide of the effluent air at the beginning of aeration was 30 parts per 10,000, and it decreased steadily throughout aeration though it decreased to the amount normally present in the atmosphere in only one experiment. The average content of oxygen of the effluent air at the start was 19.6 per cent, but before the end of aeration the amount normally in the atmosphere, 20.5

per cent, was attained. The low oxygen at the start was probably due to the high content of iron of the water. The weight of carbon dioxide in the effluent air, calculated from the average content of carbon dioxide of the effluent air and the volume of air used, was 46 to 51 g. per run. The weight of carbon dioxide originally in the water, calculated from the dissolved carbon dioxide and the capacity of the tank, was 43 to 56 g.; that is, the carbon dioxide content of the effluent agreed reasonably well with the content of dissolved carbon dioxide in the original tap water.

The alkalinity in presence of phenolphthalein resulted from the breaking down of bicarbonates naturally in the water. According to the titrations in the experiments the amounts of carbon dioxide set free varied from 52 to 64 g. per run. This gas, in accord with the law of Henry, was not liberated because the inflowing air contained carbon dioxide.

When sewage was aerated in the presence of sludge the net gain of the effluent air in content of carbon dioxide was 125 g. If 46 to 51 g. are deducted for the carbon dioxide in the effluent air obtained by blowing air through tap water, the 75 to 80 g. of carbon dioxide that remains may be considered as having been produced by bacterial action during the process of aerating sewage. That this deduction is warranted is shown by the fact that when fresh sewage was aerated without sludge the dissolved carbon dioxide disappeared and the phenolphthalein alkalinity appeared at nearly the same stage of aeration that it did when tap water was aerated. Sewage allowed to stand after the aeration period loses its alkalinity to phenolphthalein. The sewage was not alkaline in presence of phenolphthalein 17 hrs. after aeration had ceased. When tap water was used, however, the alkalinity in presence of phenolphthalein remained several days, and the total alkalinity remained unchanged. The disappearance of the alkalinity to phenolphthalein of the raw sewage was evidently due to putrefaction of the sewage because of lack of air.

Strong bacterial action does not take place for the first few hours.

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## SEWAGE DISPOSAL EXPERIMENTS AT BROCKTON, MASSACHUSETTS

By ROBERT SPURR WESTON

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The city of Brockton, which has a present population of 62,000, is located in southeastern Massachusetts, and is sewered on the separate system. The sewage drains to a low point in the city, where it collects in a subsiding basin. It is then fine-screened and pumped to the disposal area about three miles away.

The disposal works consist of 37 acres of sand beds and a trickling filter having an area of  $\frac{1}{2}$  acre. The average daily flow of sewage is 2,100,000 gal. Approximately two-thirds of the screened sewage is applied directly to 30 acres of sand beds at an average rate of 52,000 gal. per acre per day; the remainder is first applied to the 0.5 acre of trickling filter and then, after passing through a secondary subsiding basin, to 7 acres of sand beds. The rate of application on the sand beds is about 130,000 gal. per acre per day.

According to the last report of the Sewerage Commission the sewage has the average composition shown in Table I:

TABLE I—AVERAGE COMPOSITION (P. P. M.) OF SCREENED BROCKTON SEWAGE DURING 1914

Total Solids	Suspended Solids	Free Ammonia	ALBUMINOID AMMONIA	CHLORINE
			Total Dissolved	Suspended
778	204	55.8	12.6	6.9
				5.7
				138.6

The original plant, built in 1894, consisted of 27 acres of sand beds. These gave excellent results for many years after their installation, but with increase in the amount of sewage and addition of an increasing amount of shoe-factory waste,

the beds were unable to treat adequately the sewage, some of which is 15 hrs. old when it gets to the beds. A few years ago the area of the beds was increased by 10 acres and three years ago a 0.5 acre trickling filter was constructed. The results from the trickling filter have been disappointing; very little nitrification (only 4.55 parts of nitrates per million on an average in 1915) has been secured. The effluent was stable for only about two days. Furthermore, the effluent from the secondary or humus tank is always putrid and the trickling filter unloads not intermittently but continuously throughout the year. Considerable relief has been obtained by resting the filter for two hours daily, but even at rates as low as 545,000 gal. per acre per day the results were unsatisfactory.

During passage through the humus tank the nitrates in the trickler effluent were reduced from 4.55 to 3.32 parts per million and the oxygen from 2.2 to 1.6 parts per million. This is due to vigorous decomposition of the sludge, the so-called humus, which at Brockton has all the characteristics of a badly digested septic-tank sludge. When the trickler effluent was applied to sand beds at a 130,000-gal rate, free ammonia was decreased from 30.6 (which is high for a trickling-filter effluent) to 16.3 parts per million, and nitrite from 0.732 to 0.069; while, strange to say, nitrate was decreased in the intermittent sand filter from 4.55 to 2.62 parts per million. The remedy for a sewage so stale and one which cries for oxygen so loudly is obviously more air.

In 1915, aeration experiments were made with a cascade aerator 20 ft. long having a slope of 1 ft. in 10. The devices were so arranged that the sewage could be passed over this aerator ten times, but this was not enough to show the presence of the slightest trace of dissolved oxygen in the effluent. After each aeration the sewage was passed through a bed of cobbles 6 in. in diameter in order to make use of the contact action employed so successfully by Mr. Clark at Lawrence in his aerated tank but all without sufficient benefit. The effluent from this aerated contact tank passed through an Imhoff tank with little if any change, and after the effluent from the Imhoff tank had been applied to a trickling filter the results were not enough better than those obtained by the municipal filter to warrant further continuance of the experiments. The colloidal matter was not appreciably decreased in amount but was carried through the whole row of devices.

Along with the other 1915 experiments a small activated-sludge tank was operated on the fill-and-draw plan. This tank was aerated for 4-hr. periods and contained 25 per cent of sludge. The effluent was discharged on an intermittent sand filter 5 ft. thick at a rate of 500,000 gal. per acre per day. The results were excellent and in striking contrast with the results obtained by the municipal sand beds receiving the trickling filter effluent. The effluent from the activated sludge tank contained 254 parts of suspended matter, 37.6 parts of free ammonia, no nitrite, only a trace of nitrate, and 3.28 parts per million of dissolved oxygen. Nevertheless, when this effluent was applied to the experimental sand filter filled with sand from one of the beds which had been receiving trickling filter effluent, excellent results were obtained; *i. e.*, free ammonia was decreased to 6.62 parts and nitrate was increased to 13.89 parts per million on the average, while the effluent was brilliant in appearance and stable even at the high rate of 500,000 gal. per acre per day. The activated sludge experiments were so promising that they have been continued during 1916 on the continuous plan with a large aerating tank 10 ft. square and 8 ft. deep below the flow line, discharging into a settling tank and from it on a sand bed 10 ft. square and 2.5 ft. thick that operates at a half-million rate.

As the object of these experiments was to devise a process to relieve the present plant as much as possible, no attempt was made to obtain complete nitrification but only a clarified



effluent which contained some free dissolved oxygen and a sludge which would not putrefy in the tank. The experiments began with an aeration period of less than 2 hrs. and with varying volumes of air. This aeration period has been gradually increased until a period of 4 hrs is now used. This seems to be the one which gives the optimum results, when about 25 per cent of sludge is used. When a shorter period is used the sludge becomes septic and loses its efficiency regardless of the amount of air used. When the period is greatly lengthened, as shown beyond, not only is no nitrification produced—regardless of the amount of air—but the accumulated suspended matter passes again into the colloidal state and the effluent from the settling tank becomes highly colored. The sewage with which the experiments have been made had the composition given in Table II, and the results obtained by the experiment, as shown by the analyses of weekly composite samples, are given in Table III, in parts per million except as otherwise designated.

TABLE II—COMPOSITION OF SCREENED SEWAGE

Week ending (1916)	CHLORINE	FREE AMMONIA	ALBUMINOID AMMONIA	NITROGEN AS NITRITE	NITRATE	SUSPENDED SOLIDS
Jan. 1.....	108.5	33.3	8.60	0.04	0.19	196
11.....	103.5	31.6	9.80	0.22	0.22	132
18.....	92.0	31.6	8.80	0.24	0.45	166
25.....	104.5	38.7	11.00	0.07	0.16	256
Feb. 1.....	110.5	40.0	11.20	0.11	0.27	194
8.....	119.5	38.7	12.60	0.07	0.20	208
15.....	111.5	36.4	9.2	0.13	0.07	190
23.....	112.0	37.5	12.6	0.09	0.07	222
29.....	88.5	27.9	10.2	0.28	0.27	180
Mar. 7.....	74.5	24.5	7.6	0.41	0.19	108
13.....	98.0	27.3	9.6	0.24	0.28	146
21.....	89.5	35.3	9.2	0.17	0.01	126
28.....	93.0	35.3	8.2	0.19	0.01	172
Apr. 4.....	66.0	17.9	4.6	0.46	0.47	54
14.....	74.0	25.5	6.2	0.09	0.48	92

TABLE III—COMPOSITION OF WEEKLY COMPOSITE SAMPLES OF ACTIVATED EFFLUENT

Week ending (1916)	AIR PER MIN Cu. ft.	AIR VOLUMES	SLUDGE PER CENT	FREE AMMONIA	NITROGEN AS NITRITE	NITRATE
Jan. 23	45	9.7	2	3.244	0.0001	0.0155
30	46	9.9	2	3.871	0.0001	0.0190
Feb. 6	46	9.9	2	3.636	0.0001	0.0185
13	44	9.4	4	3.529	0.0000	0.0000
20	51	10.9	6	3.750	0.0000	0.0000
27	53	22.7	19	3.077	0.0029	0.0070
Mar. 5	38	16.3	16	1.876	0.0110	0.0100
12	38	16.3	23	2.308	0.0001	0.0090
19	46	23.0	28	7.727	0.0004	0.0035
26	46	31.7	39	3.428	0.0000	0.0000
Apr. 2	Tank out of service					
9	43	48.3	23	2.143	0.0260	0.0080

The most interesting feature of our experience has been the effect of plain aeration on the process. After the experiments had been in operation for two months and complete nitrification had not been obtained even when 22 volumes of air per volume of sewage were used, it was decided to stop the flow of sewage through the activated-sludge tank and continue aera-

TABLE IV—COMPOSITION OF EFFLUENT FROM PLAIN AERATION

Date	SLUDGE PER CENT	DISSOLVED OXYGEN	FREE AMMONIA	NITROGEN AS NITRITE	NITRATE
Mar. 24.....	29	0.00	30.91	0.000	0.00
25.....	26	0.00	31.88	0.104	0.09
26.....	25	0.00	35.17	0.074	0.06
27.....	22	0.00	44.34	0.089	0.06
28.....	19	6.40	46.36	0.074	0.05
29.....	18	.....	55.56	0.170	0.06
30.....	18	.....	70.34	0.190	0.07
31.....	16	6.7	80.00	0.195	0.10
Apr. 1.....	15	.....	85.00	0.330	0.10
2.....	18	.....	72.86	0.520	0.08
3.....	19	.....	71.58	0.570	0.12
4.....	24	.....	70.34	0.530	0.13
5.....	25	.....	66.91	0.630	0.15
6.....	27	.....	74.18	0.560	0.16
7.....	25	.....	75.56	0.560	0.17
8.....	21	.....	71.58	0.530	0.19
9.....	19	.....	62.77	0.590	0.17
10.....	19	.....	62.77	0.670	.....
11.....	18	.....	57.46	0.680	.....
12.....	19	.....	50.37	0.960	.....
13.....	19	.....			
15.....	19	.....			

tion until the nitrification was complete. This experiment began March 24 and is still in progress. It was conducted in the large tank until April 1 and then transferred to the smaller tank. The results of plain aeration are given in Table IV.

The clarification was good at the beginning, but 18 days

after the beginning of aeration the color of the supernatant liquid suddenly increased and the sludge began to settle imperfectly and to decrease in volume. The suspended matter evidently had been partly transformed into the colloidal state. Many spent dyes used in the Brockton shoe factories are discharged with the sewage and at present it is believed that these are at first absorbed by the activated sludge but that prolonged aeration causes them to pass into colloidal solution. The Brockton sewage, if allowed to stand, develops a strong reddish color. When further aeration will reprecipitate this color cannot be answered now. As Table IV shows, the free ammonia is beginning to decrease, after having increased, and nitrite and nitrate are on the increase. Perhaps a slow oxidation is taking place which will end in complete nitrification and reclarification.<sup>1</sup> Whatever the result may be, nitrification by aeration seems impracticable at Brockton.

The experiments at Brockton are not yet finished, although nearly so. At present we are using a 4-hr. period of aeration and about 23 per cent of sludge and are applying the effluent to a sand bed at the rate of 500,000 gal. per acre per day. We are now gradually reducing the air to ascertain the minimum required for a 4-hr. period of aeration. We feel sure that this minimum, even for clarification alone, will be considerably more than the 2 cu. ft. per minute per gallon of sewage or less determined in other experiments. The Brockton experiments have shown that the activated-sludge process is the only one which offers any relief to the overworked filter beds, sick with stale sewage. On the other hand, they have shown that it would be impracticable to use the process alone or to produce a highly nitrified effluent thereby. Never has complete nitrification been obtained or anything approaching it. The activated-sludge process would, however, allow the beds to be operated at a rate exceeding 200,000 gal. per acre. There is no difficulty in obtaining a highly nitrified effluent from a bed to which the effluent from the activated sludge process is applied; furthermore, the beds so operated are free from subsurface clogging, which now greatly interferes with the operation of the municipal plant. That this plant needs some assistance is shown by the average analyses in Table V from one representative group of beds.

TABLE V—ANALYSIS (P. P. M.) OF REPRESENTATIVE BROCKTON FILTER-BED EFFLUENT (1915)

AMMONIA {	Free..... 25.96	NITROGEN {	Nitrite..... 0.039
	Albuminoid..... 1.70		Nitrate..... 0.87

The rate of filtration at which this effluent was produced was only 52,000 gal. per acre per day, or about one-tenth of that used experimentally with the activated-sludge effluent with which a highly nitrified bed effluent was produced.

Some of the sludge contains 99 per cent of water and it is believed that tank treatment before applying it to the beds for drying, will be necessary.

14 BEACON STREET, BOSTON

## THE ACTIVATED-SLUDGE PROCESS IN TREATMENT OF TANNERY WASTES

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### GENERAL TREATMENT OF INDUSTRIAL WASTES

The activated-sludge process of sewage treatment may be particularly well adapted for the treatment of some industrial wastes. The firm with which the writers are connected is now directing activated sludge tests on paper-mill wastes at the mills of Bird & Son, East Walpole, Mass., on woolen-mill wastes at the Assabet Mills of the American Woolen Co., Maynard, Mass., and on tannery wastes at the factories of Winslow Bros. & Smith Co., Norwood, Mass. The tests on woolen-mill wastes

<sup>1</sup> On June 15th the free ammonia had been reduced to 1 P. p. M. and the nitrates had been increased to more than 1 P. p. M. The sewage was still dark colored and would not clarify by subsidence.

have not been conducted for a sufficient length of time to afford any indication as to the practicability of treating these wastes by the activated-sludge process. The tests on the paper-mill wastes are not very encouraging, although various modifications of the process, which are being tried on an experimental scale, may solve the problem. The results of the tests on the tannery wastes are very promising, although it remains to be determined whether the method will be economical. A brief account of the activated-sludge tests made thus far on these tannery wastes may prove of interest.

#### CHARACTER OF WASTES

The Winslow Bros. & Smith Co. manufacture sheep, calf, and kid leather and pulled wools. The wool-scouring liquors, amounting to about 30,000 gal. a day, are degreased by the acid-cracking process and a large part of the grease is subsequently recovered. The combined wastes from the tannery and degreasing plant average about 500,000 gal. each working day. This does not include about 250,000 gal. a day of comparatively clean rinse waters discharged into the brook without treatment other than by fine screens.

The individual wastes from the various processes are discharged at different times and in different quantities, causing a marked variation in the character of the combined wastes. The composite for the day is gray or brown in color, densely turbid, and malodorous. It contains much suspended matter, but after settling remains densely turbid. Tests showed that for each 100 parts by weight of solids settling in 24 hrs., there were 63 parts of non-settling suspended and colloidal matter. The combined wastes are frequently acid in nature, due to the discharge of certain acid wastes, but the daily composite is generally alkaline.

The average results of analyses of the crude wastes for 1915, together with the maximum and minimum monthly averages for the different constituents, are given in Table I (A). These

TABLE I TESTS OF COMBINED FACTORY WASTES AND ACTIVATED-SLUDGE TANK EXPERIMENTS AT FACTORY OF WINSLOW BROS. & SMITH CO. Results in Parts per Million (Except last column)

DETERMINATIONS	(A)—FACTORY WASTES			(B)—ACTIVATED SLUDGE		
	Av. for 1915	MONTHLY AVERAGE	TANK TESTS (a)	De- crease Per cent		
Total Oxygen Consumed...	889	979	759	785	258	67.1
Dissolved.....	554	670	386	605	244	59.6
Suspended.....	335	427	259	180	14	92.2
Total Albuminoid Nitrogen.....	29.3	36.4	21.1	21.5	5.5	73.0
Dissolved.....	16.2	21.9	10.8	16.0	4.4	72.5
Suspended.....	13.1	18.7	9.9	5.5	1.4	74.6
Ammonia Nitrogen.....	17.9	25.1	13.3	25.5	9.9	61.1
Nitrites.....	...	...	...	...	1.90	...
Nitrates.....	...	...	...	...	0.06	...
Total Residue.....	3915	4902	2882	3088	2356	23.7
Loss on Ignition.....	1352	1862	1057	836	272	67.3
Fixed Residue.....	2563	3339	1825	2252	2084	7.4
Total Dissolved Solids.....	2671	3560	1766	2726	2340	14.1
Loss on Ignition.....	520	606	375	514	258	49.8
Fixed Residue.....	2151	3025	1388	2212	2082	5.8
Total Suspended Solids.....	1243	1690	993	362	16	95.5
Loss on Ignition.....	331	1294	623	322	14	95.6
Fixed Residue.....	412	674	248	40	2	95.0
Total Sulfur.....	227	300	144	252	251	0.4
Fats by Ether Extraction..	486	780	312	255.2	48.5	81.1

wastes are several times as strong as ordinary domestic sewage. It was found that one volume of settled wastes required, on the average, about 50 volumes of unpolluted brook water to produce stability. These wastes have a marked avidity for oxygen, as much as 240 milligrams of oxygen per liter of wastes being absorbed immediately from water used for dilution. This would be enough to saturate with dissolved oxygen about 25 times this volume of distilled water at room temperature:

#### PRESENT METHOD OF TREATMENT

The combined wastes are pumped to sedimentation tanks, having a total capacity of nearly 1,000,000 gals. Lime in the form of milk of lime is added to the crude wastes whenever necessary in sufficient amount to maintain an alkaline tank

effluent. A portion of the tank effluent is applied to sand filter beds, an area of 3.5 acres being available for this treatment. The remainder is treated by dilution with water from an 800,000-gal. reservoir controlled by the company.

#### OBJECT OF EXPERIMENTS

Sufficient diluting water is not available for complete oxidation of the tank effluent during the greater part of the year. Several times the present area of filter beds would be required to filter properly the entire volume of wastes under favorable weather conditions, and it is not practicable to keep the filter beds in working order during the winter. Moreover, the cost of operation and maintenance of the filter beds has proven excessive, principally because of the very large proportion of finely divided suspended matter and colloids in these wastes.

In order to ascertain whether the trickling filter would not be better adapted for the purification of these wastes tests on a large working scale were authorized. These tests, carried on for 18 months, indicated that by this method a satisfactory effluent could be obtained at much less cost than by the sand filter method. The principal drawbacks in this process were the danger of the dissemination of foul odors by the spraying of the liquid on the filter and possible trouble from moth flies, which are common to this type of filter. The cost of construction of a one-acre trickling filter 7.5 ft. deep with dosing tank, secondary sedimentation tanks, and other equipment, capable of satisfactorily purifying all of the waste waters from the factory was estimated at \$63,480.

Before the trickling filter tests were completed the activated sludge process of sewage treatment came into prominence. This process, if it could be economically applied to the treatment of these wastes, promised to avoid any possible fly nuisance and to reduce foul odors to a minimum. Moreover, it was to be expected that a suitable activated sludge plant might be constructed for much less than the cost of a trickling filter plant. We were accordingly authorized by the company to conduct activated sludge tests on a working scale.

#### DESCRIPTION OF EXPERIMENTAL PLANT

A 1,000-gal. aeration tank approximately 6 ft. long, 3 ft. wide and 8 ft. deep was built in one corner of the press-room of the degreasing plant. This room is not very warm in cold weather, but the temperature is high enough to prevent freezing. The tank is provided with a complete false bottom of filter plates (Grade 5 R), 6 in. above the true bottom, for diffusion of the air. The air space is divided into 3 independent longitudinal ducts to make it possible to cut out the outside ducts and by sloping the sides to the middle duct to operate with one-third of the volume of air required for agitation with the complete false bottom if it should be found that a smaller volume of air is sufficient for oxidation. The air is taken from the pipe supplying compressed air for mixing the treated wool-scouring liquors in the acid-cracking tanks, under a pressure of about 50 lbs. per sq. in., which is reduced to the required pressure of approximately 3.5 lbs. by a Mason pressure-reducing valve. The consumption of air is measured by a Westinghouse gas meter supplied by the Pittsburgh Meter Co.

The joints between the filter plates were first made with Arco-Sealit roofing compound. When the liquid in the tank reached a temperature between 70° and 80° F. this material softened and the pressure of air from beneath blew holes through it. Various high-melting-point pitches and asphalts were tried, but none was found which we felt certain would not give way under the conditions of warm temperature and air pressure. The lower part of the joints was then made with one of the best pitches and the upper part was filled with rich cement mortar.

The wastes are drawn by gravity into the aeration tank, and the supernatant liquor is drawn off by means of a flexible jointed pipe. A sludge draw-off pipe is provided at the bottom of the



tank. Provision is made for sampling from the influent and effluent pipes during the filling and drawing of the tank, and 4 sampling outlets in the tank at different depths are available for making special tests.

#### PRELIMINARY TREATMENT

In view of the constantly changing character of the wastes during the day it was considered necessary to equalize them before applying the activated-sludge treatment. It was, therefore, decided to use the effluent from the sedimentation tanks for the tests. By this preliminary treatment there is removed not only the heavy matter in the wastes, which would require an excessive amount of air to keep it in suspension, but also the other settling suspended matters, which would require large amounts of air for their oxidation. No difficulty has been experienced in dewatering the sedimentation sludge on drying beds without causing complaints from foul odors. All the dried sludge is being carried away, without expense to the company, by the farmers in the vicinity who use it as fertilizer.

#### BEGINNING OF TESTS

The aeration tank was put into operation December 29, 1915, on a schedule of one filling each working day. Air was applied at a sufficient pressure to maintain a good agitation of the tank contents, and the aeration continued for about 20 hrs., when the aerated wastes were allowed to settle for a period of 2 hrs., after which the supernatant liquor was drawn off and replaced with fresh sedimentation-tank effluent. The tank was not filled on Sundays, and air was applied for about 44 hrs. from Saturday to Monday. After 9 fillings it was found that 4.6 per cent of sludge (based on 2 hrs. sedimentation) had accumulated in the aeration tank, but the treatment was effecting no perceptible change in the liquor applied.

#### ARTIFICIAL HEATING OF WASTES

It became apparent that it would be a very slow process, if indeed possible, to activate the sludge at the low temperature of the wastes, less than 50° F. It was therefore considered advisable to warm the tank liquor to expedite the tests. It is impracticable to do this by heating the air supplied. The specific heat of air is approximately 0.238 (water = 1), whence 4.2 times as much air as water by weight is required to produce a given result in heating or cooling. The specific gravity of air is 0.00129 + (water = 1), whence one volume of water weighs the same as 775 volumes of air. The relative volumes of air and water at a given temperature to have the same calorific power are, therefore, as 3,250 : 1. On the basis of the above computations 100 times the actual quantity of air being used for 20 hrs. aeration would be required at 90° F. to raise the wastes from 50° to 70° F. in 20 hrs. If the air were heated to 212° F., 500 times the quantity of air being used per hour would be required to raise the temperature of the wastes from 50° to 70° F. in 1 hr. The quickest and most economical way to heat the liquor appeared to be by live steam admitted to the tank. The application of a moderate amount of steam for 2 to 3 hrs. is sufficient to raise the temperature of the wastes to 70° F. The effect of live steam on the bacterial life within the filter was conjectural. It was found, however, that after less than one day's aeration at the higher temperature the dark gray liquor became reddish in color and showed partial clarification.

After carrying on the tests for 2 or 3 days at the warm temperature the pitch which had been used to form the joints between the filter plates softened to such an extent that the air pressure blew holes through it, thus necessitating the withdrawal of the sludge and the making of new joints with cement mortar as previously described. The tank was out of use from January 10 to January 22, during which time the sludge accumulated prior to January 10 was stored in a cool place. When it was returned to the tank on January 22, it had become very foul—in odor like decaying fish. In spite of this fact, there was a de-

cided improvement from the first in the appearance of the tank liquor on aeration at the warm temperature. The top liquor drawn January 28, was free from disagreeable odor and was only slightly turbid.

#### ACTIVATION OF SLUDGE

By February 7 there had accumulated 20 per cent of sludge based on a working capacity 7 ft. 6 in. deep and a period of sedimentation of 2 hrs. It was then decided to aerate continuously without further addition of liquor until the sludge became activated. Steam was applied from time to time with a view to maintaining a temperature between 65° and 75° F. Occasionally the temperature dropped below 60° F., but the liquor was not allowed to remain at that temperature for any considerable length of time.

The nitrite and nitrate nitrogen in the liquid being aerated gradually increased from a trace on February 8 to 3.5 parts per million on February 17. It then jumped to 12 parts per million on the following day and continued to increase, reaching about 35 parts per million on February 24, which is higher than has ever been obtained in the effluent from the sand filters. Nearly all of this was nitrite nitrogen. The continuous aeration was extended until March 6 to ascertain whether it would be possible to convert the nitrite into nitrate. This was not accomplished, presumably because the nitrate-forming organisms were absent.

On February 18, after 11 days' continuous aeration, the settled tank liquor was found to be perfectly stable. A chemical analysis of a sample collected February 25 showed 4.9 parts per million albuminoid nitrogen—a reduction of 63 per cent from that in the influent—and 0.5 part per million of ammonia nitrogen, a reduction of 97 per cent from that in the influent. Shortly after this the air was accidentally turned on at full pressure. This broke up the coagulant to a marked degree so that much fine suspended matter remained in the liquor after settling for 2 hrs. This fine suspended matter did not coagulate again on further aeration and continued to render the tank liquor exceedingly turbid.

The continuous aeration started February 7 caused the sludge to become more granular in nature so that it tended to be more compact on standing and thus to occupy less space. Further, the continued application of air and the occasional introduction of steam tended to break up the coagulant, thus rendering the sludge resulting from sedimentation of the liquor denser and of less volume. The sludge volume of 20 per cent on February 17 was reduced to 13 per cent on February 25 and after the excessive application of air to only 7.6 per cent on March 5.

#### RESULTS OF OPERATION AT ONE FILLING A DAY

Beginning March 6, the tank was again put into operation on the schedule of one filling each working day. Air was applied at the rate of about 0.5 cu. ft. per gal. per hr., or approximately 10 cu. ft. per gal. per day, based on 20 hrs. aeration. By the end of March the accumulation of sludge, based on 2 hrs. sedimentation, was equivalent to 17.8 per cent of the working capacity of the tank.

The character of the effluent of the activated-sludge tank continued to improve until it became practically clear and nearly free from suspended matter. Beginning March 16 the effluent was perfectly stable by the methylene-blue test. No considerable amount of nitrification, however, is yet taking place. The last weekly analyses of sterilized composite daily samples of influent and effluent are given in Table I (B). It will be seen that a very large proportion of the fine suspended matter and a considerable proportion of the dissolved organic matter in the influent are being removed by the activated-sludge treatment.

#### CHARACTER OF ACTIVATED SLUDGE

The sludge from the aeration of these tannery wastes is reddish brown in color and flocculent in nature, being very similar

to that resulting from the aeration of sewage. It is free from offensive odor and comparatively stable. Partial analyses of this sludge, made during March, gave the results appearing in Table II.

TABLE II—PARTIAL ANALYSES OF ACTIVATED SLUDGE (PERCENTAGES)

DATE 1916	MOISTURE	DRY SOLIDS	COMPOSITION OF DRY SOLIDS ORGANIC	MINERAL	FATS
March 5.....	98.79	1.21	66.1	33.9	7.3
10.....	98.58	1.42	71.1	28.9	9.1
18.....	98.16	1.84	72.3	27.7	9.4
27.....	97.70	2.30	74.8	25.2	11.6

The increasing percentage of dry solids, organic matter, and fats in the accumulating sludge is worthy of note.

The analyses in Table II were made on sludge resulting from 2 hrs.' sedimentation. That there is a wide difference in the volume of sludge after different periods of sedimentation is shown by Table III.

TABLE III—VOLUME OF ACTIVATED SLUDGE AFTER DIFFERENT PERIODS OF SEDIMENTATION IN MEASURING GLASSES

Sedimentation Periods (Hrs.)	1/4	1/2	3/4	1	1 1/2	2	3	4	18
Sludge (per cent of sample)	25.0	22.0	20.7	18.6	16.6	14.7	13.3	12.8	11.3

## PERIOD OF SEDIMENTATION REQUIRED

The amount of suspended matter remaining in the aeration tank liquor after different periods of aeration on April 6, 1916, gave the results noted in Table IV.

TABLE IV—SUSPENDED MATTER (P. P. M.) IN AERATION TANK LIQUOR AFTER DIFFERENT PERIODS OF SEDIMENTATION

Period of Sedimentation, hours.....	1/4	1/2	1	2	4	8
Suspended Matter in Supernatant Liquor.....	260	86	64	50	32	22
Reduction by Sedimentation in Succeeding Period.....		174	22	14	18	10
Reduction per Hour.....		696	44	14	9	2.5

Though a very large proportion of the suspended matter was removed by 1/2 hr.'s sedimentation considerable fine suspended matter continued to settle after that. Undoubtedly mass action in a large tank would bring about more rapid sedimentation.

## AMOUNT OF AIR REQUIRED

Considerable trouble has been experienced from frothing due to the soapy character of the wastes aerated and caused principally by the necessity of discharging some wool-scouring liquors into the wastes channel without degreasing until certain improvements in the degreasing plant have been completed. This trouble has necessitated cutting down the air supply to the minimum which will furnish sufficient agitation. At a rate as low as 0.25 cu. ft. per hr. of air per gal. of wastes aerated, 20 hrs.' aeration was insufficient to produce stability. There are indications that double this rate of applying the air will be more economical. Even at the higher rates of application of air the aeration-tank liquors show only about 15 per cent saturation of dissolved oxygen after 20 hrs.' aeration. It is hoped that the period of aeration may be materially shortened as the tests progress. The effect of an increasing proportion of activated sludge, of reduction in the temperature of aeration, and of variation in the depth of liquor aerated remain to be studied.

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## TREATMENT OF PACKING-HOUSE SEWAGE BY AERATION IN THE PRESENCE OF ACTIVATED SLUDGE

By PAUL RUDNICK AND G. L. NOBLE

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This paper is a brief account of experiments with the activated sludge process<sup>1</sup> on sewage from the plant of Armour & Co., at Chicago.

An idea of the extreme variation in the nature and composition of the different kinds of sewage involved may be obtained

from the following list of the more important departments where this sewage originates: Hog, beef and sheep abattoirs, power plant, lard refinery, oleomargarine, meat-canning, meat-curing and sausage departments, rendering tanks, fertilizer plant, several other smaller departments, and the domestic sewage of 10,000 employees. This sewage is much more concentrated than domestic sewage, containing approximately four times as much suspended solids. Averages of recent analyses, including analyses of night and holiday sewage, show the composition in Table I. The suspended solids consist largely of organic material. The high content of inorganic matter is caused to great extent by the deep-well water used in many departments, the total solids of which is more than 2,000 parts per million.

TABLE I—SOLIDS IN RAW SEWAGE: PARTS PER MILLION

Organic.....	560	Organic suspended solids.....	425
Inorganic.....	2990	Inorganic suspended solids.....	75
Total.....	3550	Total suspended solids.....	500

Sewage from each of the three main outlets is pumped into a weir box, which also acts as a small grit chamber. From this the sewage passes into an aerating tank 10 ft. by 20 ft. by 10 ft., where it is aerated for 10 hrs. A partition is arranged so that the path of the flow is about 40 ft. long. Sludge containing 99.5 per cent water, which has been aerated for 3 hrs., is introduced into the aerating tank at the same point as the raw sewage at the rate of 30 per cent of the raw sewage flow. The aerating tank is fitted with underflow and overflow baffles, and the air is distributed by means of 3/4 inch pipes perforated with 1/25-in. holes, 2 in. apart and staggered, the pipes being placed at 4-ft. intervals at right angles to the line of flow. After leaving the aeration tank the sewage is allowed to settle 40 to 60 min. in a separate chamber. The sludge is siphoned continuously into the sludge storage and the effluent continuously flows over the edges of the settling chamber. The air is measured by means of an orifice and differential manometer: 3 cu. ft. of air are required per gal. of sewage. This includes the air used for siphoning the sludge from the settling chamber to the sludge storage and from the sludge storage to the aerating tank for inoculation. The effluent is fairly clear and practically odorless. The methylene blue test<sup>1</sup> shows that it is nonputrescible for at least 4 days. Typical sanitary analyses of the effluent are shown in Table II.

TABLE II—NITROGEN CONTENTS OF EFFLUENT: PARTS PER MILLION

Albuminoid	Ammonia	Nitrite	Nitrate
2.40	23.80	0.60	None
7.40	16.20	0.07	None
3.00	31.20	0.25	None
4.10	27.90	0.15	None
2.50	28.60	Trace	None

The change in the composition of the sewage caused by the aeration process is concisely shown in Table III, which gives the percentage of decrease of certain constituents.

TABLE III—APPROXIMATE PERCENTAGE REDUCTION OF CERTAIN CONSTITUENTS BY AERATION

Albuminoid nitrogen	Ammonia nitrogen	Total organic nitrogen	Total organic matter	Suspended solids
96	71	66	70	95

A very important factor in the decomposition of the sludge is its high content of moisture and the difficulty of dewatering it in large quantities. A summary of a series of analyses of

TABLE IV—ANALYSES OF SLUDGE: RESULTS IN PERCENTAGES

	MOISTURE	AMMONIA	NITROGEN	FATS
Number of analyses.....	12	18	18	17
Maximum.....	99.70	7.81	6.46	9.36
Minimum.....	99.10	3.60	2.96	1.98
Average.....	99.48	5.57	4.59	5.54

(a) Calculated to a commercially dry (10 per cent moisture) basis.

sludge obtained from the experimental unit is given in Table IV, which shows also the limits which may be expected for the fertilizer value and the fat content of the dried sludge.

<sup>1</sup> Am. Pub. Health Assoc., "Standard Methods for the Examination of Water and Sewage," 2nd Ed., 1912, 63.

<sup>1</sup> G. J. Fowler, E. Arden and W. T. Lockett, *J. Soc. Chem. Ind.*, **31** (1912), 471; E. Arden and W. T. Lockett, *Ibid.*, **33** (1914), 533 and **34** (1915), 937; E. Bartow and F. W. Mohlman, *This Journal*, **7** (1915), 318 and **8** (1916), 16; T. C. Hutton, *Eng. News*, **74** (1915), 134 and *Eng. Rec.*, **72** (1915), 481.



The dry sludge contains very small proportions of phosphoric acid (approximately 2 per cent calculated as  $P_2O_5$ ) and potash (approximately 0.4 per cent calculated as  $K_2O$ ) and its fertilizer value therefore lies entirely in its content of nitrogen.

Much work has been done to find some practicable means of dewatering the sludge so that it may be obtained in a form in which it can be dried in the driers regularly used for handling fertilizer materials. The moisture content of the wet sludge coming from the settling chamber must be reduced from 99.5 to 50 per cent if possible. The importance of this problem is brought out much more clearly when it is considered that such reduction involves the removal of almost 99 per cent of the weight of the wet sludge as it comes from the settling chamber.

Filter pressing in the ordinary type of filter press and in the newer forms, such as Kelly or Sweetland presses, has proved entirely unsuccessful. The filter cloths are very rapidly clogged. A special type of filter press may be developed for this purpose and experiments in that direction are under way. Centrifuges of the imperforate-bowl type have also been tried, but it will be difficult to construct a machine of sufficient capacity to bring the cost of installation to a nonprohibitive amount. After the sludge has been reduced to a 50 per cent moisture content it can be readily and cheaply dried in the usual driers employed for drying organic ammoniates for fertilizers. As available space is an important consideration, an investigation into the possible depth of aerating tanks was made. Two pipes 14 in. in diameter were erected, one 36 ft. and the other 18 ft. high. The air, which was discharged through perforated pipes, was allowed to pass into each unit in equal amounts. The sewage used for this experiment came from the beef abattoir. Samples were taken at regular hours covering several days and the albuminoid, ammonia, nitrite and nitrate nitrogens, and the putrescibility were determined. As the results in either pipe were practically identical it was concluded that an aerating tank of any depth to 36 ft. will produce as good results as a more shallow tank in respect to purification of sewage. Economy in consumption of air should also be considered in this connection.

The bacteriological data are too meagre to warrant conclusions, but two facts are apparent: (1) three or four hours' aeration of the sludge from the settling chamber increases the number of organisms, but further aeration reduces them somewhat; (2) the organisms grow better at 20° C. than at 37° C. as might be expected. Throughout the records there seems to be a correlation between warm sewage temperatures above 75° F. and inactivity of the organisms, which results in an inactive sludge. This may be an obstacle that will prevent the placing of a disposal plant close to the abattoir where the sewage temperature may suddenly change from cold to hot or *vice versa*.

The results of the experimental work warrant the belief that this process offers more promising possibilities than any of the other methods of disposing of packing-house wastes hitherto proposed. The relatively small area required for installation, the comparatively high nitrogen content of the sludge, the comparative clarity and stability of the effluent, and the relatively short time of treatment are perhaps the most important features of the process.

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## CHEMICAL OBSERVATIONS ON THE ACTIVATED-SLUDGE PROCESS AS APPLIED TO STOCKYARD SEWAGE

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The Sanitary District of Chicago began experiments with the activated-sludge process of sewage purification on the sewage of Stockyards and Packingtown in April, 1915. The operation on the fill-and-draw plan was conducted in two 200-gal.

galvanized iron tanks well into the cold season, being discontinued when the contents of the tanks froze. Certain observations can be explained by the effect of low temperatures on the process. These observations were substantiated on the larger 4-unit installation of the Sanitary District designed to treat 30,000 to 100,000 gals. a day on the continuous flow basis. This installation was put into operation early in 1916 under the direction of Langdon Pearse.

The object of this paper is to elaborate certain chemical and biological facts, which have presented themselves in the course of operation, and not to furnish any prescription for the treatment of the stockyard waste. The features of operation now being worked out will require much time and experience before final recommendations can be made. Economically the continuous-flow process seems preferable, but it has certain disadvantages which the fill-and-draw plan avoids. Experience from our own experiments and those of others will probably indicate the solution. Like other sewage-treatment processes, this is governed primarily by the composition of the waste. The process, being largely biological in nature, is greatly influenced by the temperature of the sewage. In this respect the stockyard waste lends itself readily to the process, the temperature varying between 60° and 90° F. throughout the year at the Center Avenue outlet. The fall of temperature in the plant is only a few degrees in the coldest winter weather. By far the greater percentage of the sewage treated is packing-house waste. The variation in discharge and composition between day and night waste is extremely marked. The free oxygen demand is approximately 8 to 10 times greater than that of the domestic sewage of Chicago. The changes of the nitrogenous constituents during the aeration process have been carefully studied. Our experience has coincided, so far as I am aware, with the experience of other observers. During the warmer season a decrease of ammonia nitrogen to about 1 or 2 parts per million and an increase of nitrite nitrogen to 5 or 10 parts per million indicate complete oxidation and clarification. When colder weather set in, however, this ceased to be the condition with the small galvanized iron tanks, which were easily affected by changes in temperature of the air. Absolute stabilities were reached in cold days with ammonia nitrogen actually increasing several hundred per cent and with little, if any, change in the nitrite and nitrate nitrogen. The reduction of the organic nitrogen was just as marked as in summer. Clarification was very satisfactory. The results mentioned are those noted when the effluent showed a relative stability of 100 or thereabouts. With the small galvanized iron tanks, in which the warm sewage quickly chilled, it took longer in cold weather to obtain such high stability, but the chemical results were consistently as noted.

It is clear that the mechanical features of the process outweighed the biological features. The higher putrescible colloids have simply been whipped out of suspension by the continuous agitation. Repeated observations indicate that the mere mechanical removal of the colloidal matter from sewage brings about an improvement far out of proportion to the actual percentage of substance removed. There is no doubt, however, that there is some biologic activity even in a liquid near freezing; otherwise the persistent increase in ammonia nitrogen could hardly be explained. Various active protozoa, such as infusoria and trachelomonads, also were noted in the sludge at all times. More highly developed animal or plant organisms were not found. Our work indicates that the temperature of the liquid treated will be a controlling factor. On a large scale changes in temperature will probably be much smaller than on the very small scale of 200-gallon steel tanks exposed to weather.

During cold weather, removal of colloidal matter was the only immediate indication of accomplished oxidation. Determina-

tions of turbidity in connection with the methylene-blue putrescibility test can establish a fairly definite working relation. Tabulation of a large number of results shows that the stability is 100 with turbidities of 10 parts per million or less. With a turbidity of 15 parts per million the relative stability varies usually between 50 and 100. With turbidities exceeding 15 the quality of the effluent shows rapid deterioration. With turbidities ranging from 20 to 25 the stabilities are usually less than 50. To compare turbidities exceeding 25 parts per million with stabilities appears unsafe; such stabilities are, without exception, very low. Recently, with the advent of warmer weather, nitrite nitrogen is again increasing in the effluent and no doubt the ammonia index will again serve the purpose. The determination of other constituents, such as the organic nitrogen, albuminoid nitrogen, permanganate oxygen consumed, chlorine, and the bacterial content are merely of scientific interest. They are not essential to routine control. This holds good to a certain extent for the dissolved oxygen, but it is quite conceivable that the rate of deoxygenation at a given temperature can be made to serve as an index of the degree of stabilization accomplished. The quantity of the settling suspended matter in the final effluent merely indicates the efficiency of the settling process and has nothing to do with the activated-sludge process proper. Packingtown sewage completely oxidized by the activated-sludge process is clear with a slightly yellowish tint barely noticeable in small bulk.

39TH ST. PUMPING STATION  
CHICAGO, ILLINOIS

## DEVELOPMENT OF THE PURIFICATION OF SEWAGE BY AERATION AND GROWTHS AT LAWRENCE MASSACHUSETTS

By H. W. CLARK

Chemist and Director, Water and Sewage Laboratories  
Massachusetts State Department of Health

What is now known as treatment of sewage by the activated sludge process has been in operation at the Lawrence Experiment Station of the State Department of Health of Massachusetts since early in 1912. During a series of experiments made at the station in 1911 it was found that the presence of certain algal growths in bottles of weak sewage caused a purification of this sewage. This happened even in sealed bottles and with the liberation of oxygen. It was found also that these growths, aided by forced aeration, effected remarkable purification.<sup>1</sup> Immediately following this early work, *i. e.*, in the spring of 1912, extensive experiments were begun in regard to what could be accomplished in the actual purification of sewage by aeration aided by growths. For several months this work was carried on in gallon bottles and carboys and we found that by 24 hrs.' aeration of sewage containing growths of various kinds we could obtain an effluent which was stable with nitrates at times equal to 15 parts per million and containing only 33 per cent as much organic matter as the untreated sewage. A shorter period of aeration gave clarification and stability but nitrates were not formed. The sewage was emptied from the bottles daily, only the growths and sewage slime being left.<sup>2</sup> This work was shown to Dr. Gilbert Fowler of Manchester, England, in the fall of 1912, and was his first view of sewage purified by what is now known as the activated sludge process. On his return to England he and his colleagues, Ardern and Lockett, began similar work and when Ardern and Lockett's paper was published<sup>3</sup> a year and one-half after his visit to Lawrence, Fowler's statement in regard to this English work and its results was as follows:

"It is only right to admit that the work was really due to a visit to the Experiment Station at Lawrence where he (Fowler) saw sewage which had been completely purified by 24 hrs.' aeration."

<sup>1</sup> Mass. State Bd. Health Rept., 1912, 344-45.

<sup>2</sup> *Ibid.*, p. 291.

<sup>3</sup> J. Soc. Chem. Ind., 33 (1914), 18.

Ardern and Lockett state in the paper just mentioned:

"In November, 1912, Dr. Fowler visited the States \* \* \* \*. Shortly after his return he described to the authors, work in progress at the Lawrence Experiment Station on the purification of sewage in the presence of organisms. Dr. Fowler suggested that work might be carried on on similar lines."

As a result of the first few months' work at Lawrence it appeared that offering a considerable surface to which growths would become attached might favor the purification of sewage by this method; hence, a tank containing a few pieces of slate separated from each other at intervals of an inch or more was put into operation late in 1912. Spongy gelatinous growths, brown and gray in color, soon covered these slate layers and sides of this tank, and, of course, sewage slime was also prominent.<sup>1</sup> These growths, aided by aeration and the circulation of sewage in the tank by the air currents, collected not only the suspended matter of the sewage but also a large percentage of the colloidal matter. Oxidation occurred and again, as in the bottle experiments, stable and well clarified effluents low in organic matter were obtained.

This Lawrence work to the end of 1912 was summarized by Dr. McLean Wilson of England, in his recent address at Manchester as President of the Association of Sewage Works Managers, as follows:

"Many investigators, including Drown, Dupre and Dibdin, Mason and Hine, Black and Phelps, Fowler and others, had sought to purify sewage by direct chemical oxidation by means of air currents and had failed. At Lawrence, however, the efficiency of growths in the purification of sewage by aeration was discovered" \* \* \* \* and this changed the current of investigation along this line of work.

During the past three years the work at Lawrence has been continued both along the aerated slate-tank method and also by that method known more commonly now as the activated-sludge process, and various articles have been published by us in the *Engineering Record* and elsewhere in regard to it. Fairly complete accounts have been given also in the report of the Lawrence Experiment Station during recent years. More than a year ago an article of mine appeared in the *Engineering Record* comparing Lawrence and Manchester (England) work along this line. Up to that time we had shown, as stated in that article, that it was possible by 5 hrs.' aeration of sewage in the Lawrence tank, with the use of 50,000 cu. ft. of air per hour per million gallons of sewage treated ( $\frac{1}{4}$  cu. ft. per gal.), to render the tank effluent stable during more than 70 per cent of the time. 10 hrs.' aeration with the same volume of air per hour per million gallons of sewage rendered the tank effluent stable 90 per cent of the time. By 5 hrs.' aeration, 80 per cent of the total suspended matters were collected and removed from the sewage, and by 10 hrs.' treatment, 90 per cent. Five hours' aeration removed the soluble organic nitrogen, including colloids, to the extent of 35 to 40 per cent, and this removal was increased to 60 per cent by 10 hrs.' aeration. The albuminoid ammonia was reduced about 60 per cent by 5 hrs.' and 80 per cent by 10 hrs.' aeration.

Statements have been made in engineering journals in this country and abroad that the Lawrence aerating tank containing slate is a contact filter. This is not true, however. In a contact filter at least 65 per cent of the total space is filled with filtering material allowing 35 per cent for air and sewage. In our aerating tanks, of slate colloids not more than 3 to 7 per cent is filled with slate or other material, leaving 94 or 95 per cent of space free for sewage and air. It has been stated, also, that at Lawrence the object of our work was to prepare a sewage for filtration. This is untrue, of course, for as mentioned above we produced by aeration as early as 1912, an effluent practically

<sup>1</sup> Mass. State Bd. Health Rept., 1912, 292.



stable and containing nitrates equal to 15 parts per million. We have at times studied filtration of these effluents, however.

It is not my purpose in the present paper to review all the Lawrence work along this line but to give some comparative results obtained during the past six or eight months by the two ways of working the process followed at Lawrence. The comparisons are made with two aerated slate tanks containing sludge and growths, Nos. 449 and 449B, and two activated-sludge tanks, so called, Nos. 465 and 482. These tanks hold only 110 to 200 gallons of sewage, each. The results appear in Table I.

From Jan. 10 to March 29 (3-cycle period with one-hour sedimentation at the end of each period in Tank No. 465), there were periods when a digestion of sludge occurred and the albuminoid ammonia in solution in the tank effluent averaged

slightly greater than 40° F. and activated-sludge tanks were operated at different temperatures, that of Tank 465 averaging 42° F. and of Tank 482 averaging 55° F. Little difference in results was noted at first at these temperatures, but a period of digestion of sludge occurred during a portion of the winter in activated-sludge Tank 465 and much organic matter went into solution. On the whole, except for this period of several weeks when the organic matter of the sewage in Tank 465 was going into solution, the effluents from these two activated-sludge tanks operated at different temperatures were about equal, showing a general clearing of the effluent, and 80 per cent of the samples stable. The work of the slate tanks during the winter period were much better, showing removals of 50 to 60 per cent of the organic matter and practically every sample stable.

TABLE I—COMPARATIVE RESULTS: AERATED SLATE TANKS (NOS. 449 AND 449B) AND ACTIVATED-SLUDGE TANKS (NOS. 465 AND 482)

TANK No.	Av. Winter Temp.	Date of Treatment	Period of Aeration	CUBIC FEET OF AIR USED Per Hour	OF AIR USED Per million gals. Treated	REDUCTION (IN PERCENTAGES)					STABILITY OF EFFLUENTS Per cent of Samples Stable
						Free NH <sub>3</sub>	Alb. Ammonia To- tal	Dis- solved	Oxygen Con- sumed	Sus- pended Matter	
449	41° F.	July 1 to Oct. 6, Oct. 6 to Feb. 15 Feb. 15 to Mar. 29	5 hrs. 6 hrs. 3 hrs.	50,000 50,000 250,000	250,000 300,000 750,000	..	40	46	57	65	78
449B	45° F.	(a)	10 hrs. (b)	500,000	250,000	59	88	86	80	80	100
465	42° F.	Oct. 6 to Jan. 10	(Period of settling, 1 hr.) 3-hr. Sample 8-hr. Sample	250,000 750,000 2,000,000	250,000 750,000 2,000,000	11 22 48	56 68 49	49 63 ..	74 74 63	75 .. 75	(3 cycles) 86 (1 cycle) 100 (3 cycles) 100
482	55° F.	Jan. 11 to Mar. 29	(Operated same as 465)								

(a) Tank 449B receives effluent from Tank 449. Nitrification to 2.5 parts per 1,000,000.

(b) Total aeration period including aeration in Tank No. 449.

66 per cent greater than the albuminoid ammonia in solution in the sewage entering the tank and 12 per cent greater than the total albuminoid ammonia in the sewage entering the tank. This phenomenon was at first a rather disquieting element in this investigation but its causes were easily controlled.

If these figures are compared it will be seen that at Lawrence the results are about as follows: The slate process, as exemplified by Tanks 449 and 449B, gives considerably better purification in 10 hrs., calculated upon removal of organic matter, than activated-sludge Tank 465 in 3 hrs. and practically the same as Tank 465 in 8 hrs. By the slate tank method only 66 per cent as much air is used in 10 hours as by the activated-sludge tank in 3 hrs. and only 37 per cent as much as is used by the activated-sludge tank in 8 hrs. Both methods give stable effluents, generally speaking, the slate-tank method requiring generally more time to accomplish this result but less air and the effluent of the activated-sludge tank being the clearer in appearance. During the winter, as shown in the tables, the aerated slate tanks were operated at temperatures

At Lawrence the sludge from both methods has lost the offensive characteristics of sewage sludge; it is more dense, that is, more easily drained, and more or less granular when dried. It is of greater agricultural value, not only on account of the changes mentioned and increased nitrogenous contents, but also because a large percentage of the fatty matters present before treatment is destroyed.

The governing factors in the success of this process of sewage treatment, as I have stated in previous articles, are: (1) The cost of power for supplying the large volume of air necessary; (2) a sewage that readily yields itself to this method of treatment. It is not impossible to believe that certain sewages cannot be purified in this manner.

In conclusion, I wish to state that we cannot at Lawrence work out certain points in regard to such a method, these needing experiments upon a larger scale. It is probably true, however, that the method as first carried on by us at Lawrence, without the use of slate, is the more practical.

STATE DEPARTMENT OF HEALTH, BOSTON

## CURRENT INDUSTRIAL NEWS

### HOT MECHANICAL PULP

All attempts to make hot ground pulp with the aid of old or weakly constructed apparatus are futile, says the *Paper-Maker*. In one mill experiments have been made in this direction but failed and were even dangerous to life owing to the bursting of the stones which, for want of axles thick enough, could not stand the increased pressure. Since, however, new machinery has been built for making hot pulp, the manufacture proceeds steadily and without trouble. The advantage of the hot grinding process compared with others may be recognized by the fact that four or five mills were hardly able to take care of the resultant coarse stuff, whereas now a single mill handles it easily.

For tissue papers of less than 18 g. per sq. meter weight and which must contain 25 to 30 per cent of mechanical pulp, it is advisable to allow the pulp-wood logs that are to be converted into hot mechanical pulp to soak for some time before grinding in hot water. The mechanical pulp thus obtained is exceedingly

feltable and like wadding, so that on open, as well as on automatic machines, steady working and a very strong product will result. For the production of cheap kinds of imitation parchment, such a previously warmed stuff is to be highly recommended. The pulp combines more intimately, is not so plainly visible and the sheet of paper possesses remarkable toughness. McMILLAN.

### BEST OIL FOR DIESEL ENGINES

The best results with Diesel engines are obtained, says the *National Petroleum News*, with an oil of between 20 and 40° Baumé gravity. Oils with a higher gravity have a flash point too low for cheap storage and also do not furnish as many heat units per gallon, while an oil with a gravity below this is usually not fluid enough to be piped in cold weather without heating. Oils as heavy as 14° can be used if precautions be taken in heating, so that the oil can be readily handled and the lighter dis-

tillates not driven off. The oils used should have a fairly uniform distillation curve and practically all should distil at from 700 to 900° F. The best fuel should be between 150 to 250° F. as regards flash point. An oil with a flash point less than 150° has to be treated with great care in storage because of the proportion of light oil in it, while an oil with a flash point greater than 250° causes trouble in starting or running with a variable load. Further, the oil should contain no water and the storage at plant should be arranged so that water will drain off. Again, good Diesel engine oils should not contain over a very small percentage of sulfur as this burns to sulfur dioxide and, as sulfurous acid, attacks the metal. Fuel-oil should be free from solid matter although this can be removed by oil filters which should be used in conjunction with all heavy oil engines. Oils with a large percentage of asphalt can be used successfully, provided there is thorough preparation of the fuel before being injected into the cylinder. With the semi-Diesel or what is known as the hot bulb type of engine, there are some limitations to the oils which may be used, as the tendency of most oils when brought into contact with the hot bulb or plate is to "crack," leaving a solid residue which clogs up the working chamber of the engine. This can, however, be obviated by carefully arranging the temperature of the hot plate to suit the particular oil being used.—M.

#### TILTING CRUCIBLE FURNACE

A new crucible melting furnace of the tilting type has been introduced by the Monometer Manufacturing Company, of Aston, Birmingham, England. One of the features of the furnace is that the combustion chamber is made in the form of an annular chamber concentric with, but situated below the crucible and connected to the melting chamber by inclined ducts. The object of this arrangement is to delay the escape of the burnt gases and to distribute the heat evenly over the crucible so as to obtain simultaneous melting of the whole metal. The furnace takes standard crucibles without special spouts and the arrangement for pouring is such that the pouring lip does not deviate more than  $\frac{1}{8}$  in. from the vertical so that the contents can be poured into a 1-in. hole until the furnace is emptied. The tilting mechanism consists of a transverse shaft at the back of the furnace, a toothed wheel on the shaft and a high-speed silent chain which connects the wheel and the furnace body, and is accommodated in a quadrantal grooved runway on the bottom of the latter. By turning a handwheel the tilting shaft is rotated through reduction gearing, and the chain is wound on the toothed wheel, thus elevating or tilting the body about the axis of the trunnions. Two batteries of nearly 30 of these furnaces, intended to be fired with oil, are being constructed for use in melting copper, brass, nickel alloys and other metals at some newly-erected works.—M.

#### THE UTILIZATION OF WASTE HEAT IN ENGLAND

The growing attention that is being paid to methods of utilizing the large quantity of surplus heat which is everywhere a by-product of British manufacturing is a hopeful sign. A public discussion on this question took place recently at Sheffield, England, and attracted the attention of representatives of the iron and steel trades and scientific men, as well as those associated with gas, electricity and colliery undertakings. The suggestion that there should be established a Government Department to control the supply of power and electric current is a somewhat drastic one and not likely to be accepted unless a very strong case were advanced in its favor. On the other hand, the proposal to harness all the energy of the South Yorkshire coal field, at present running waste, and to employ it in the form of gas or electricity in the iron and steel trades of the district has certainly much to be said for it. This would mean that the individual manufacturer in the Sheffield district would

cease to provide his own power plant but would draw supplies from a large central station which would generate current from the waste energy available in the local coal field. If this plan were carried into operation, it has been calculated that manufacturers in the district could be supplied with current for power purposes at one-half cent per unit.—M.

#### SUGGESTED SOURCES OF SULFATE OF AMMONIA

A paper on "Kerogen and Kerogen Shales," read recently before the Institute of Petroleum Technologists, London, by Mr. E. H. Cunningham Craig, contained suggestions as to fresh available sources of sulfate of ammonia. Vast masses of highly inspissated oil sands are known to exist in different parts of the Empire, the most important being the tar-sands of Athabasca. Large areas of material which could be worked from outcrop are also found at Trinidad and Barbados. The recovery of oil from these deposits has been suggested often but the cost of extraction would be so great compared with the cost of drilling for petroleum that the exploitation of these dried up oil rocks has never been carried out on a commercial basis. If, however, such a valuable by-product as ammonium sulfate could be obtained in sufficient quantity, the working of these oil-sands might prove a commercial success. It has been shown that nitrogen compounds become concentrated in proportion to the state of inspissation, and it has been ascertained that the nitrogen content of such strata as Athabasca and La Brea oil-sands is not negligible. It was the production of ammonium sulfate which saved the Scottish oil shales from extinction through the competition of American oil; in the same way, a yield of this valuable product may be the means of these great oil-sand deposits being utilized and worked at a profit.—M.

#### GAS PRODUCTION FROM WOOD IN AUSTRALIA

Wood is regularly used, says *Gas and Oil Power*, in connection with gas production in many of the smaller Australian gas works. Only certain classes of timber are suitable, the best being those of the box and red gum varieties intermixed with coal to the extent of 25 per cent. The resulting gas is said to offer advantages over ordinary coal gas, chiefly owing to the elimination of naphthalene, while there is a reduction of the scurf deposited on the retort walls. In Australia, the average yield of gas amounts to 12,000 cu. ft. per ton of wood carbonized. The charcoal is usually separated from the coke and made use of for heating the retort furnace. When employed for power purposes, wood gas is usually made from waste material such as sawdust, shavings, or even leaves, and, except for de-tarring and washing, is consumed in the crude form and unmixed with any other gas. The presence of moisture in the wood has an important effect on the results and, if the water content exceeds 60 per cent, preliminary drying of the wood must be resorted to. Wood gas as obtained by distillation in gas works has a calorific value of about 400 B. t. u. per cu. ft., whereas that generated by suction plant is approximately 160 B. t. u. A system known as the Brook's dual method is stated in the *Times Engineering Supplement* to be successful for using wood waste. According to this method, the wood is primarily carbonized in retorts in the ordinary way when a gas equivalent to about 13,000 cu. ft. per ton and having a calorific value of from 375 to 390 B. t. u. is obtained. The resultant charcoal, which amounts to  $\frac{1}{3}$  of the original weight of wood, is then transferred to suction producers and the mixed gas used for power purposes.—M.

#### JAPANESE DYESTUFFS

According to a report in the *Chemical Trade Journal*, a number of well-known dye merchants of Tokyo, Osaka, and Nagoya have formed a dyestuffs trust called the Kokuryu Kai with



offices at Osaka, with the object of preventing speculative transactions by amateurs, and of regulating the market when the inevitable slump comes. The production of aniline dyes is still increasing but manufacturers still keep the monthly output secret. However, it is thought that the monthly production of aniline oil at the different works exceeds 60,000 lbs. In Tokyo alone, there are four large works capable of producing about 24,000 lbs. per month. Of these, the largest is the Toshima Tokusan Kaisha, which produces from 10,000 to 15,000 lbs. per month. In Osaka there are large works which devote the entire plant to the manufacture of aniline oil. These are the Sankyosha, the Osaka Chemical Works and the Yura Dye Company, which, between them, produce about 40,000 lbs. per month. In addition, some small factories have been built at Kobe and Kyoto, the combined output of which reaches 4,000 lbs. per month. As a result of the extraordinary rise in price, the demand has declined so that dyers' requirements probably do not exceed 25,000 lbs. per month, while military requirements absorb not more than 25,000 lbs. in addition. The output, therefore, exceeds the total demand by something like 10,000 lbs. a month. No further increase in the market price of aniline oil is anticipated unless the cost of benzole imported from the United States rises materially.—M.

#### ANALYSIS OF PRUSSIAN BLUE

Mr. James E. Heckel, in *Drugs, Oils and Paints*, points out the difficulty of estimating iron in Prussian blue by Penny's method; *i. e.*, by adding mercuric chloride to a solution of the material in acid containing stannous chloride and then titrating with potassium permanganate solution. The method recommended by the above author is to ignite the Prussian blue, dissolve the residue in concentrated hydrochloric acid with sufficient stannous chloride added to give an apple-green tint with chrome oxidized blues or to become colorless with chlorate oxidized blues. Mercuric chloride and manganous sulfate solutions are then added in definite proportions and the combined solution titrated with *N/10* potassium permanganate.—M.

#### RUSSIAN RESOURCES COMMISSION

A series of monographs is at present being published dealing with the natural resources of the Russian Empire, under the auspices of a Commission appointed by the Imperial Academy of Sciences of Petrograd. No. 5 of the series (Petrograd, 1916) treats of natural sources of tungsten and tin ores. The author, P. P. Sušinskij, says that hitherto neither the mining nor the smelting of these ores has been organized on a regular basis in Russia, but that quite recently, in response to the requirements of Russian industry and of the Imperial Defence Committee, an electro-metallurgical company has been formed in Petrograd for the preparation of special kinds of steel for the admiralty. The article concludes with an illustrated description of the Russian tungsten and tin mines.—M.

#### FERTILIZERS FROM MINERAL PHOSPHATE

In the *Journal of the Society of Chemical Industry* (Vol. 35, No. 4), Mr. G. S. Robertson brings forward the question of the possibility of procuring phosphate from basic slags and mineral phosphates. He puts forth the plea that these phosphatic bodies might become a fruitful source for fertilizers and does not place much reliance on the usual test for phosphates, *i. e.*, 2 per cent citric acid test, on account of the low solubility of the phosphatic materials in this solvent. It is further shown that quite as much phosphoric acid can be dissolved out of the minerals as out of the slags if sufficient extractions are made and the mineral ground very finely. Results obtained at English centers and also in the United States have shown the high value of rock phosphate as a fertilizer.—M.

#### JAPANESE SULFUR AND ZINC

It is reported that the high price of sulfur will seriously affect the bleaching industry in Japan. The Hokkaido producers, says a contemporary, have announced the suspension of sales up to the end of June. While the supplies are running short, orders still pour in from Europe and America, and a further advance in price is expected. The brisk export trade has kept the sulfur market on the up-grade since last October. The price of zinc on the Japanese market has also increased at an alarming rate and several zinc-producing plants have been established to meet the demands as the imports of zinc have almost entirely ceased. By this means, it is hoped that, besides supplying home orders, some shipments abroad may be made. One company in Osaka is now able to turn out 200 tons per month and is preparing to enlarge the scope of its business.—M.

#### ESTIMATION OF NAPHTHALENE IN AMMONIA

The naphthalene present in ammonia liquor can be estimated by the picric acid method in the following manner: A known quantity of the solution is cooled in ice water and neutralized by gradual addition of sulfuric acid, cooling being maintained during the process. The liquid is then distilled and about 30 cc. of distillate collected. This is then extracted with ether and the condenser washed out with a little ether. The ethereal extracts are treated with a *N/20* solution of picric acid. After being allowed to stand for 2 minutes, the ether is evaporated under reduced pressure and the residual solution cooled in ice-water and titrated with *N/10* caustic soda solution with litmus as indicator. Naphthalene is soluble in ammonia liquid containing 5 per cent  $\text{NH}_3$  to the extent of 0.030 g. per 1000 g. of liquid, in a solution containing 100 per cent  $\text{NH}_3$  to the extent of 33 g. per 1000 g. solution. The solubility is increased if traces of pyridine are present. The distillation of ammonia liquor containing naphthalene results in blocking up the condenser tubes unless the temperature is kept above  $30^\circ \text{C}$ .—M.

#### BRITISH BOARD OF TRADE

During the month of May the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply of the following articles. Firms that may be able to give information regarding these things are asked to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall Street, London, E. C.:

Aluminum and other bronze powders	Leather for football covers
Bags, paper, blue, for sugar	MACHINERY FOR MAKING:
Beads, insulating, glass or porcelain	Pins, hair-pins, safety-pins
Boards, compressed leather, for boot manufacture	Press buttons, all sizes
Boxes, wood fiber, suitable for ointment	Paper and cardboard
Bottles, sample, 6 oz. and 8 oz., for oil	Boot-lace, braid
Buckles for clothing	Margarine
Buttons, boot, also pearl	Paper tubes
Cane-pith	Asbestos roof slates
Celluloid eyelets for boot trade	Cardboard, mounts
CHEMICALS:	Cement tiles
Cellulose acetate	Tin boxes
Ferric chloride	Wire of hexagonal section
Flowers of sulfur	Wood-floor
Paraphenylenediamine	Mirrors, small, for Kaffir trade
Selenium dioxide	Mooring, rings and tackle, forged in iron or steel
Sodium selenite	Needles
Electric roof lamps for motor cars	Paper and cardboard
Frames, nickel, for tobacco pouches	Paper, felt, white
Frames, suitable for silk bags	Pins
Glass taps	Press studs
Glass tubing for tubes for aerated water siphons	STRAPONERY:
Glassware suitable for mounting with electro-plate	Rubber bands
Glass chimneys for incandescent burners	Envelopes
Handles for tea-trays	Account books
Hangers, chain, for coats	School books
Hoops for cask making, hazel or chestnut	Writing pads
	Straw-boards
	Tinder lighters
	Thermometers for incubators
	Wicks, lamp
	Vacuum flasks
	Yarn waste

M.

## SCIENTIFIC SOCIETIES

### AMERICAN INSTITUTE OF CHEMICAL ENGINEERS EIGHTH SEMI-ANNUAL MEETING, CLEVELAND, OHIO, JUNE 14 TO 17, 1916

The opening session of the 8th Semi-annual Meeting of the American Institute of Chemical Engineers was held at Hotel Statler, Cleveland, Ohio, with an attendance of about fifty. Professor J. H. James called the meeting to order, as President Rosengarten was unable to attend on account of a serious automobile accident. The address of welcome was given by Ralph L. Fuller, president of the Chamber of Commerce, and vice-president of the Harshaw, Fuller & Goodwin Company. Mr. Fuller spoke of the large number and variety of chemical industries in Cleveland and vicinity, many of which were afterwards visited. He called attention to the effect of the tariff upon these industries, especially in view of conditions likely to be met with after the war, and suggested the advisability of concerted effort by the American Institute of Chemical Engineers and similar organizations toward securing adequate and effective protection for the chemical industries which have been started or have expanded to meet present conditions. Secretary Olsen responded to the address of welcome and expressed appreciation of the fact that the Institute had been welcomed to Cleveland by a chemist who understood both technical and business problems. The suggestion as to securing suitable tariff legislation seemed to be feasible as had been shown during the existence of the Patent Committee of the Institute.

The report of the treasurer showed a very substantial balance on hand. The secretary reported that 27 applications for membership had been received since the winter meeting; 9 new members had been elected.

The *Committee on Meetings* reported that invitations had been received from St. Louis and New York for the winter meetings: New York seemed to be favored, by those present, for the next meeting. The *Committee on Patents*, Dr. Baekeland, chairman, reported very little progress on account of interest in preparedness and the European war. The *Committee on Chemical Engineering Catalog* reported that the catalog would be issued by September 1st.

#### SOCIAL FEATURES

The Tuesday evening session was held at the University Club, with Prof. J. H. James presiding. After the reading of the papers the members were entertained as guests of the Local Committee by a musical program and a smoker. On Thursday, luncheon was served at the Case School of Applied Science, the address of welcome being made by Prof. Mabery, who gave a short account of the foundation and development of the school. Secretary Olsen responded, stating that the chemical engineers recognized that the varied and prosperous chemical industries of Cleveland owed their existence to Case School, which had furnished most of the technical men who carried on the industries. Following the afternoon session, the physical and chemical laboratories of the Case School were inspected. On Friday the company was taken by automobile to the Country Club, where an elaborate luncheon had been arranged by the Grasselli Chemical Company in honor of the visiting chemical engineers. On Saturday the party went to Akron by special trolley. A complimentary luncheon was served by the Goodrich Rubber Company at the Akron Country Club, after which the party returned to Cleveland by trolley and the meeting adjourned. The attendance had been the largest in the history of the Institute, and was unusually large even on the Saturday excursion.

A program for the ladies was also carried through, including an automobile trip to Lorain and Elyria with complimentary supper at the Country Club at Elyria, an automobile trip through the Cleveland park system, and a theatre party.

The subscription dinner was held on Thursday evening in the beautifully decorated library of Hotel Statler: about sixty-five persons were present. Prof. A. W. Smith acted as toastmaster, introducing Dr. William C. Moore, chairman of the local section of the American Chemical Society, who spoke of the work of the local chemists; Mr. F. H. Lee, of the Grasselli Chemical Company and chairman of the *Local Committee of Arrangements* for the meeting, who spoke of the efforts of this committee to make the visitors welcome; Dr. T. B. Wagner was introduced as the only ex-president of the Institute present at the meeting, and amused the company by telling of his efforts to be relieved of the duties of being ex-president. Mr. John C. Hebdon related his experience in building the plant of the Federal Dyestuff and Chemical Company at Kingsport, Tenn., which is now in successful operation. Prof. A. H. White told many amusing stories as well as of the progress of chemical engineering education at the University of Michigan. Secretary J. C. Olsen, in a toast to the "Institute," spoke of the substantial growth and bright prospects of the Institute.

#### PAPERS

**The Production of the Rarer Metals.** By JOSEPH W. RICHARDS. This paper was of special interest on account of several suggestions of the lines along which improvement in the manufacture of rarer metals is possible.

**The Effect of Storage on Mixed Paints.** By E. E. WARE and R. E. CHRISTMAN. It was shown in this paper that deterioration in mixed paints is frequently due to the presence of zinc oxide.

**Nitric Acid Sophistication.** By JAMES R. WITHROW. The examination of a shipment of nitric acid from which crystals of sodium nitrate had been deposited was the occasion for a study of the solubility of sodium nitrate in nitric acid of various strengths. It was shown that as much as 6 per cent of this salt could be dissolved, producing a considerable increase in specific gravity. The presence of considerable amounts of calcium chloride in muriatic acid was reported during the discussion.

**Water Powers of the Western United States,** by HERMAN STABLER of the U. S. Geological Survey, gave a list of water powers which have been developed in our western states, aggregating 1,396,000 h. p. Most of this power is used for light, traction and general municipal purposes and not for electrochemical industries. A list of possible developments aggregating 5,708,000 h. p. was also given. During the discussion of this paper it was brought out, especially by Dr. F. A. Lidbury, that on account of cost of transportation, electrochemical industries cannot be located west of the Mississippi. Only in the eastern states is it possible to carry on these industries at a profit. On account of the limited amount of power available at Niagara Falls, electrochemical industries cannot expand and are being re-located in France or Norway.

**Purification of Sewage by Activated Sludge,** an illustrated lecture by EDWARD BARTOW, described the experiments which had been carried out at the Illinois University. Analyses of the gases evolved showed considerable oxidation of the carbon in the sewage.

**Public Lecture: "Sound,"** By D. C. MILLER. Special interest was shown in the Phonodyke, an instrument devised and built by Dr. Miller, by which the curve of any sound may be thrown on the screen. The audience was delighted to watch the ever varying curves produced by the music of a phonograph, as well as those produced by the cheers and encores which greeted Prof. Miller's wonderful achievement. The sound waves were magnified 40,000 times. The mirror of the phonodyke weighed 2 mg. and could vibrate 12,000 times per second.



A joint meeting with the Cleveland Section of the American Chemical Society was held at Hotel Statler on Friday evening, Dr. T. B. Wagner presiding. A paper on **Acid Resisting Alloys**, by W. C. CARNELL, was read and discussed at considerable length. Dr. LIDBURY spoke on the **Electrochemical Industries of the United States** and the report of the Committee of the New York Section of the American Chemical Society on the Universities and Industries was read (see below for full report).

#### EXCURSIONS

**The Central Furnaces and Semet-Solvay Company By-Product Coke Oven Plant of the Cleveland Furnace Company.** The steel was first melted in open-hearth furnaces of which there are 100 of 50-ton capacity each, then it was cooled in the soaking pits, after which it passed through the rolling mills. In order to obtain a uniform product two mixers of 400 tons' capacity were used. The Garrett continuous rod mill was inspected with interest, also a Bessemer converter in operation. At the Semet-Solvay plant a bank of 100 ovens of 800 to 1000 tons daily capacity was inspected. The ammonia and light oils were recovered from the gas which was worked with petroleum to recover the light oils.

**The Ore Docks of the Pennsylvania Railroad.** Here much interest was shown in the three Hulett unloaders which were transferring the ore from an ore boat to railroad cars. The capacity of the buckets is 17 tons each; the best record for unloading a 11,800-ton boat is 3 hrs. and 35 min., including weighing and loading on cars, the usual time being 4 hrs.

**The Cleveland Filtration Plant** is built for 85,000,000 gallons. The purification consists of precipitation and clarification with ferrous sulfate, sedimentation, rapid sand filtration and chlorination. Mechanical sand filters are installed.

**The National Carbon Company Plant (W. C. MOORE, guide).** The manufacture of electric arc carbons was inspected, special interest being shown in the carbons used for the flaming arc lamps, and in the brushes for electric dynamos. Fifty grades of these brushes are manufactured and the methods in use for testing them were shown. The manufacture of dry cells and methods of testing them were also seen.

**The National Lamp Works of the General Electric Company at Nela Park.** Here incandescent lamp bulbs are blown. The modern glass furnace and clean and orderly condition of the entire plant was greatly admired. The time of blowing a bulb was found to be 20 seconds. The Smith Gas Producer used to furnish the gas supply was inspected. The cutting and decorating of the globes was demonstrated as well as the methods of testing the bulbs, not only for life of the bulb but also for candle power. Of especial interest was the photometric room, which is the best equipped in the world. Tests are made of the light emitted by a lamp at any angle with an accuracy of 0.1 per cent. The research laboratories were then visited where methods of producing artificial daylight were shown.

**The Cleveland Experimental Sewage Disposal Plant (R. WINSLOW PRATT, guide).** A 1,000,000-gallon unit for the purification of sewage by means of activated sludge is in operation. The sewage is subjected to the air for about one hour,  $\frac{3}{4}$  cu. ft. being used per gallon of sewage. The raw sewage contains about 98 parts of iron per 1,000,000 gallons. This iron is precipitated, giving the sludge a brown appearance. The sludge contains about 3.5 per cent N, 2 per cent  $P_2O_5$ , 0.23 per cent  $K_2O$  and 7 per cent fat.

**The Goodrich Rubber Company Works, Akron, Ohio.** The manufacture of automobile tires was first shown, including both cloth and silver wire cord tires. The manufacture of waterproof clothing, conveyor belts and hard rubber articles was seen; especial interest was shown in the very large jars for submarine batteries.

COOPER UNION

NEW YORK, June 21, 1916

JOHN C. OLSEN, *Secretary*

#### NEW YORK SECTION AMERICAN CHEMICAL SOCIETY UNIVERSITY AND INDUSTRY COMMITTEE REPORT

1—This Committee was appointed at the April, 1916, meeting to consider the papers presented at the meetings in November and December, 1915, and in April, 1916, and to report at the June, 1916, meeting—this report to embody the findings, conclusions and recommendations of this Committee based upon the foregoing material, supplemented by such other as this Committee was able to consider.

2—The Committee was divided into three sub-committees to examine the above subject matter from three different points of view: *First*, that of the university; *second*, that of the industries; and *third*, that of the consulting chemists. Each of these sub-committees reached its conclusions separately and these conclusions were then submitted in writing to the full Committee. The work of the whole Committee is given below.

#### FINDINGS

- (a)—Research is the source of all added knowledge.
- (b)—The universities are properly institutions of research.
- (c)—The proper development of university research requires unlimited and unrestricted publicity as to all its activities and results.
- (d)—Not all research activities of the industries can be published and it is only in those cases where publicity is compatible with industrial progress, that full coöperation between the universities and the industries can be effected.
- (e)—When a faculty-member as an individual works in conjunction with an industry and the results of that work are kept secret, that is not that coöperation between universities and industries which this committee is considering.
- (f)—Industrial or similar fellowships when founded by industrials or groups of industrials, coupled with publicity of the results, are effective modes of coöperation; the effectiveness of these fellowships diminishes as the number of contributing industrials decreases and the liberty to publish is restricted.
- (g)—In the case of problems of the industries where the results shall be held exclusive or secret or subject to patent, no general solution can be offered, but in each such case the individual industrial and the individual faculty-member or the individual institution must work out the best plan under the given set of conditions.
- (h)—No matter how efficiently the university may train its men, the industries that take up such men must be prepared to expend considerable of their own time, effort and money in training such men for the specific work before them.
- (i)—The tuition and fees paid by students cover only a small part of the cost of their education at the universities.
- (j)—Apprenticeship of chemists during summer vacations in the industries is not in general feasible, and in general is limited to routine experience in the analytical laboratory and not in the manufacturing plant proper.
- (k)—Scientific problems and the scientific side of technical problems are proper subjects for university treatment and investigation; the bringing of the university professor into the industries by having him examine the problem in the plant and determine the scientific aspect of the problem, and the pursuit of that problem in the university, is a promising point of entry for increased coöperation.

#### CONCLUSIONS

I—Coöperation, such as has been had heretofore, between associations of industries and institutions of learning for the solution of scientific problems or the scientific side of industrial problems, which are common to such specific industries, and the appropriate publication of the results of such investigations, has been productive of great public good, and the greatest immediate prospect for expansion of coöperation between universities and industries lies in coördinated effort along the above lines.

II—There are industrial problems not common to any group or number of plants and which cannot properly be published, and these are, therefore, not adapted to university treatment; problems of this kind in the course of time do become common to the entire industries; to increase coöperation in this class of problems it is needful to accelerate the transfer of problems of this class to problems of the preceding class.

III—In order that there may be as little duplication of effort and labor as possible, and the greatest acceleration of coöperation, a permanent central committee should be created and appointed by representatives of the universities and the industries, and such committee should study opportunities and make public recommendations for coöperation along the lines laid down in these conclusions.

IV—Coöperation between universities and industries as to uniform requirements in the fundamentals of instruction seems possible, feasible and mutually profitable.

V—Such universities as aim to produce technical men should equip them with a working acquaintance with the fundamental types of machinery likely to be used in actual practice.

VI—In order to increase opportunity for research on the part of qualified faculty-members, relief from routine and administrative work within the university should be encouraged and executed to its reasonable limit.

VII—Our universities have a training capacity for branches of industry not now existent in this country; such unexploited training opportunities should be published by the universities to the end that our industrials and others might take up the advisability of creating such non-existent industries.

VIII—The industries can stimulate research by publishing such specific problems as may be common to the industry and yet not of sufficient importance to the industry to undertake their solution directly; such problems would afford valuable training for students and give them live material upon which to work.

IX—The industries, through associations and otherwise, when submitting problems for research, would facilitate the work if they were to make reasonable provision for the financial reimbursement of the university for its expenditure of time, effort and material, and thereafter provide for suitable stimulus and encouragement for expansion of coöperative effort, such as endowments, fellowships and the like.

#### RECOMMENDATION

In view of the foregoing, this Committee is unanimous in recommending that the American Chemical Society take the initiative in creating the Committee suggested in Conclusion III.

CHARLES BASKERVILLE, *Chairman*

E. G. LOVE	RUSSELL W. MOORE
W. S. ALLEN	MAXIMILIAN TOCH
VIRGIL COBLENTZ	J. C. OLSEN
GEO. A. HULETT	F. G. WIECHMANN

NEW YORK CITY, June 1, 1916

#### OBITUARY—JONAS WALTER AYLSWORTH

Jonas Walter Aylsworth, technical director of the Condensite Company of America, died at his home in East Orange, New Jersey, on June 7, 1916. Mr. Aylsworth was born in Indiana in 1868. He gave early indication of his genius for invention and aptitude for scientific study. At the age of twenty he engaged in the manufacture of lamp filaments, in the City of Orange, New Jersey, where he quickly attracted the attention of Thomas A. Edison, who induced him to enter his laboratory as an assistant in the year 1888, and from that time until his death, a period of twenty-eight years, he was in daily association with Mr. Edison either in the Edison laboratories and shops, or in his own laboratory in East Orange, where the "Old Man" was a frequent visitor.

During this time Mr. Aylsworth applied himself to the development of the Edison enterprises, the chief products of which

were electric lamp filaments, the storage battery, and the phonograph. Among the many other notable fields of investigation incidental to this work, was the comprehensive study of waxes and similar substances. Those who are familiar with the character of the work done in the Edison laboratories, will appreciate just what the word "comprehensive" means as applied to any series of experiments or investigations made there. In this case it meant the determination of all the characteristics of every substance of the kind known in the world.

One of Mr. Aylsworth's earliest inventions or discoveries was the use of tungstate of calcium in the fluoroscopic screen, used with Roentgen rays.

Several hundred patents were granted to Mr. Aylsworth for his inventions, and while most of these had to do with the Edison enterprises, chiefly the storage battery and phonograph, a goodly number of them related to chemical and mechanical apparatus and processes of a more general nature. Chief among his latter-day inventions, however, were those relating to phenolic condensation products and chlorinated naphthalene, or as they are better known, "Condensite," and "Halowax," the products manufactured by the Condensite Company of America, Bloomfield, N. J., of which Mr. Aylsworth was the technical director. But the last work on which he was engaged, it is said, promises to be the most important, and that is a continuous autoclave working at high temperatures and corresponding pressures. A few weeks before his death a demonstration of this device was made before some visitors to his laboratory, when a reaction was carried on at a temperature of 750° F. and a pressure of 2500 lbs., the product coming from the autoclave in a continuous stream.

Mr. Aylsworth was a self-taught man in large measure, having had the advantage of only an ordinary public school education and one year at Purdue. When questioned on this point by one of the visitors to the International Congress of Applied Chemistry in this country, he replied that he had pursued his studies in the greatest university in the world, the Edison laboratories: a true statement, but one that might well be amplified by the assertion that he played no mean part in making it the great university that it is; as the result of an industry that never slackened he has left a notable volume of achievement in the chemical and mechanical arts—a life well spent. Mr. Aylsworth was of a very modest and retiring disposition, else the world might have heard more of him. His lovable disposition endeared him to all who knew him. He was a member of the American Chemical Society and the Society of Chemical Industry.

CONDENSITE COMPANY OF AMERICA  
BLOOMFIELD, NEW JERSEY

KIRK BROWN

#### ANNUAL CONVENTION OF FERTILIZER ASSOCIATIONS HOT SPRINGS, VA., JULY 10 TO 14, 1916

The 23rd Annual Convention of The National Fertilizer Association and the 11th Annual Meeting of the Southern Fertilizer Association will be held jointly at The Homestead, Hot Springs, Va., during the week of July 10, 1916. Practically the entire week will be devoted to the discussion, especially by the Soil Improvement Committees of the two organizations, of the important factors that make for a *larger average yield per acre of better crops*.

**President's Annual Address**, PRESIDENT GEORGE BRADEN, Louisville, Kentucky.

**The Need of Coöperation between Manufacturers and Bankers in the United States**, MR. F. C. SCHWEDTMAN, National City Bank of New York.

**The New Agriculture**, PROF. G. I. CHRISTIE, Superintendent of the Department of Agricultural Extension, Lafayette, Indiana.

**Appraisals and Depreciation of Fertilizer Plants**, MR. W. S. RANKIN, General Manager of The Appraisal Company of the South, Savannah, Georgia.

Everybody in any way interested in the fertilizer industry, directly or indirectly, whether his company is a member of the association or not, will receive a cordial welcome.



## NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES NEW YORK—SEPTEMBER 25 TO 30, 1916

The many favorable comments received on the showing of the motion picture films at the 1915 Exposition of Chemical Industries led the management of the coming Second National Exposition of Chemical Industries to be held at the Grand Central Palace, New York City, Sept. 25 to 30, to arrange a motion picture program broader in scope than that prepared for the former exposition. Among the films secured during the past six months from large industrial corporations throughout the

country through the Bureau of Commercial Economics at Washington, are included the following:

The Match Industry	Mining and Manufacturing of Iron
The Rubber Industry	Making of Blotting Paper
Manufacture of Explosives	Accident and Fire Prevention
Varnish Manufacture	Manufacture and Use of Fertilizers
Silver Mining	Manufacture of Steel
Members of the American Chemical Society in Danville during their Spring Meeting in April	

The managers report that they have at this time twice the number of exhibitors they had at the Exposition last year, and that much new apparatus and many processes will be exhibited for the first time at the coming Exposition.

# NOTES AND CORRESPONDENCE

## ON THE EXTRACTION OF RADIUM, ETC., BY THE U. S. BUREAU OF MINES

*Editor of the Journal of Industrial and Engineering Chemistry:*

The remarks of Dr. Charles L. Parsons, of the Bureau of Mines, *THIS JOURNAL*, 8 (1916), 469-473, go to show that he cannot refute the statements which I have made in a previous letter with regard to the production of radium by the Bureau of Mines. A great deal that he brings forward has little or nothing to do with the question under discussion: however, some of the points I feel require a further statement, for which I trust you will allow me the space.

Since the whole of this argument grows out of a disinclination on my part to accept unreservedly as facts the statements about radium emanating from Dr. Parsons and the Bureau, it is not remarkable that I have declined to reprint these statements. The repeated misstatements in the public press with regard to the work of the Bureau of Mines in the production of radium, etc., have, as far as I know, brought forth no call for correction from Dr. Parsons or any of the others concerned with the propaganda of publicity. These misstatements have not been made once, but repeatedly on each occasion of the issue of a news bulletin from Washington, and their effect on the radium market has been disastrous, especially as the foreign market has been practically closed to producers from the outbreak of the war. But it is not only the newspaper misrepresentations that are to be criticized, but the official utterances coming from the Bureau of Mines, as, for example, the report of the director of the Bureau of Mines for the fiscal year ending June 30, 1914, page 19, where we read (the italics are mine):

"Chemists and engineers of the bureau have demonstrated that a process they have devised for the extraction of radium from its ores can be successfully used on a large scale and will prove more efficient than that used by the largest foreign producers of radium. *Through this process it is possible that the cost of radium to the consumer will be reduced to one-third of the present price.* The process is to be patented and dedicated to the public."

Oddly enough nothing whatever is said in this report of the cooperative agreement entered into with the National Radium Institute, Inc., although the arrangement was made during the year covered by this report and this company was to receive the radium produced. It is true, as Dr. Parsons says, that the agreement with the National Radium Institute, Inc., was printed on page 195 of a report of the Hearing before the House Committee on Mines and Mining, which took place in January, 1914. The letter in question is sandwiched in with a number of letters to the Secretary of the Interior, commending his course in trying to withdraw from entry the public radium lands, and in this way was overlooked by the writer in preparing the article which was printed over a year ago. The Committee report in which this agreement was published is not for general distribution, and to my knowledge in neither the hearing before the House Committee nor the Senate Committee was the agreement read.

The difference between the cost of production of radium from

high-grade ore and the selling price of radium seems to have dawned upon some one in the Bureau of Mines, for in the next annual report of the director of the Bureau of Mines (1915, pages 12-13) we read (the italics are mine):

"Probably, however, the most striking of the mineral-technology investigations have been that dealing with radium. In 1912 the bureau showed that large quantities of ore were being mined in Colorado and shipped abroad for the production of radium, some of which was sold back to this country at a price far in excess of any just proportion of that received by the American miner for his raw material.

"Through the cooperation of the National Radium Institute 1,000 tons of ore are being mined in the Paradox Valley of Colorado and a plant was built at Denver for producing radium. This plant has now been in successful operation for several months, and nearly 4 grams of radium have been extracted, which will be used in the treatment of cancer and malignant tumors. The bureau's work has shown that the price formerly paid the miners for the carnotite ore was entirely out of proportion to the value of the mineral contained, and that the *cost of producing radium by the methods developed by the bureau is so low that from Government-owned ore, at least, radium can be supplied to the hospitals of the Army, Navy and Public Health Service at a cost not exceeding \$36,500 per gram, or one-third of prices that have been obtained by foreign producers.*

"One of the most important features of the radium investigations has been the *development of methods whereby the large wastes of low-grade carnotite ore heretofore common may be prevented*, and the main part of the valuable minerals they carry may be readily shipped to market and utilized as a source of radium. This result will add greatly to the radium resources of the country, for heretofore probably five tons of low-grade ore have been mined and wasted for each ton of marketable ore shipped.

"Incident to this work several new methods for the determination of radium and the extraction of uranium and vanadium from radium ores have been developed. Application has been made for patents, which, if granted, will be dedicated to the public."

In a preliminary report (Bureau of Mines, *Bull.* 70) and in other statements coming from the bureau (see report of Director just quoted) a great deal was said about the conservation of the low-grade carnotite ore which must be mined in taking out the high-grade ore. This very important matter from the standpoint of large scale radium production has been accorded scant attention by the Bureau of Mines in the frantic endeavor to produce cheaply a few grams of radium for the National Radium Institute, from high-grade ore. Concentration of low-grade carnotite has been talked of by the Bureau and apparently given some thought, with the result that Dr. Parsons admits that they have adopted the air-separator method that has been in use by the Standard Chemical Company for several years, and a method which certainly differs from the dry concentration method described on page 38 of Bulletin 70, and as mentioned on pages 111-112 in the appendix to the revised edition of that bulletin, a method that has since apparently proven a failure.

The concentration figures given by Dr. Parsons in answer to a question by the writer, after his lecture at the Chemists' Club in New York, on Dec. 15, 1915, were not quoted in my previous letter, owing to the fact that Dr. Parsons, in giving the figures, asked his hearers not to remember them, presumably

as they were but preliminary figures which might need to be altered. It was in the course of this same general discussion that the output of the Standard Chemical Company was given by the writer as 5,000 tons of ore averaging about 1.7 per cent  $U_3O_8$ . Dr. Parsons in later taking me to task for changing this figure in my letter to 1.6 per cent has conveniently forgotten my use of the word about, for in December I did not have accurate statistics.

Dr. Parsons seems to be supremely contented with the air-separator concentration process and the efficiency which it gives. The figures he gave in December he has since cited in the course of a lecture in Pittsburgh, on March 16, 1916, so that these results are presumably the best obtained up to that time. A little thought will show that if this method of concentration were applied, the efficiency of extraction of radium from Colorado carnotite would not be the 85 per cent, which the bureau attained on *unconcentrated high-grade* ore, but would be from 60 to 75 per cent, depending upon the proportion of low-grade ore concentrated. It is difficult to state with any degree of approximation the proportion of low-grade carnotite ore to high-grade. Certainly there is enormously more low-grade than high-grade, and if, as Dr. Parsons formerly felt, there is not enough radium in the carnotite field to satisfy the world's requirements, he can hardly countenance as satisfactory a process which applied to concentrates would yield him an extraction of about 53 per cent of the radium, for he says that six tons of carnotite ore containing 0.8 per cent uranium oxide would give one ton of concentrates approximating 3 per cent of uranium oxide. This concentrate contains 3 out of the 4.8 parts of uranium oxide and the extraction efficiency to concentrates is about 62.5 per cent. A subsequent extraction of 85 per cent of the radium from the concentrates makes the extraction efficiency 53.1 per cent, a result which is hardly satisfactory. Depending upon the proportion of concentrates to raw high-grade ore, the extraction of radium will vary between 53 and 85 per cent, and the tendency, as far as workable ore is concerned, will be towards the lower efficiency, as the high-grade ore is worked out. It is for this reason, and not the ingenious reasons which Dr. Parsons kindly supplies, that the Standard Chemical Company acknowledges that its air-concentrating plant, constructed at a considerable expense in the Colorado field, is not a success when this method is applied to ore containing about 1 per cent of uranium oxide.

Had Dr. Parsons given the context, where he quotes me as saying that radium could be extracted from ordinary soil, it would alter the sense of his quotation, as he well knows, for I qualified the statement by saying this would be possible *if the price justified the extraction*.

Dr. Parsons will be pleased to learn that in the several years elapsing since the Congressional Hearing a market has developed for the vanadium from carnotite ore, and a metallurgical use for uranium which will no doubt insure a sufficient market for all of the uranium which may be produced.

As regards the form in which the uranium was recovered by the Bureau of Mines it is difficult for one not acquainted with the actual facts to draw definite conclusions from statements made in *Bull. 104*, since on page 107 we find:

"The recovery of uranium as sodium uranate has, of course, varied with the losses, the extremes being between 75 and 94 per cent. The average on the last 10-carload lots treated has been 84.4 per cent."

while on page 116 we read:

"All the uranium and vanadium has been recovered by the National Radium Institute plant as sodium uranate or uranium oxide and iron vanadate, the whole plant being designed with this object in view."

Further, on page 117, occurs the statement:

"also there have been extracted 31,650 pounds of uranium oxide and 11,528 pounds of vanadium oxide."

If Dr. Parsons will indicate how one may ascertain from these

statements that 85 per cent of the uranium in the ore has been recovered in the form of a high-grade black oxide of uranium, he will no doubt favor a circle of puzzled readers of *Bull. 104*.

As regards the prices offered to miners for ore by the Standard Chemical Company, it must be remembered that the Standard Chemical Company is itself the largest individual producer of carnotite ore in Colorado, and would, under the circumstances, mine all necessary ore from its own properties, unless able to secure the ore at a lower price from an independent producer. The Standard Chemical Company, unlike the Bureau of Mines and the National Radium Institute, is a corporation in business for other than philanthropic and altruistic purposes, and must make endeavors to pay dividends to its stockholders.

The telegram signed "Carroll," was quoted in good faith in my former letter, Mr. Carroll's denial in the *Norwood Post*, which Dr. Parsons mentions, not having come to my attention.

In conclusion I would summarize a few of the many objections to the work of the Bureau of Mines and the National Radium Institute, with radium, objections which Dr. Parsons has not met in his letter. If we believe the statements of Dr. Parsons, this work was to be primarily a work of conservation (see preface to Bureau of Mines, *Bull. 70*). It was also

"\*\*\*\*\* to enable the miner and prospector to obtain a just return for the ores, and to convince the public that the radium ores on the public lands of the United States should be mined and treated under Government supervision and the radium placed in the hospitals of the Army, Navy, and Public Health Service for the benefit of the people of this country \*\*\*\*\*" (see *Bull. 104*, p. 13); and "\*\*\*\*\* it was the desire of the Bureau to show beyond doubt that, if authorized by Congress, the radium could be procured from ores now owned by the people at a cost approximating one-third the market price, and that it was a much better policy for the Government to obtain the radium so greatly needed in the hospitals of the Army, Navy and Public Health Service at a cost not exceeding one-third the present market price, than to give these ores to large corporations and then purchase as radium salts material that had belonged to the people, at a price insuring large profits to the possessors." (*Bull. 104*, pp. 13-14.)

What the bureau has accomplished according to *Bull. 104*, and to Dr. Parsons' statements, falls far short of the original aims.

Being most important, the conservation work, apparently, has been left for the last. We have analyzed Dr. Parsons' ore concentration figures above, and it is evident that the process will not be satisfactory, neither was it original with the Bureau.

The miners and prospectors are engaged in a hazardous calling and they have fared little better in selling their ore to the National Radium Institute than they did in selling their ore abroad. With the foreign ore market closed, and with the domestic market for radium adversely influenced by the Bureau's propaganda, the ore producers have little to do but sit tight and await the time when there is a demand for their ore, or else to sell their claims for what they can get. Dr. Parsons seems to have hypnotized himself into the belief that if radium were sold at a lower price the miner would somehow receive a price more commensurate with the value of the material in the ore. Certainly cheaper radium will not incline producers to pay more for their ore.

As regards the cost of production of radium by the Bureau we may read between the lines in the introduction to *Bull. 104*, where we find the statement:

"With ore obtained from Government land or purchased at a cost as low as that maintained in the operations of the bureau, it has been shown that the cost of producing radium need not exceed \$40,000 per gram and that the extraction of at least 90 per cent of the radium present may be obtained from good quality ore, such as the bureau has been able to procure."

One of the "jokers" in this statement is the "good quality ore." In the Congressional hearing it was testified that it was difficult for miners to supply quantities of 2 per cent ore, and certainly it would be only fair for the Bureau of Mines to base its figures



on average ore, rather than on the exceptional ore which cannot be available to large scale producers. Taking the average ore as it is now mined, unquestionably it must be concentrated, to be treated economically. Why then base efficiency and the cost of production figures on *high-grade unconcentrated ore*? The answer is that the public had to be convinced of the truth of the statements made by the officials of the Bureau of Mines before they had a process of extraction and before they had produced a milligram of radium in the form of a high-grade salt. Reading between the lines in *Bull. 104*, it is possible to note some of the inconsistencies. However, the average physician who plans to use radium does not consult an abstruse technological bulletin. He reads in the newspapers stories about government production of radium which are based on press notices from the Bureau of Mines and Secretary of the Interior such as:

"The Bureau of Mines \* \* \* \* \* devised methods for the production of radium from the carnotite ores of Colorado and Utah at an average cost of \$36,500 a gram, two-thirds cheaper than the market price of \$120,000 asked by foreign producers, the new, cheaper methods making it much more certain that medical institutions will be able to procure a sufficient quantity of radium for the treatment of cancer and other malignant growths. With an adequate supply of radium for therapeutic use, it is intimated that the progress in the future in curing cancer will rival that made in wiping out diseases that once were prevalent. Physicians who have been enabled to make cures by reason of obtaining a greater quantity of the radium through Bureau of Mines methods say that radium in cancer will prove an inestimable boon to man."

Is it fair and honest for the Bureau of Mines to countenance such chicanery?

In spite of all of the publicity by the Bureau of Mines, which includes official bulletins, newspaper statements, Dr. Parsons' moving picture lectures, etc., the Bureau admits that it does not necessarily follow that the price of radium will be reduced as a result of the development of "cheaper methods of production" (*Bull. 104*, p. 12), and it is the writer's conviction that the condition of free competition will soonest result in the establishing of a competitive market price for radium; and in the establishing of this market price the work of the Bureau of Mines can play no more important part than it has in supplying the immediate requirements of the world's radium market.

In this discussion of the work of the Bureau of Mines on radium production, etc., the writer has tried to confine his remarks to the subject. Dr. Parsons in his letter has clouded the issue by discussing the Standard Chemical Company, the efficiency of its processes, etc., in part on the basis of testimony given several years ago, and in part on the basis of data given in connection with my previous letter, etc. The writer, unlike Dr. Parsons, is not at liberty to discuss publicly the processes, efficiency, etc., relating to the treatment of carnotite ore by the Standard Chemical Company. Suffice it to say that in two years it is possible to effect considerable changes in process methods and efficiency. Our failure to discuss these matters in no way weakens what we have said about the work of the Bureau of Mines, since they have stated what they proposed to do and have later published a statement of what has been done, and a little consideration, even by one not familiar with the technology of radium extraction, shows how far the results have fallen short of that which was to be accomplished. In the meanwhile the sick must continue to suffer, the radium industry must bear the set-back as best it can, and the progress of radium therapy is hindered so that the National Radium Institute, Inc., may secure a few grams of radium through the work of the Bureau of Mines.

CHARLES H. VIOL

STANDARD CHEMICAL COMPANY  
PITTSBURGH, May 22, 1916

## LABORATORY PROBLEMS IN INDUSTRIAL CHEMISTRY

*Editor of the Journal of Industrial and Engineering Chemistry:*

I have read with considerable interest Dr. H. K. Benson's article on "Laboratory Problems in Industrial Chemistry," which appeared in the June number of *THIS JOURNAL* and believe that he struck the right note in suggesting an interchange of views on the subject by those teaching industrial chemistry.

I believe with Dr. Benson that previous personal experience has considerable to do with the courses in industrial chemistry which are offered in our colleges and I also think that another factor which has a strong influence in shaping a course is local manufacturing, especially if there happens to be a predominating industry in the neighborhood. This is only natural, perhaps, but it is likely to cause the course to lean a bit toward that one industry since the instructor will probably be more or less interested in it. It seems to me that considerable effort should be made to evolve a course as well balanced as possible so that the student who has been able to work out only one or two problems in the laboratory may get a good idea of other lines of work in the class conferences.

The laboratory course in industrial chemistry at this university is offered in the first term of the senior year to students in chemistry and chemical engineering; they have at this time covered inorganic chemistry, qualitative and quantitative analysis, organic chemistry and some physical chemistry and have reached a point when they can be given a course of work in which they can apply not only the chemistry but also the engineering which they have been absorbing for three years. To this end the students are given problems in commercial chemical manufacturing which involve such general operations as solution, filtration, evaporation, etc., and the use of suitable apparatus for the carrying on of these and other operations which are commonly met with in manufacturing processes. The work is carried out on fairly large quantities of material so that the student comes to realize that there are other measures of weight than the gram, and the course of the work is followed by chemical analyses to ascertain where the losses occur, all the operations being carried out quantitatively.

When the laboratory work on the problem is complete the student turns in a report, written from his notes, taking up a consideration of the process as a whole, the relation of the various steps to each other, the reasons for carrying out the various operations and finally cost sheets for each step of the process. Toward the end of the term each student is required to prepare drawings showing the layout of a plant for the manufacture of some material based on work done in the laboratory, giving also rough specifications.

The accomplishment of this work requires that the student shall do considerable outside reading, thus becoming acquainted with chemical and engineering literature and his attention is particularly directed toward the use of trade catalogues of the various manufacturers of chemical and metallurgical appliances and machinery.

Some of the problems which we have been handling in this laboratory in regular class work as outlined above, are:

- 1—Production, from bauxite, of newspaper alum complying with the tentative specifications of the *Alum Committee of the Division of Industrial Chemists and Chemical Engineers of the American Chemical Society*.
- 2—Production of beta-naphthol from commercial naphthalene.
- 3—Fractionation of fusel oil with special reference to the recovery of the propyl alcohol and the subsequent conversion of the amyl alcohol into amyl acetate.
- 4—Production of ultramarine from china clay.
- 5—Production of dichromates of soda or potash from chrome iron ore or chrome cobbing with special reference to the proportions of soda ash and lime as affecting not only the yield of di-

chromate but also the physical condition of the furnace product, which bears directly upon the proposition of leaching.

6—Recovery of values (silver and gold), from zinc retort residues by some method of leaching.

7—Production of aniline oil from crude benzole.

8—Production of nitrate of potash from Chili salt peter and muriate of potash by fractional crystallization.

9—Coking of coal with recovery of the by-products, paying particular attention to the yield of ammonia.

10—Electrolytic production of bleach liquor.

11—Electrolytic production of permanganate of potash.

12—Electrolytic production of carbonate of lead.

13—Fractionation of water gas tar and determination of the constituents of the light oil fraction.

LABORATORY OF INDUSTRIAL CHEMISTRY S. H. SALISBURY, JR.  
LEHIGH UNIVERSITY, June 15, 1916

## ON PRECIPITATION OF MANGANESE

*Editor of the Journal of Industrial and Engineering Chemistry:*

It may be of considerable interest to chemists to note that in precipitating manganese by ammonium hydroxide and an oxidizer that sodium and hydrogen peroxides may be used in the place of bromine or bromine water now so generally used.

Sodium peroxide added to a manganese solution precipitates the dark brown manganic hydroxide similar to the precipitate with ammonia and bromine water. Sodium peroxide supplies both the alkali, NaOH, and the oxidizer, oxygen. The powdered  $\text{Na}_2\text{O}_2$ , in small quantities, is added to the hot manganese solution until the reaction is alkaline. This precipitates all of the manganese as a dark brown manganic hydroxide in a granular form which quickly settles. If the introduction of sodium into the solution is objectionable, hydrogen peroxide should be used. In such cases a few drops of a 10 per cent hydrogen peroxide solution are added to the manganese solution. After heating to boiling, ammonia is added until the solution is strongly alkaline. Dark brown manganic hydroxide is instantly precipitated. The hydrogen peroxide must be added to the manganese solution before the ammonia is added, otherwise the manganese is incompletely precipitated as a yellow-brown precipitate which is very difficult to filter.

These reagents have many advantages against the use of bromine as they do not produce annoying fumes, do not increase the volume of the solution, and are far more effective and cheaper than bromine as only small quantities are necessary to oxidize manganese.

ANALYTICAL LABORATORY  
NATIONAL CARBON CO., CLEVELAND  
April 18, 1916

GREGORY TOROSSIAN

## ON THE FORMOLITE REACTION OF OIL RESIDUALS, ETC.

*Editor of the Journal of Industrial and Engineering Chemistry:*

The writer has read with some surprise the paper entitled "The Formolite Reaction of Nastukoff as Applied to Oil Residuals and Natural Asphalts," by Mr. Clifford Richardson, appearing in THIS JOURNAL, 8 (1916), 319.

Mr. Richardson's experiments are based upon only those constituents of the various asphalts which he dissolves out by means of a vague solvent designated "naphtha" yet he neglects the proportions and characteristics of the insoluble constituents in his deductions as to the proper constitution of asphalts. The work, therefore, is open to the serious criticism of incompleteness from the scientific standpoint.

The most amazing feature, however, is that paragraph on page 321 wherein two asphalts are differentiated from three other materials and misleading intimations presented as to their relative industrial behavior. When it is realized that the author of the paper is the paid expert of the company handling the two first mentioned asphalts, the commercial aspect of the article becomes at once apparent and it is difficult to understand how

such paragraphs received the approval of your editorial staff.

As a matter of fact the bitumen constitutes at best only from 9 to 12 per cent of an asphalt pavement and the other constituents, as well as the workmanship of their mixing and laying, are certainly important factors bearing on the serviceability of the construction. Furthermore, in view of these conditions, it is quite possible to find both good and bad examples with all of the asphalts mentioned so the association of the formolite reaction with industrial behavior is by no means established.

As the technical representative of a prominent asphalt refining company holding corporation membership in the Society, I wish to enter a strong protest against the publication in our journals of such papers of advertising nature and request that this communication be given due prominence.

U. S. ASPHALT REFINING COMPANY LEROY M. LAW  
EAST BROOKLYN, BALTIMORE, April 24, 1916

*Editor of the Journal of Industrial and Engineering Chemistry:*

We wish to protest against the publication of the article by Clifford Richardson entitled "The Formolite Reaction of Nastukoff as Applied to Oil Residuals and Natural Asphalts" which appeared in THIS JOURNAL, 8 (1916), 319.

Mr. Richardson's article would appear to be an advertisement for Trinidad and Bermudez asphalts, two products controlled by the Barber Asphalt Company for which company Mr. Richardson is the chief chemist.

Mr. Richardson's statement that the "deficiencies of the artificial asphalts in their industrial behavior, as demonstrated by service tests, may be considered to be satisfactorily explained" is particularly objectionable in that it is not in accordance with the facts. The various grades of asphalt referred to by Mr. Richardson under the term "artificial asphalt" have been used for paving purposes in this country over a period of from ten to twenty years and with success so marked that in the case of some of the larger cities Trinidad asphalt has been excluded and Bermudez asphalt permitted only under the general specification that would admit the grades of asphalt described by Mr. Richardson under "artificial asphalts."

17 BATTERY PLACE, NEW YORK CITY  
April 26, 1916

JOHN BAKER, JR.

## POTASSIUM PERMANGANATE FOR SULFUR DIOXIDE DETERMINATIONS

*Editor of the Journal of Industrial and Engineering Chemistry:*

Considering the high cost of iodine and potassium iodide, a cheaper reagent for determining sulfur dioxide in routine tests is desirable. A solution of potassium permanganate serves admirably for such work, giving very constant and close agreement with iodine solution. In making up such a solution only 0.9 the theoretical amount should be taken. Thus 10 g.  $\text{KMnO}_4$  to 1 liter should theoretically give a solution, 1 cc. of which would be equivalent to 0.01 g.  $\text{SO}_2$ , but the amount actually required is almost exactly 9 g. per liter. In standardizing the solution, titrate against a sulfur dioxide solution of known strength as determined by an iodine solution.

CLINTON SUGAR REFINING COMPANY  
CLINTON, IOWA, April 21, 1916

A. P. BRYANT

## THE NEW NATIONAL FORMULARY

The Committee on Publication of the *American Pharmaceutical Association* makes the following announcement: The National Formulary, 4th Edition (N. F. IV), will be ready for distribution about July 1, 1916. The prices of the book in the various bindings will be as follows. *Muslin*, plain, \$2.50; *Buckram*, plain, \$2.75; *Buckram*, interleaved, \$4.00.

The Midland Publishing Company, Columbus, Ohio, has been appointed General Sales Agent with the following sub-agents: The Baker-Taylor Company, New York City; The Chicago Medical Book Company, Chicago; L. S. Mathews Company, St. Louis, Mo.; The Pacific Drug Review, San Francisco and Portland.



## PERSONAL NOTES

The American Leather Chemists' Association held their annual meeting at Atlantic City, June 1, 2 and 3, 1916. The program included a "Symposium on the Disinfection of Hides and Skins." The meeting was one of the most successful in recent years and was attended by members of the society and representatives of the leather industry, extract, oil and allied trades. The full proceedings will be published in the July issue of the *Journal of the American Leather Chemists' Association*.

Following the calling out of the military forces of the states, the Rhode Island Section of the American Chemical Society have formally proffered their cooperation to the Governor of the State in order that their professional knowledge and organization may be available for the common good.

The twenty-fourth annual meeting of the Society for the Promotion of Engineering Education was held at the University of Virginia, University, Va., on June 19 to 22, 1916.

Isaac H. Levin has resigned his position as chief engineer and chemist of the International Oxygen Company in order to devote his time to chemical research and as a specialist in the electrolytic field. Mr. Levin's temporary address is 186 Hillside Avenue, Newark, N. J.

William M. Barr, recently manager of the Mallinckrodt Chemical Works, Jersey City, N. J., has been appointed consulting chemist for the Union Pacific Railroad Company, with headquarters at Omaha, Nebraska. His address will be, Office of the General Manager, Union Pacific R. R., Omaha, Nebraska.

Dr. George Rosengarten recently met with a serious automobile accident. In turning aside to avoid running down a pedestrian, Dr. Rosengarten's machine turned turtle, pinning him beneath. He was very painfully injured and has since been confined to his bed.

Mr. James A. Branegan, member of the Philadelphia Section of the A. C. S., is now in charge of the intermediate department of the General Chemical Company, with headquarters at 25 Broad Street, New York City.

Mr. Charles R. Oberfell of the Philadelphia Section of the A. C. S. has been elected president of the American Leather Chemists' Association. Mr. Oberfell has the distinction of being the youngest man to receive the honor.

The death at Budapest, on May 21st, of General Arthur Goergei has been reported; he was 98 years old. General Goergei was commander in chief of the Hungarian Army during the war of liberation in 1848. He was also prominent as a chemist.

President MacLaurin of the Massachusetts Institute of Technology, Boston, has announced that the Institute in establishing its new school of chemical engineering practice will maintain stations in connection with certain selected manufacturing organizations in representative industries. The Institute is to maintain a professor in each station, and a well-equipped laboratory. One station will be established at Somerville, Mass., in connection with the works of the New England Gas & Coke Company; a second at Bangor, Me., with the Eastern Manufacturing Company; the third at Niagara Falls in connection with the Exolon Manufacturing Company; and a fourth at the works of the Atlas Cement Company in Allentown, Pa.; the fifth station has not yet been definitely fixed upon, but will be with one of the great chemical industries near New York or Chicago. An article on the dedication of the new buildings of the school and a description of its five-year course in chemical engineering will appear in the August issue of *THIS JOURNAL*.

A committee of the American Chemical Society, consisting of President Charles H. Herty, Leo H. Backeland and Willis R. Whitney, has been appointed as an advisory committee to the Bureau of Mines on chemical problems in connection with its investigations.

Dr. J. F. Norris, of Vanderbilt University, will take charge of research work and applied chemistry with fifth-year students in the new chemical engineering course of the Massachusetts Institute of Technology. Dr. Norris was recently appointed as the A. C. S. representative on the Tennessee State Board of the Organization for Industrial Preparedness.

Mr. Stanley H. Rose, formerly in charge of the New York office of the Bureau of Foreign and Domestic Commerce of the Department of Commerce, has been engaged by the Barber Asphalt Paving Co. to direct its foreign trade department.

Sir Corbet Woodall, prominently identified with the gas industry in England, died on May 18th at his home in London, aged 75 years. He was governor of the Gaslight and Coke Company of London, and was twice president of the Institute of Gas Engineers.

At the recent commencement of the University of Virginia, Mr. Richard K. Meade, of Baltimore, was elected to membership in the Phi Beta Kappa Society of that institution, in "recognition of his attainments in the field of chemical engineering and especially hydraulic cements." As the University of Virginia confers no honorary degrees, election to this society is the highest gift the University may confer on its alumni.

Silvanus Phillips Thompson, noted as an electrical engineer and physicist, and a former president of the Institution of Electrical Engineers, died in London, June 13th, in his sixty-sixth year. He was professor of physics at the University of London, and a past president of the Physical Society, the Röntgen Society, the Optical Society, and the Illuminating Engineers' Society. Prof. Thompson visited the United States in 1893, when he was received by many scientific societies and delivered several lectures.

George M. Kendall, for a number of years manager of the New York office of The Pfaunder Company and widely known among the dairy and pharmaceutical trades, died on May 22nd, at the home of his father, in Ludlow, Vermont.

Prof. G. T. Morgan, F.R.S., has been appointed to the chair of chemistry at Finsbury College, London, in succession to the late Raphael Meldola.

At the meeting of the Board of Directors of the American Electrochemical Society held in the New Willard Hotel, Washington, D. C., April 26, 1916, the Board voted that the past-presidents of the Society, with the president of the Society as chairman, shall constitute an Advisory Committee to be known as the Committee on Public Relations, to recommend to the Board action on public affairs, and with such other powers as the Board may delegate to it. This committee was authorized to send word of its existence to the working committees of Congress, and to say that it is ready to advise such committees upon electrochemical questions.

The United States Civil Service Commission announces the following open competitive examinations: *Chemists* (male), salary \$3.84 per diem, on July 5, 1916; *assistant alloy chemist* (male), salary \$1,620 per annum, on July 5-6, 1916. Further information may be had from the United States Civil Service Commission, Washington, D. C.

# GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

## DEPARTMENT OF AGRICULTURE

**Methods for the Determination of the Physical Properties of Road-Building Rock.** FRANK H. JACKSON, JR. Department Bulletin 347. 27 pp. Paper, 10 cents. "The present bulletin has thus been limited to a description of methods employed by this office for testing rock for road building, and is intended to serve as a more or less permanent laboratory manual for those who have occasion to make such tests."

The physical tests reported are the specific gravity, weight per cubic foot, water absorption, Deval abrasion test, hardness, toughness, cementing value, and compression test. Appendices include a discussion of the selection and shipment of samples and a description of laboratory equipment required for this work.

**The Utilization of Cherry By-Products.** FRANK RABAK. Department Bulletin 350. 24 pp. Paper, 5 cents. The following summary of the available by-products indicates the results of this investigation.

"1—The fixed oil, which is perhaps the most important product, is, in its properties and general characteristics, so closely related to the commercial oil of almonds that it is placed in an important position with respect to usefulness and value. The oil expressed from the fresh kernels is quite similar to almond oil and its use as an article of commerce, applied along pharmaceutical and therapeutical lines, or as a condimental oil, or even for soap-making purposes, should be assured.

"2—The volatile oil which can be produced from the press cake after the fixed oil has been extracted is practically identical with the oil of bitter almonds, thus rendering its usefulness the same in every way as that of bitter-almond oil.

"3—The meal, which is the final residue, has been shown to possess nourishing properties, much the same as those of the more common feeding stuffs on the market.

"4—The juice has been shown to be capable of being transformed into alcohol, sirup, or jelly, and it is reasonable to assume that there should be a demand for such products."

**Moisture Content and Shrinkage of Forage.** H. A. VINAL AND R. MCKEE. Department Bulletin 353. 37 pp. Paper, 10 cents. The only matters of chemical interest in this bulletin are those which have to do with methods which can be employed for the determination of moisture in various materials similar to hay, alfalfa, etc.

**A New Penetration Needle for Use in Testing Bituminous Materials.** CHARLES S. REEVE AND FRED P. PRITCHARD. Journal of Agricultural Research, 5 (March 13), 1121-6.

**Relation of Green Manures to the Failure of Certain Seedlings.** E. B. FRED. Journal of Agricultural Research, 5 (March 20), 1161-76.

**Relation of Carbon Bisulfide to Soil Organisms and Plant Growth.** E. B. FRED. Journal of Agricultural Research, 6 (April 3), 1-19.

**Soluble Nonprotein Nitrogen of Soil.** R. S. POTTER AND R. S. SNYDER. Journal of Agricultural Research, 6 (April 10), 61-4.

**Determination of Stearic Acid in Butter Fat.** E. B. HOLLAND, J. C. REED AND J. P. BUCKLEY, JR. Journal of Agricultural Research, 6 (April 17), 101-113.

**Effect of Pasteurization on Mold Spores.** CHARLES THOM AND S. HENRY AYERS. Journal of Agricultural Research, 6 (April 24), 153-166.

**Effect of Water in the Ration on the Composition of Milk.** W. F. TURNER, R. H. SHAW, R. P. NORTON AND P. A. WRIGHT. Journal of Agricultural Research, 6 (April 24), 167-178.

**Development of Sugar and Acid in Grapes during Ripening.** WILLIAM B. ALWOOD. Department Bulletin 335, from the Bureau of Chemistry. 28 pp. Paper, 5 cents. This publication is primarily of interest to growers of grapes for commercial purposes.

**Ground-Wood Pulp. Part I—The Grinding of Cooked and Uncooked Spruce. Part II—Substitutes for Spruce in the Manufacture of Ground-Wood Pulp.** J. H. THICKENS AND G. C. McNAUGHTON. Department Bulletin 343, from the Forest Service. 151 pp. and 12 plates. This professional paper is not available for distribution nor is it for sale by the Superintendent of Documents. It can be consulted only in libraries receiving department bulletins.

**Relation of Mineral Composition and Rock Structure to the Physical Properties of Road Materials.** E. C. LORD. Department Bulletin 348, from the Office of Public Roads and Rural Engineering. 26 pp. and 8 plates. Paper, 10 cents. This is principally of interest to road contractors and engineers.

**Bacteria in Commercial Bottled Waters.** MAUD M. OBST. Department Bulletin 369, from the Bureau of Chemistry. 14 pp. Paper, 5 cents. This is a report of results obtained from a bacteriological examination of bottled waters from 110 American and 57 foreign springs.

**Commercial Production of Thymol from Horsemint (*Monarda Punctata*).** S. C. HOOD. Department Bulletin 372, from the Bureau of Plant Industry. 12 pp. Paper, 5 cents. Methods of cultivation and harvesting the mint and the procedure for extraction and distillation of the oil is given in some detail in this bulletin.

**Legal Standards for Dairy Products.** Unnumbered leaflet from Bureau of Animal Industry. 3 pp. Paper, 5 cents. This revision is complete to July 1, 1915; issued May 1, 1916.

## NATIONAL MUSEUM

**Proceedings of the National Museum.** Volume 49 contains the following four articles of chemical interest:

1—Notes on Composition and Structure of Indarch, Russia, Meteoric Stone. GEORGE P. MERRILL.

2—Peculiar Oölite from Bethlehem, Pennsylvania. EDGAR T. WHERRY.

3—Report on Some Carbonic Acid Tests on Weathering of Marbles and Limestones. GEORGE P. MERRILL.

4—Notes on Allophanite, Fuchsite and Triphylite. EDGAR T. WHERRY.

## BUREAU OF STANDARDS

**Effect of Certain Pigments on Linseed Oil.** E. W. BOUGHTON. Technologic Paper 71. 16 pp. This report describes the effect of storage on the constants of oil in paint. It gives data as to the combination of oil and pigment during drying and other changes.

**Invar and Related Nickel Steels.** Circular 58, 1st Edition. Issued April 4, 1916. 68 pp. "The present circular, issued in response to many requests received by the Bureau for information concerning invar, describes some of the most important



properties of nickel steels in general, but with particular reference to that alloy which owes its name to its extremely small thermal expansion at ordinary temperatures.

"The account is largely a compilation of results obtained during the last 25 years by various investigators, from the writings of whom figures, tables, and text have been freely taken."

The discussion of this circular includes the following properties: Equilibrium diagram; microstructure and constitution; magnetic and electrical properties; thermal expansion and the constance of the dimensions of invar (in this section the behavior of different types of invar, according to the heat treatment, is fully discussed); density, strength, elastic limit, elongation, reduction of area; hardness and abrasion; elasticity and its change with temperature; polish; and resistance to corrosion. The various applications and sources of the supply of these steels are discussed and a bibliography of the more important articles is included.

**Constants of the Quartz-Wedge Saccharimeter and the Specific Rotation of Sucrose. I—The Constants for the 26-gram Normal Weight.** FREDERICK BATES AND R. F. JACKSON. Scientific Paper 268. 62 pp. Issued April 6, 1916. A full description of the method used for purification of sucrose by concentrating aqueous solutions in vacuum below 35° C. and crystallizing while in motion, is included. The reducing action of pure sucrose on cuprous oxide is demonstrated by a study of the reaction velocity of sucrose and of invert sugar on such solutions. The speed of formation of caramel at various temperatures is determined and the permissible time of heating is plotted as a function of temperature. These data were applied to the drying operations. It has been shown that moisture can be eliminated from finely divided sugar by heating in a vacuum of 50° C. for a few hours. The absence of moisture has been shown by two direct qualitative tests of high sensitivity. The ratios of the rotations of quartz and sugar for two wave lengths are given and it is shown that the reading for a normal sugar solution on the Herzfeld-Schönrock scale is 99.89<sub>s</sub> S. Other constants of the saccharimeter and the details as to disagreement in accepted and correct values are discussed in detail.

**General Design of Critically Damped Galvanometers.** FRANK WENNER. Scientific Paper 273. 34 pp. Issued April 12, 1916. "The paper shows how the sensitivity to current, to voltage, to current impulse, and to voltage impulse, and also the period and conditions for critical damping depend upon the construction constants. These are the constants which depend upon the size, shape, and kinds of material used in the construction. The paper also gives a procedure for finding the magnitudes the various construction constants must possess if the galvanometer is to meet definite performance specifications.

"The paper is highly technical and was not written for the general reader. It may, however, be of interest to students in electrical measurements and to others especially concerned in the use of galvanometers or in their construction."

**Interference Measurements of Wave Lengths in the Iron Spectrum. (3233Å. to 6750Å.)** KELVIN BURNS, W. F. MEGGERS AND PAUL W. MERRILL. Scientific Paper 274. 29 pp. Issued April 11, 1916. "Between the limits 3233Å. and 6750Å., some 400 iron lines were either remeasured or measured for the first time by the interference method. The work was done in conformity with the recommendation of the international wavelength committee. Where it was found possible, faint lines as well as strong ones were measured. Satisfactory standards were found at intervals of 10 or 15 Ångströms throughout the greater part of the spectrum; there are no sharp iron lines of even moderate intensity in the region 5775Å. to 5934Å., and the number is insufficient in the extreme red."

**Relation between Composition and Density of Aqueous Solutions of Copper Sulfate and Sulfuric Acid.** H. D. HOLLER

AND E. L. PFEFFER. Scientific Paper 275. 9 pp. Issued April 7, 1916. "In connection with an investigation on the regulation of solutions for electrodeposition, especially of acid copper sulfate solutions for electrotyping, it was found desirable to devise a simple method of determining and adjusting their composition. Since the solutions usually employed for the above purpose contain only copper sulfate and sulfuric acid, the composition of any given solution is fixed if the acid content and density at a given temperature are known. The density can be readily determined with a hydrometer, and the acidity can be ascertained with sufficient accuracy by titration with standard alkali, using methyl orange as indicator, as described by Wogrinz. In order, therefore, to learn the content of copper sulfate, all that is required is a table showing the density of solutions containing known amounts of copper sulfate and of sulfuric acid."

#### BUREAU OF THE CENSUS

**The Gas Industry.** Unnumbered Circular, released for use June 12th, giving the Census Bureau's summary concerning the gas industry for 1914. The following tabulation indicates the number of establishments:

Carbureted water gas.....	427
Straight coal gas.....	274
Mixed coal and water gas and coal, water, and oil gas.....	156
Oil gas.....	150
Acetylene.....	165
All other (chiefly gasoline) gas.....	112
Number of establishments.....	1,284

"The value of all products in 1914 was \$53,423,410, or 32 per cent, more than in 1909; and the output of manufactured gas in 1914 exceeded that in 1909 by 52,894,308,000 cu. ft., or 35.1 per cent, in quantity, and by \$36,450,621, or 26.3 per cent, in value.

"In addition, there is a large amount of gas made in coke establishments and used for illuminating and for domestic fuel. The gas purchased by the gas companies is largely retort coke-oven gas. The following tabular statement gives the by-products obtained in the manufacture of coke in retort ovens in 1914, as reported by the Geological Survey:

Gas:	
Cubic feet (thousands).....	61,364,375
Value.....	\$6,009,583
Tar:	
Gallons.....	109,901,315
Value.....	\$2,867,274
Ammonia, sulfate or reduced to equivalent in sulfate:	
Pounds.....	170,763,906
Value.....	\$4,696,590
Ammonia liquors:	
Gallons.....	5,938,233
Value.....	\$658,497
Anhydrous ammonia:	
Pounds.....	25,370,509
Value.....	\$2,300,137
Other by-products, value.....	\$997,007

"The mileage of mains increased from 45,119 in 1909 to 58,727 in 1914, or by 30.2 per cent. There were reported 5,168,924 gas stoves and heaters in use in 1914, as compared with 3,603,435 in 1909, the increase being 43.4 per cent. The number of gas stoves and heaters reported can not, however, be considered as representing the actual number in use, since the establishments reporting them in many instances say that their records show only those supplied by themselves and that they have no knowledge of the number obtained from other sources."

#### CONGRESSIONAL COMMITTEE REPORTS

The following reports, obtainable in most cases from the Document Room of the appropriate branch of Congress, contain material of chemical interest:

**Investigation of High Price of Gasoline and Other Petroleum Products.** This is the report of a hearing on House Resolution 118, adopted March 10th. It contains an article entitled "Price of Gasoline and Dissolution Decree," by R. L. WELCH.

**Metalliferous Minerals on Indian Reservations.** This is a report accompanying House Bill 12,426 which authorizes mining for metalliferous minerals on Indian Reservations in Arizona. It is numbered House Report 533, dated April 12, 1916. 4 pp.

**Coal and Asphalt Deposits in Choctaw and Chickasaw Nations.** Report of hearings before subcommittee on House Bill 12,544 which provides for the sale of coal and asphalt deposits in the segregated mineral lands of these reservations.

**Government Armor-Plate Factory.** Report to accompany Senate Bill 1417 which provides for the erection or purchase of an armor-plate factory. Numbered House Report 497, Part I, issued April 6, 1916. 2 pp. Paper, 5 cents. For sale by the Superintendent of Documents. A similar document—House Report 497, Part II, issued April 13, 1916, is a 5-page pamphlet also for sale at 5 cents.

**Experiment Stations in Connection with State Colleges.** This is a memorandum relative to Senate Bill 4874 which proposes to establish experiment stations in engineering and in other branches of mechanical arts in connection with colleges established in several states under the provision of earlier congressional acts. This report is Senate Document 353, issued March 10, 1916. 10 pp.

**Withdrawal of Water-Power Sites and Construction of Water-Power Plants for Manufacture of Nitrates.** Two reports have been issued on hearings on Senate Bill 4971. Part I of this is 77 pp., issued during March. Part II is Senate Report 325.

#### GENERAL SUPPLY COMMITTEE

**Method of Sampling Coal Deliveries.** Appendix A to specifications and proposals for the purchase of coal which is Class 14 of the General Supply Committee specifications for the fiscal year 1917. This appendix describes the methods of sampling which are required by those supplying coal under Government contract.

#### NAVAL ENGINEERING EXPERIMENT STATION

**The Volatile Matter of Coal.** J. G. O'NEILL. Reprint from the Journal of the American Society of Naval Engineers, 28 (1916), 11-19.

#### BUREAU OF MINES

**Instruments for Recording Carbon Dioxide in Flue Gases.** J. F. BARKLEY and S. B. FLAGG. Bulletin 91. 52 pp. Paper, 10 cents.

"In the course of the tests the following details were determined:

"1—The lag in recording changes of composition of a flowing gas.

"2—The accuracy of each type of recorder.

"3—The variable factors affecting the operation and accuracy of each type.

"4—The repairs and renewals necessary.

"5—The kind and amount of attention required."

**The Feldspars of the New England and North Appalachian States.** A. S. WATTS. Bulletin 92. 180 pp. Paper, 25 cents. "The investigations presented in this bulletin have been undertaken by the Bureau with a view to a better understanding of the conditions which confront the producer of commercial feldspar and also with the object of determining wherein the various deposits of feldspar differ. This information will enable the manufacturer to choose the source of supply which is best suited to his needs, and in case a change is necessary to choose more intelligently the location from which to draw for his future supply.

"Such an investigation was deemed necessary, not only because of the continued and increasing consumption of these minerals, but especially because of the demand for better technical control of the raw materials that are used by the white-ware industries of the United States. Most manufacturers of white pottery wares have only a limited knowledge

of the origin, mode of occurrence, and methods of mining and preparation of the materials that they use."

**The Analysis of Permissible Explosives.** C. G. STORM. Bulletin 96. 84 pp. Paper, 15 cents. "Permissible explosives are those that have passed the test prescribed by the Bureau of Mines for explosives intended for use in coal mines, and are therefore recommended by the Bureau as suitable for this class of work when used under the prescribed conditions.

"This bulletin is published primarily for the purpose of informing manufacturers of such explosives as to the methods used by the Bureau of Mines in the analysis of samples received for tests to determine their permissibility. Such information may be of value in cases of possible controversy over the results obtained in the analysis of a field sample as compared with those obtained in analyzing the sample originally tested by the Bureau. Also a description of the methods used by the Bureau of Mines in the analysis of explosives should be of assistance to the many chemists engaged in similar analytical work."

**The Inflammability of Illinois Coal Dusts.** J. K. CLEMENT and L. A. SCHOLL, JR. Bulletin 102. 68 pp. Paper, 15 cents. "The present paper is a report of a detailed study of the bituminous dusts of Illinois mines, and is a part of the investigations conducted by the Bureau in cooperation with the Illinois State Geological Survey and the department of mining engineering of the University of Illinois.

"Laboratory tests of inflammability have been made on more than 500 samples of dust from 100 representative Illinois mines. As a result of these tests it may be stated that:

"1—The coals of Illinois when ground fine enough yield highly inflammable dusts which when suspended in air may give rise to violent explosions.

"2—In the majority of the mines of the State the dusts adhering to the ribs are inflammable. In about one-fourth of the mines the quantity of rib dusts present in the entries is sufficient to form an explosive mixture with air.

"3—Most of the road dusts are inflammable when ground to a sufficient degree of fineness."

**Some Properties of the Water in Coal.** HORACE C. PORTER and O. C. RALSTON. Technical Paper 113. 28 pp. Paper, 5 cents. "In connection with the analysis of coal, its destructive distillation, its alteration during storage, and other phases of its industrial utilization, the question of its water content is of interest and importance. This paper deals with the manner in which water may be held in coal, and how its properties and those of the coal are affected by the condition in which it is held. Water formed in the decomposition of the coal substance by heat is not considered in this paper."

**Effects of Atmospheres Deficient in Oxygen on Small Animals and on Men.** GEORGE A. BURRELL and G. G. OBERFELL. Technical Paper 122. 10 pp. Paper, 5 cents. "The results of these experiments may be summarized as follows:

"Atmospheres that are deficient in oxygen begin to affect men when the percentage of oxygen is about as low as that affecting canaries and mice. Canaries are slightly more susceptible to 'oxygen want' than are mice. In mixtures of air and nitrogen containing about 7.6 to 7.8 per cent oxygen, canaries show pronounced distress. When the oxygen content is about 7 per cent, mice show considerable distress, and a man is in grave danger of dying; hence canaries and mice should not be used by exploring parties in mines to show when men unequipped with breathing helmets should retreat, because the atmosphere is low in oxygen.

"Mice and canaries, especially the latter, are chiefly of value for indicating to exploring parties the presence of dangerous proportions of carbon monoxide. In an atmosphere in which oil-fed lamps will not burn, an exploring party should not depend upon canaries for further guidance, but should use breathing apparatus in advancing into the atmosphere."



**The Sand Test for Determining the Strength of Detonators.** C. G. STORM AND W. C. COPE. Technical Paper 125. 64 pp. Paper, 10 cents. "The results obtained in the tests described in this report justify the conclusion that the sand test provided an exact means of grading commercial detonators. As regards each of the fulminate compositions tested, the value established by the sand test has been shown to be a definite function of the weight of charge. It has also been demonstrated that the weight of charge of a given composition in a detonator may be closely estimated from the quantity of sand pulverized in the sand test of the detonator."

"The relative efficiencies of the various fulminate compositions tested, as indicated by the quantity of sand crushed by each when subjected to the sand test, have been shown to be comparable with their relative efficiencies in causing complete detonation of nitro-substitution compounds of varying degrees of sensitiveness to detonation."

**The Casting of Clay Wares.** TAINIE G. McDOUGAL. Technical Paper 126. 26 pp. Paper, 5 cents. "Casting, as a rule, is undertaken by potteries that are at the time using one of the plastic processes. The object of this paper is to point out, in the light of experiments and factory observations, the difference in procedure necessary and the precautions advisable when changing from a plastic to a casting process. The paper is addressed especially to the practical potter, and the matters considered are discussed with regard to factory rather than laboratory problems, only as much theoretical discussion being given as is deemed necessary to a better understanding of the practical application."

**Explosibility of Gases from Mine Fires.** GEORGE A. BURRELL AND GEORGE G. OBERFELL. Technical Paper 134. 31 pp. Paper, 5 cents. "This report presents the results of observations of gases produced during mine fires, and the liability of such gases to explode. The first part deals with a fire that resulted in an explosion. Information obtained regarding the gases that caused the explosion allowed some conclusions to be reached regarding the parts played by the combustible gases produced by the fire and regarding the methane that was normally given off by the coal seam."

"Only those facts are reported herein that have a distinct bearing on the study of the gases produced during the fire investigated. No attempt is made to describe in detail the fighting of the fire or all of the expedients that were adopted in quenching it."

#### HYGIENIC LABORATORY

**I—Chemical Changes in Central Nervous System as Result of Restricted Vegetable Diet. II—Chemical Changes in Central Nervous System in Pellagra.** MATHILDE L. KOCH AND CARL VOEGTLIN. Bulletin 103. 135 pp. Paper, 20 cents. Also available as House of Representatives Document 620.

#### COMMERCE REPORTS—MAY, 1916

A comparison of the American dyestuff production in 1914 and as estimated for 1916, by the Census Bureau, may be summarized as follows:

OUTPUT.	1914	1916
Benzene.....	9600 tons	90,000 tons
Toluene.....	3200	22,440
Naphthalene.....	1500	12,500
Phenol.....	75	10,000
Aniline.....	900	15,000

The output of natural dyes, including logwood extract, quercitron, fustic, cutch, archil, etc., shows a marked increase. The value of mineral dyes has increased, but not the actual output, except of ultramarine. (Pp. 406-8.)

Promising deposits of pitchblende have been discovered in the Gaya district, India. (P. 408.)

A large list of tanning and dyeing materials available in Brazil is given. While mangrove is the most abundant source of tannin, its exportation is not permitted under existing laws. (Pp. 410-3.)

Shipments of nitrate and copper ore from Chili have been almost suspended, owing to lack of shipping facilities. (P. 433.)

The government railways in Brazil are about to adopt crude oil as fuel, owing to the shortage of coal. (Pp. 490-2.)

Canada is using measures similar to those in the United States for conserving the supply of paper. (P. 503.)

The chief mineral exports of Seville, Spain, are copper, copper ore, and iron pyrites. (P. 504.)

The Geological Survey has discovered that lake muds about 60 miles west of the Great Salt Lake, Utah, contain appreciable potash. (P. 512.)

There has been a great increase in the production of asbestos in the United States, especially in Arizona and Georgia, thus in part compensating for the shortage due to the embargo on shipments from Canada. (P. 517.)

In a new method proposed for dyeing wool with prussian blue, the ferrocyanide is converted to ferricyanide by the addition of sodium hypochlorite just before dyeing. (P. 523.)

For the first time, the sale of oleomargarine is permitted in France (under restrictions). (P. 529.)

Small deposits of potassium nitrate and chloride are found in Peru. (P. 537.)

The world's supply of araroba, a tree growth containing the drug "chrysarobin," comes from Brazil. (P. 568.)

Efforts are being made to develop electrochemical industries in South Africa, especially the manufacture of carbide, cyanide, cyanamide and nitrates. (P. 676.)

Shipments of linseed from Argentina to the United States, which were formerly very large, but smaller in recent years, are now increasing. (P. 700.)

The limited output of tungsten ore from Argentina is now being shipped entirely to the United States. (P. 702.)

Owing to serious shortage of coal in Sweden, efforts are being made to increase the output of peat. (P. 722.)

An electrolytic copper refinery and a zinc smelter are being erected at Trail, British Columbia. (P. 731.)

The sugar production of Porto Rico shows a marked increase. (P. 739.)

In order to avoid possible losses of glycerine, the manufacture of soap in Germany, by other than licensed factories, is prohibited. (P. 768.)

In order to meet better the anticipated competition abroad, all the German dyestuff manufacturers have formed a combination. (P. 770.)

Shipments of oil from Tampico show a marked increase. (P. 777.)

The natural gas fields of Hungary have been leased by the government to a company which will immediately develop them. (P. 786.)

Zinc foil is now being used in Germany as a substitute for tin foil. (P. 803.)

Supplies of logwood, fustic and Brazil wood are now available in the Dominican Republic, Cuba, Nicaragua, and Brazil. (P. 812.)

#### SPECIAL SUPPLEMENTS ISSUED IN MAY

Italy, Florence and Venice—8a	Honduras—31a
United Kingdom, Ireland—19c	Paraguay—45a
United Kingdom, Wales—19d	China, Hongkong—52b
Canada, Manitoba—23c	Japan, Taiwan (Formosa)—55b

EXPORTS TO THE UNITED STATES. (PP.)

LONDON—626	CARDIFF—Sup. 19d	HONDURAS—Sup. 31a
Rubber	Coal	Gold
Tin	Glue	Hides
Hides	Paints	Rubber
Platinum	Paper stock	Sarsaparilla
Indigo		Silver
Cresote oil	WINNIPEG—Sup. 23c	Antimony
Copper	Glycerine	HONGKONG—Sup. 52b
VENICE Sup. 8a	Hides	Chemicals
Beet pulp	Paper	Chinaaware
Glycerine	Senega root	Peanut oil
Hides	PORT ELIZABETH, So.	Aniseed oil
TAIWAN (FORMOSA)	AFRICA—803	Cassia oil
Camphor	Wool grease	Paper
Camphor oil	Hides	Sugar
	Wattle bark	Tin

# NEW PUBLICATIONS

By IRENE DEMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

- Agriculture:** Exercises in Agriculture. S. H. DADISMAN. 12mo. 160 pp. Price, \$0.60. Lyons & Carnahan, Chicago.
- Analysis:** Elementary Qualitative Analysis. BENTON DALES and O. L. BARNEBY. 12mo. 206 pp. Price, \$1.50. John Wiley & Sons, Inc., New York.
- Chemical Plants:** A Manual of Chemical Plants. S. S. DYSON. Issued periodically. Parts 1-4 have been published. 8vo. Price of entire work \$5.25, of each part \$0.75. The Dover Printing & Publishing Co., Dover, England.
- Coal:** Its Economical and Smokeless Combustion. J. F. COSGROVE. 8vo. 273 pp. Price, \$3.00. Technical Book Publishing Co., Philadelphia.
- Concrete Construction for Rural Communities.** R. A. SEATON. 8vo. 225 pp. Price, \$2.00. McGraw-Hill Book Co., New York.
- Concrete:** General Specifications for Concrete Bridges. W. J. WATSON. 3rd Ed. 4to. 70 pp. Price, \$1.00. McGraw-Hill Book Co., New York.
- Concrete:** General Specifications for Concrete Work. W. J. WATSON. 4to. 56 pp. Price, \$1.00. McGraw-Hill Book Co., New York.
- Copper:** From the Ore to the Metal. HUGH K. PICARD. 8vo. 140 pp. Price, \$0.50. Sir Isaac Pitman & Sons, New York.
- Drugs:** The New National Formulary. 4th Ed. American Pharmaceutical Association. (See page 663, this issue).
- Electrical Engineering:** The Electrical Contractor. L. W. MOXEY. 8vo. 87 pp. Price, \$1.50. McGraw-Hill Book Co., New York.
- Flotation:** List of References on Concentrating Ores by Flotation. JESSE CUNNINGHAM, Comp. 8vo. 106 pp. School of Mines and Metallurgy, University of Missouri.
- Furnace Heating.** W. G. SNOW. 8vo. 259 pp. Price, \$2.00. D. Williams Co., New York.
- Gases:** Dynamical Theory of Gases. J. H. JEANS. 2nd Ed. 444 pp. Price, \$4.00. Cambridge University Press.
- Humidifying Apparatus.** 48 pp. Bulletin No. 100, Carrier Engineering Corporation, 39 Cortlandt Street, New York.
- Hydraulics.** R. L. DAUGHERTY. 8vo. 270 pp. Price, \$2.50. McGraw-Hill Book Co., New York.
- Inks:** Their Composition and Manufacture. C. A. MITCHELL and T. C. HEFORTH. 2nd Ed. 8vo. 272 pp. Price, \$2.00. Charles Griffin & Co., London.
- Locomotive Breakdowns.** G. L. FOWLER. 16mo. 301 pp. Price, \$1.00. Norman W. Henley Publishing Co., New York.
- Materials:** Elementary Strength of Materials. E. S. ANDREWS. 8vo. Price, \$1.12. Chapman & Hall, London.
- Mechanical Engineers' Handbook.** L. S. MARKS. 16mo. 1800 pp. Price, \$5.00. McGraw-Hill Book Co., New York.
- Metal Trades.** R. R. LUTZ. 12mo. 129 pp. Price, \$0.25. Cleveland Foundation, Survey Committee, Cleveland.
- Metals:** A Class-Book of Chemistry. Part IV. G. C. DONINGTON. 8vo. 133 pp. Price, \$0.50. Macmillan & Co., London.
- Mine Gases and Ventilation.** J. T. BEARD. 16mo. 216 pp. Price, \$2.00. McGraw-Hill Book Co., New York.
- Minerals:** The Deposits of the Useful Minerals and Rocks; their Origin, Form and Content. Vol. 2. FRANZ BEYSCHLAG and OTHERS. 3 Vol. 8vo. 711 pp. Price, \$5.25. The Macmillan Co., New York.
- Minerals:** Microscopical Determination of the Opaque Minerals. JOSEPH MURDOCH. 8vo. 165 pp. Price, \$2.00. John Wiley & Sons, Inc., New York.
- Organic Agricultural Chemistry;** a Textbook of General Agricultural Chemistry for Use in Colleges. J. S. CHAMBERLAIN. 12mo. 319 pp. Price, \$1.60. The Macmillan Co., New York.
- Textiles.** P. H. NYSTROM. 8vo. Price, \$1.50. D. Appleton & Co., London.
- Valves:** Slide Valves and Valve Gearing. PETER YOUNGSON. 2nd Ed. 4to. 194 pp. Price, \$2.00. J. Munro, London.
- Cobalt:** The Volumetric Determination of Cobalt and Nickel. W. K. SCHOELLER and A. R. POWELL. *The Analyst*, Vol. 41 (1916), No. 482, pp. 124-131.
- Coke:** By-Products of Coke Making. W. H. CHILDS. *Iron Trade Review*, Vol. 58 (1916), No. 22, pp. 1215-1218.
- Coke:** By-Products Recovery in Coke Production. W. H. CHILDS. *Blast Furnace and Steel Plant*, Vol. 50 (1916), No. 6, pp. 277-279.
- Corrosion:** Effect of Rust on the Rate of Corrosion. JAMES ASTON. *Steel and Iron*, Vol. 50 (1916), No. 5, pp. 150-153.
- Cost-Accounting in the Construction and Operation of a Copper Smelter.** E. E. THOM. *Metallurgical and Chemical Engineering*, Vol. 14 (1916), No. 11, pp. 660-662.
- Cyanidation:** The Discovery of Cyanidation. J. S. MACARTHUR. *Mining and Scientific Press*, Vol. 112 (1916), No. 24, pp. 851-855.
- Cyanidation:** Effect of Black Slate on Cyanidation. H. FISCHER. *Mining and Scientific Press*, Vol. 112 (1916), No. 21, pp. 743-745.
- Electric Furnace in Steelmaking.** JOHN A. MATHEWS. *Iron Trade Review*, Vol. 58 (1916), No. 23, pp. 1264-1267.
- Electric Power:** The Inherent Economic Advantage of Electric Power. C. P. STEINMETZ. *General Electric Review*, Vol. 19 (1916), No. 6, pp. 431-433.
- Fat:** A Rapid Method for the Estimation of Fat in Powders. S. P. PHILLIPS. *The Analyst*, Vol. 41 (1916), No. 482, pp. 122-123.
- Fuel:** Cost of Coal and Oil as Fuel. PERRY BARKER. *Power*, Vol. 43 (1916), No. 22, pp. 765-767.
- Furnaces:** Mechanical Feeding as Applied to Silver-Lead Blast Furnaces. L. D. ANDERSON. *Engineering and Mining Journal*, Vol. 101 (1916), No. 21, pp. 885-888.
- Gas:** The Combustion of Gas, and Flame Temperatures. FREDERICK PEITER. *Journal of the Cleveland Engineering Society*, Vol. 8 (1916), No. 6, pp. 439-455.
- Gases:** Mixing Air and Furnace Gases. S. H. VIAL. *Power*, Vol. 43 (1916), No. 23, pp. 788-790.
- Gasoline:** The Gasoline Question. *Mining and Scientific Press*, Vol. 112 (1916), No. 21, pp. 753-756.
- Gears:** On Reduction Gears. J. H. MACALPINE. *Engineering*, Vol. 101 (1916), No. 2629, pp. 478-492.
- Iron and Steel Wire for Transmission Conductors.** T. A. WORCESTER. *General Electric Review*, Vol. 19 (1916), No. 6, pp. 488-492.
- Lubricating Oils and Cutting Compounds for Shop Use.** W. R. CONOVER. *American Machinist*, Vol. 44 (1916), No. 23, pp. 993-998.
- Manganese in South Carolina.** R. W. PETRE. *Engineering and Mining Journal*, Vol. 101 (1916), No. 24, pp. 1019-1020.
- Motors:** Selecting Industrial Motors. THOMAS R. HAY. *Engineering Magazine*, Vol. 51 (1916), No. 3, pp. 344-354.
- Oils:** Refining Vegetable and Animal Oils. CHARLES BASKERVILLE. *Journal of the Franklin Institute*, Vol. 181 (1916), No. 6, pp. 733-746.
- Ores:** The Dry Chlorination of Complex Ores. S. A. IONIDES. *Mining and Scientific Press*, Vol. 112 (1916), No. 22, pp. 781-787.
- Petroleum:** The Refining of Petroleum. ANDREW CAMPBELL. *Petroleum Review*, Vol. 34 (1916), No. 722, pp. 417-418.
- Porcelain:** Testing of Electrical Porcelain. E. E. F. CREIGHTON and P. E. HOSGOOD. *General Electric Review*, Vol. 19 (1916), No. 6, pp. 479-483.
- Portland Cement.** G. A. RANKIN. *Journal of the Franklin Institute*, Vol. 181 (1916), No. 6, pp. 747-784.
- Samples and Their Interpretation.** E. H. DICKENSON and H. J. VOLKER. *Engineering and Mining Journal*, Vol. 101 (1916), No. 22, pp. 933-936.
- Silver:** The Distribution of Silver between Metallic Lead and Litharge-Containing Slags. BOYD DUDLEY, JR. *Metallurgical and Chemical Engineering*, Vol. 14 (1916), No. 11, pp. 636-641.
- Sintering Plant Installed at Toledo.** H. V. SCHIEFER. *Iron Trade Review*, Vol. 58 (1916), No. 21, pp. 1155-1160.
- Steam:** How to Use Superheated Steam. CHARLES L. HUBBARD. *Engineering Magazine*, Vol. 51 (1916), No. 3, pp. 413-419.
- Steel Production at New Minnesota Plant.** C. C. LYNDE. *Blast Furnace and Steel Plant*, Vol. 50 (1916), No. 6, pp. 251-260.
- Sulfate Pulp Manufacture.** CARL MOR. *Paper*, Vol. 18 (1916), No. 12, pp. 11-16.
- Turbines:** The Exhaust Steam Turbine. J. BRESLAY. *Power*, Vol. 43 (1916), No. 23, pp. 801-805.
- Turbines:** Recent Advances in Large Steam Turbine Practice. J. F. JOHNSON. *The Electric Journal*, Vol. 13 (1916), No. 6, pp. 258-262.
- Water:** Impure Boiler Waters. W. N. BEKKELEY. *Power*, Vol. 43 (1916), No. 23, pp. 795-796.

## RECENT JOURNAL ARTICLES

- Air:** The Action of Air in Surface Condensers. PAUL A. BAUCEL. *Power*, Vol. 43 (1916), No. 24, pp. 834-836.
- Ammonia:** Calculating the Quantity of Ammonia Needed. CHARLES H. BROMLEY. *Power*, Vol. 43 (1916), No. 24, pp. 843-844.
- Blast Furnace:** Handling the Blast Furnace Charge. G. W. VREELAND. *Iron Trade Review*, Vol. 58 (1916), No. 23, pp. 1289-1273.
- Blasting:** Modern Blasting Practice. P. B. McDONALD. *Mining and Scientific Press*, Vol. 112 (1916), No. 22, pp. 788-795.
- Coal:** More Economical than Oil. JAMES ROSS. *Power*, Vol. 43 (1916), No. 21, p. 723.



# INORGANIC CHEMICALS

Acetate of Lime gray.....	100 Lbs.	7.00	@	7.05
Alum lump ammoniac.....	100 Lbs.	4.00	@	—
Aluminum Sulfate, high grade.....	100 Lbs.	5.00	@	6.00
Ammonium Carbonate, domestic.....	Lb.	9 1/2	@	10
Ammonium Chloride, gray.....	Lb.	9	@	10
Ammonium Phosphate, commercial, 98-100%.....	Lb.	—	@	—
Aqua Ammonium, 16°, drums.....	Lb.	—	2 3/4	@
Arsenic, white.....	Lb.	6 1/4	@	—
Barium Chloride.....	Ton	110.00	@	—
Barium Nitrate.....	Lb.	15	@	16
Barytes, prime white, foreign.....	Ton	—	@	—
Bleaching Powder, 35 per cent.....	100 Lbs.	5.00	@	—
Blue Vitriol.....	Lb.	12	@	—
Borax, crystals, in bags.....	Lb.	6 3/4	@	7
Boric Acid, powdered crystals.....	Lb.	11 3/4	@	15
Brimstone, crude, domestic.....	Long Ton	35.00	@	—
Bromine, technical, bulk.....	Lb.	3.50	@	—
Calcium Chloride, lump.....	Ton	11.75	@	12.00
Calcium Chloride, granulated.....	Ton	14.78	@	15.00
Caustic Soda, 74 per cent.....	Lb.	4 1/2	@	—
Chalk, light precipitated.....	Lb.	4 1/2	@	5 1/4
China Clay, imported.....	Ton	15.00	@	18.00
Feldspar.....	Ton	8.00	@	12.00
Fuller's Earth, foreign, powdered.....	100 Lbs.	80	@	1.05
Glauber's Salt, in bbls.....	100 Lbs.	55	@	65
Green Vitriol, bulk.....	100 Lbs.	1.25	@	1.50
Hydrochloric Acid, commercial, 18°.....	100 Lbs.	2.50	@	3.00
Hydrochloric Acid, C. P., conc., 22°.....	100 Lbs.	3 1/4	@	—
Iodine, resublimed.....	Lb.	4.25	@	4.50
Lead Acetate, white crystals.....	Lb.	15 3/8	@	15 7/8
Lead Nitrate.....	Lb.	16	@	17
Litharge, American.....	Lb.	—	9 1/4	@
Lithium Carbonate.....	Lb.	90	@	1.00
Magnesium Carbonate.....	Lb.	18	@	21
Magnesite, "Calcined".....	Ton	—	@	—
Nitric Acid, 36°.....	Lb.	7 3/4	@	8
Nitric Acid 42°.....	Lb.	8 1/4	@	—
Phosphoric Acid, sp. gr. 1.750.....	Lb.	30	@	31
Phosphorus.....	Lb.	—	@	—
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, casks.....	Lb.	45	@	50
Potassium Bromide (granular).....	Lb.	4	@	4 1/4
Potassium Carbonate, calcined, 80 @ 85%.....	Lb.	80	@	85
Potassium Chlorate, crystals, spot.....	Lb.	53	@	70
Potassium Cyanide, bulk, 98-99 per cent.....	Lb.	—	@	—
Potassium Hydroxide.....	Lb.	85	@	95
Potassium Iodide, bulk.....	Lb.	3.90	@	—
Potassium Nitrate.....	Lb.	—	@	—
Potassium Permanganate, bulk.....	Lb.	1.65	@	1.80
Quicksilver, flask, 75 lbs.....	Lb.	76.00	@	—
Red Lead, American, dry.....	Lb.	9 3/4	@	—
Salt Cake, glass makers'.....	Ton	8.00	@	10.00
Silver Nitrate.....	Oz.	39 3/4	@	—
Soapstone in bags.....	Ton	12.00	@	—
Soda Ash, 48 per cent.....	100 Lbs.	—	2.50	@
Sodium Acetate.....	Lb.	15	@	16
Sodium Bicarbonate, domestic.....	100 Lbs.	1.75	@	2.00
Sodium Bicarbonate, English.....	Lb.	3 1/2	@	3 3/8
Sodium Bichromate.....	Lb.	35	@	—
Sodium Chlorate.....	Lb.	35	@	—
Sodium Fluoride, commercial.....	Lb.	—	@	—
Sodium Hyposulfite.....	100 Lbs.	2.00	@	—
Sodium Nitrate, 95 per cent, spot.....	100 Lbs.	3.10	@	—
Sodium Silicate, liquid.....	100 Lbs.	1.25	@	1.75
Sodium Sulfide, 30%, crystals, in bbls.....	Lb.	2	@	2 1/2
Sodium Bisulfate, powdered.....	Lb.	6	@	7
Strontium Nitrate.....	Lb.	42	@	45
Sulfur, flowers, sublimed.....	100 Lbs.	2.30	@	2.70
Sulfur, roll.....	100 Lbs.	1.95	@	2.25
Sulfuric Acid, chamber, 60°.....	Ton	\$25.00	@	—
Sulfuric Acid, conc., sp. gr. 1.842.....	100 Lbs.	2.50	@	3.00
Sulfuric Acid, oleum (fuming).....	100 Lbs.	5	@	—
Talc, American white.....	Ton	9.00	@	12.00
Terra Alba, American, No. 1.....	100 Lbs.	75	@	80
Tin Bichloride, 50°.....	Lb.	15 1/4	@	16
Tin Oxide.....	Lb.	49	@	51
White Lead, American, dry.....	Lb.	8 3/4	@	—
Zinc Carbonate.....	Lb.	21	@	28
Zinc Chloride, commercial.....	Lb.	13	@	15
Zinc Oxide, American process.....	Lb.	8 3/8	@	8 7/8
Zinc Sulfate.....	Lb.	6 1/2	@	7 1/4

# ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.....	Lb.	1.00	@	1.25
Acetic Acid, 28 per cent, in bbls.....	Lb.	6	@	—
Acetic Acid, glacial, 99 1/2% in carboys.....	Lb.	45	@	50
Acetone, drums.....	Lb.	40	@	50
Alcohol, denatured, 180 proof.....	Gal.	59	@	61

Alcohol, grain, 188 proof.....	Gal.	2.64	@	2.70
Alcohol, wood, 95 per cent, refined.....	Gal.	65	@	68
Amyl Acetate.....	Gal.	5.50	@	—
Aniline Oil.....	Lb.	55	@	—
Benzoic Acid, ex-toluol.....	Lb.	6.75	@	7.50
Benzol, 90 per cent.....	Gal.	70	@	—
Camphor, refined in bulk, bbls.....	Lb.	52	@	—
Carbolic Acid, U. S. P., crystals, drums.....	Lb.	65	@	70
Carbon Bisulfide.....	Lb.	8 1/2	@	—
Carbon Tetrachloride, drums, 100 gals.....	Lb.	17	@	—
Chloroform.....	Lb.	44	@	50
Citric Acid, domestic, crystals.....	Lb.	67	@	—
Cresol, U. S. P.....	Gal.	1.35	@	1.40
Dextrine, corn (carloads, bags).....	100 Lbs.	3.30	@	3.40
Dextrine, imported potato.....	Lb.	9	@	—
Ether, U. S. P., 1900.....	Lb.	15	@	20
Formaldehyde, 40 per cent.....	Lb.	13 1/2	@	14
Glycerine, dynamite, drums included.....	Lb.	45	@	60
Oxalic Acid, in casks.....	Lb.	65	@	—
Pyrogalllic Acid, resublimed bulk.....	Lb.	2.75	@	—
Salicylic Acid, resublimed.....	Lb.	3.00	@	3.25
Starch, cassava.....	Lb.	3 1/4	@	4 1/4
Starch, corn (carloads, bags).....	100 Lbs.	2.25	@	—
Starch, potato.....	Lb.	—	@	—
Starch, rice.....	Lb.	8	@	10
Starch, sago.....	Lb.	3 1/2	@	4
Starch, wheat.....	Lb.	5	@	6
Tannic Acid, commercial.....	Lb.	60	@	64
Tartaric Acid, crystals.....	Lb.	75	@	80

# OILS, WAXES, ETC.

Beeswax, pure, white.....	Lb.	47	@	55
Black Mineral Oil, 29 gravity.....	Gal.	13 1/4	@	—
Castor Oil No. 3.....	Lb.	16 3/4	@	20
Ceresin, yellow.....	Lb.	10	@	14
Corn Oil, crude.....	100 Lbs.	—	8.75	@
Cottonseed Oil, crude, f. o. b. mill.....	Gal.	69	@	71
Cottonseed Oil, p. s. y.....	Lb.	10 3/4	@	—
Creosote, beechwood.....	Lb.	4.50	@	—
Cylinder Oil, light, filtered.....	Gal.	21	@	—
Fusel Oil, crude.....	Lb.	4.50	@	—
Japan Wax.....	Lb.	15 1/2	@	16
Lard Oil, prime winter.....	Gal.	1.04	@	1.08
Linseed Oil, raw (car lots).....	Gal.	65	@	—
Menhaden Oil, crude (southern).....	Gal.	48 1/2	@	—
Naphtha, 68 @ 72°.....	Gal.	33	@	—
Neat's-foot Oil, 20°.....	Gal.	1.10	@	1.20
Paraffine, crude, 118 & 120 m. p.....	Lb.	5	@	—
Paraffine Oil, high viscosity.....	Gal.	29 1/2	@	—
Rosin, "P" Grade, 280 lbs.....	Bbl.	—	5.40	@
Rosin Oil, first run.....	Gal.	32	@	—
Shellac, T. N.....	Lb.	24 1/2	@	25
Spermaceti, cake.....	Lb.	25	@	26
Sperm Oil, bleached winter, 38°.....	Gal.	80	@	82
Spindle Oil, No. 200.....	Gal.	24	@	25
Stearic Acid, double-pressed.....	Lb.	13	@	13 1/4
Tallow, acidless.....	Gal.	88	@	92
Tar Oil, distilled.....	Gal.	30	@	31
Turpentine, spirits of.....	Gal.	44	@	—

# METALS

Aluminum, No. 1, ingots.....	Lb.	63	@	65
Antimony, ordinary.....	Lb.	—	20 1/2	@
Bismuth, N. Y.....	Lb.	3.15	@	3.25
Copper, electrolytic.....	Lb.	—	27 1/2	@
Copper, lake.....	Lb.	—	27 1/2	@
Lead, N. Y.....	100 Lbs.	—	6.75	@
Nickel, electrolytic.....	Lb.	50	@	—
Nickel, shot and ingots.....	Lb.	45	@	—
Platinum, refined.....	Oz.	—	75.00	@
Silver.....	Oz.	—	64 3/4	@
Tin.....	100 Lbs.	—	41.00	@
Zinc, N. Y.....	Lb.	—	12 3/4	@

# FERTILIZER MATERIALS

Ammonium Sulfate.....	100 Lbs.	—	3.55	@
Blood, dried.....	Unit	—	2.50	@
Bone, 4 1/2 and 50, ground, raw.....	Ton	—	—	@
Calcium Cyanamid.....	Unit of Ammonia	—	2.55	@
Calcium Nitrate, Norwegian.....	100 Lbs.	—	—	@
Castor Meal.....	Unit	—	—	@
Fish Scrap, domestic, dried, f. o. b. works.....	Unit	3.75	@	10
Phosphate, acid.....	Unit	80	@	85
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	2.75	@	3.00
Tennessee, 78-80 per cent.....	Ton	5.00	@	5.50
Potassium "muriate" basis 80 per cent.....	Ton	350.00	@	—
Pyrites, furnace size, imported.....	Unit	15	@	15 1/2
Tankage, high-grade; f. o. b. Chicago.....	Unit	2.65	@	10

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## EDITORIALS

### THE CHEMICAL INDUSTRIES

After the war then what? What is to become of our newly developed chemical industries? These questions seem to be constantly on the minds of many. To-day we may be suffering for want of dyestuffs, potash, pharmaceuticals and a great host of other chemical products—but we are hustling at breakneck speed to remedy matters.

In our great rush in building plants to take care of our home demands there have necessarily been many costly blunders. Plants have been erected and torn down to be rebuilt on the experience of the first attempt. Old processes, old methods have been called into use, only to be discarded again and replaced by newer and better ones. The country is suffering a dearth of trained and experienced chemical engineers, but our country is young. We lacked many of the chemical industries because we have heretofore been able to obtain supplies cheaper abroad. The necessity of developing completely our home chemical industries was not existing before the war. Necessity still remains the mother of invention, and we are a race of inventors.

The development of certain industries is largely a matter of geography—just as the growing of oranges is largely a matter of geography. The location of the necessary natural resources determines the location of industries for utilizing them.

We are peculiarly fortunate in our deposits of coal, sulfur, oil, salt, phosphate rock, etc., etc. We lead the world in their production. Naturally we should lead the world in the industries depending on them and this includes the whole range of chemical industry.

We have had a wall more insurmountable than any tariff wall with absolutely no holes in it, for the last two years, which has resulted in a very acute famine in certain chemical products. This condition has given us a tremendous opportunity for building up some chemical industries we lacked, rounding out the cycle of our industrial activity.

The Exposition of Chemical Industries this fall will show in a measure what American Chemical Engineers have accomplished. It will be a Clearing House for ideas and plans for the future. Already there are more exhibits, and of greater variety, promised than have ever been brought together before. It will, without doubt, be the world's largest and most important exposition of strictly chemical industry, and will indicate clearly the position we shall aim to assume among the Chemical Industries of the world.

### OUR RESPONSIBILITIES

Added opportunity means increased responsibility. The holocaust now raging in Europe has forced opportunities upon American chemists and has correspondingly increased our responsibilities. The world in general and our own public in particular, has been thoroughly awakened to the important, though unobtrusive, part played by chemical operations in al-

most every phase of every-day life; chemistry and chemists have been drawn forth into public view and subjected to such inspection and examination as has never before been accorded them. Their past efforts have been scrutinized, their every-day vocations have been studied, and lessons have been learned there-through that otherwise would not have been learned. In the enthusiasm of a newly acquired knowledge, imagination was by many given free rein; flights into the realms of fancy became the order of the day, and miracles more fantastic than any the alchemists ever claimed, were confidently heralded as accomplished facts, and echoed and re-echoed by our daily press.

### PUBLIC CONFIDENCE NECESSARY

The admirable counsel of courage and caution by Professor M. C. Whitaker [THIS JOURNAL, 6 (1914), 794] is as fitting to-day as it was in October, 1914, when it was given; and its value and usefulness must inevitably grow and become greater in the difficult days ahead. Misguided enthusiasm may be as detrimental to progress as habitual and obstinate lethargy. Confidence is of slow growth; it is quickly checked by adverse happenings and by promises unfulfilled. Our industrial progress in chemistry to-day requires, more than anything else, solid and substantial public confidence in us. One unfulfilled, extravagant promise has potentialities for greater retardation upon the growth of that confidence than can be overcome by a dozen moderate, reasonable promises wholly redeemed and completely fulfilled. Constructive work is slow and of limited range of influence; destructive work is rapid and of far-reaching consequences; bad news travels far and fast.

### RESPONSIBILITY TO THE PUBLIC

Our first responsibility is to check the super-enthusiastic, to put the bridle of reason upon unconstrained expectation, to bring back the public from its intellectual orgy to the stern reality that progress is not meteoric and that permanent, substantial progress is, like confidence, of exasperatingly slow growth; if all the chemists in the world could accomplish one real "thriller" a year, that would be a most satisfactory and satisfying record.

In spite of much diligent and convincing teaching to the contrary, there are many who still believe in the possibility of perpetual motion; there are many more who still believe that they can get something for nothing, and their misadventures in applying this doctrine to chemical enterprises do more harm over night than many earnest men can undo in many a month and year of hard and serious labor. We can have enthusiasm without extravagance, prudence without pessimism, courage without foolhardiness, caution without timidity, and confidence without bluster. Progress cannot be had without taking chances nor without failure, but there is a reasonable and an unreasonable kind of each, and it is our first responsibility to teach this to the public, however unwilling a pupil it may be or may profess to be.

<sup>1</sup> Address before the Chicago Section of the A. C. S., June 7, 1916.

This is not only our first responsibility but also the most difficult to discharge. Hosts of men and phalanxes of minds are daily contending with untold numbers of problems; the finished work of so many is so frequently being brought to public attention that consideration cannot be given to what may, for lack of a better expression, be termed "reports of progress;" progress alone does not arrest public attention nor excite public comment; conclusive, or at least moderately conclusive, achievements alone can engage the general public.

To bring the nature of this problem nearer home to us: How many of us chemists displayed breathless enthusiasm in the monthly reports that used to come up from Panama setting forth the number of cubic yards excavated? How many of us open our morning papers in haste to find out what the balance in the Federal Treasury was the day before? How many of us watched with nervous interest the daily progress of the bridge over Hell Gate? The only time we paid attention to Panama was when the Canal was opened; Hell Gate Bridge is not yet finished and has come in for but little comment, and the only time we take an acute interest in the Federal Treasury is when tax-paying time rolls around. That being so, by what stretch of the imagination can we expect the public to work itself up into a fit of excitement because some chemist has a new theory of solutions, or another has discovered a new chemical which he burdens with a baptismal appellation that exhausts all the letters in the alphabet and then some, or still another chemist has a new theory for the constitution of the terpenes? The public, however, will give attention to a new incandescent lamp that gives more light for less money, to a water purification process that really purifies, or to a new paint that stays put.

This being the situation, what are we going to do about it? This is a problem that can profitably engage the attention of each and every member of the American Chemical Society. How shall he make his thought bear fruit? At the Urbana meeting of our Society a committee on publicity was appointed to consider this very problem. Let each of our sections appoint a committee of one, two or three members to act for the section in connection with and under the direction of our parent society; when that parent committee has determined, with the help of sectional committees or otherwise, upon the course to pursue, then let all the members of each section and each sectional committee pitch in with a will and make that plan a success; with 49 publicity centers in 32 states of the Union and the District of Columbia, beneficial results ought to be forthcoming. But in this connection we too must bear in mind that progress will not only be difficult but also distressingly slow. We must not expect too much in a hurry and we must not lose heart.

#### RESPONSIBILITY TO PUBLIC OFFICIALS

Our second responsibility is to those who make our laws and shape our public policies. Questions of this kind involve so many elements that generally a dogmatic or categorical answer cannot be given; more

often than not the answers are of necessity compromises and hence embrace both advantage and disadvantage. The best that our lawmakers and our public officials can hope to accomplish under those circumstances, and the most we should expect of them, is to select that course out of the large number usually possible, where the preponderance of advantage to the community or to the country is the largest. It is out of reason to expect no disadvantage at all. That being so, it is our privilege and our responsibility to see to it that in cases involving chemistry all the elements needful to the determining of the correct location of that preponderance are properly placed before those whose duty it is to decide and determine such questions for us. In such presentation of elements we should, to the very best of our ability, present every essential fact or consideration regardless of our own individual political or economic beliefs. Determining facts is one thing; drawing conclusions from facts or basing laws or public policy upon facts, is quite another thing; correct conclusions and correct public policies cannot be reached or arrived at if the underlying facts be wrong or incomplete in any essential. However much latitude we each and all of us do have and take in drawing our own conclusions from facts, that latitude ceases absolutely and instantly the moment we presume to present facts; facts are not always agreeable to ascertain or to state, but they are absolutely essential to a correct answer. No legislation and no public policy can be better than the reasoning which led to them, and this reasoning can be no better than the facts upon which it was based. A statement of facts is essential to all good legislation and all good public policy; such statement is not always easy to make, but it is always a distinctly worth-while thing to provide.

#### RESPONSIBILITY TO BUSINESS OF THE NATION

Our third responsibility is to the business of the nation. It is our duty to produce as many things in this country, from other things in or out of this country, as commercial conditions make possible. That we are doing so and have been doing so to the best of our ability and information is true beyond question. The one weak point in our armor is our information; that is reasonably complete as to production within the country, but it is unreasonably, unpardonably and woefully incomplete as to our business with other nations. European governments disseminate information better adapted and more useful to their own chemical industrial than does our own Government. Yet our Government is not to be blamed. It has done things in its own way and since we have not told the Government that we want and need better service and have not suggested how such better service could be obtained, why blame Washington? We ourselves are to blame and we should face the situation. The remedy is absolutely and wholly in our own hands, and it has been indifference, lack of time, or sheer indisposition to labor, that has kept us from telling Washington what we should have, in such a way as to make it clear that we really know what we want and are in



substantial agreement as to the remedy. Let no one think that it will be easy to get together a list of items that will satisfy the makers of and dealers in the products of and for our industry. Each member of the Central Committee appointed by the *American Chemical Society* at the Seattle Meeting in September of last year will have to be prepared to sacrifice two hundred or more hours of real hard labor to complete his share in the work; his work can be no better than the work of the various sections of the *American Chemical Society*, and when in next September these various sections get their allotments of work, as sent to them from that Central Committee, they will have to take their coats off in earnest and work hard to see to it that each have all their suggestions in on time. This word of warning of an impending avalanche of labor is given thus early that there may be no avoidable obstacle to prompt disposition of the work assigned. The Central Committee cannot get down to business until the sections have finished. When normal use of international trade channels is available, the information proposed to be asked for will be of the greatest help in preventing products of foreign make, and which can be made in this country, from gaining such a foothold that sudden drying-up of foreign sources of supply can seriously affect us. But this information when available will largely fail of its purpose if our makers of chemicals do not cut loose from the traditions of the past that have enchaind substantially all our manufacturers of all kinds—namely, a sort of contempt for small outputs or tonnages. To be able to make a large number of different things, each of relatively small annual tonnage, or even poundage, is quite as essential to our national business life, as is ability to make large annual amounts of relatively few things. Times have changed and we will have to change with them. Also our industrials of all kinds, inclusive of our chemical industries, will have to learn that quality and price *do* count, and that there is no brand of patriotism that will, for long, withstand the lure of a profit. With individuals, patriotism is said to stop at the stomach; with business it may similarly be said to stop at the pocket-nerve.

#### RESPONSIBILITY TO EDUCATIONAL INSTITUTIONS

Our fourth responsibility is to our educational institutions. It is inconceivable that in the wealth of information and in the large ability of our university men there is not more opportunity for efficient, effective and valuable cooperation between them and our chemical industrials for the benefit of the nation. It is a knotty problem, there is no denying it, but the prospects of results of almost incalculable, potential national value seem so reasonable that it is worthy of the most serious attention of every chemist, be he university man, technical man, merchant or banker.

#### RESPONSIBILITY TO AMERICAN CHEMICAL SOCIETY

Our fifth responsibility, and the last I shall touch upon in this paper, but by no means the last of our responsibilities, is to the *American Chemical Society* itself. Our Society places on our desks four times each month publications which can challenge comparison with any similar publications in the world and can come out of such comparison with credit to themselves and honor to the American chemical profession; this is done at an annual cost to each member of about two-thirds the cost of the same service abroad. How is it done? The most of us take these publications as a matter of course, but we are indebted for these magnificent results to an untiring devotion, the unstinting labor, and the most generous loyalty of a relatively small number of our fellow-members; they give of their time, their strength and their ability far beyond their just share. Take love of labor and pride of profession out of the make-up of these men, and the quality and amount of their work would drop to such a point that the net result would not be creditable to us nor to our country. The real hard work of the *American Chemical Society* is performed substantially as a labor of love; that condition ought not be permitted to last one instant longer than it requires to remedy it. We will be asked in September next to provide the remedy. Let us not fail the *American Chemical Society*! She has served us and our country well!

B. C. HESSE

25 BROAD STREET, NEW YORK CITY

## ORIGINAL PAPERS

### THE THERMAL DECOMPOSITION OF THE PROPANE-BUTANE FRACTION FROM NATURAL GAS CONDENSATE

By J. E. ZANETTI

Received June 10, 1916

Practically every fraction of petroleum and many of its individual constituents, from natural gas to the residues from the distillation of crude petroleum have been submitted to decomposition at high temperatures, so-called "cracking," with one notable exception: the fraction which contains propane and the butanes. The reason is not far to seek; it has not been until the last few years that the separation of this fraction from "wet" natural gas<sup>1</sup> and its use as a commercial product

<sup>1</sup> For description of this process of separation and analyses of various fractions see U. S. Bureau of Mines, *Bull.* 88 and *Tech. Paper* No. 10.

under the name of "liquid gas," "gasol," etc., has become of commercial importance.

This fraction, which condenses along with the lower boiling pentanes, is usually allowed to escape in the air in the process of "ripening" and is the so-called "wild gasoline" which, because of its low boiling point, is useless for the purposes of "blending" with refinery naphthas. In some places, by further compression of the "wet gas" after the first gasoline condensate has been formed, this fraction is condensed together with ethane and put up in steel cylinders for use as an illuminant or for welding with oxygen.

For the study of the decomposition products, the "pyrogenetic reactions" of hydrocarbons, this fraction furnishes a very satisfactory material. Being

a gas at ordinary temperatures its rate of flow through a heating chamber can be regulated with nicety, no previous vaporizer is necessary as with higher boiling fractions, the formation of lower unsaturated compounds by splitting off of hydrogen as well as condensation of these to aromatics are exhibited, and finally, the products formed, outside the aromatics, are gases, and any undecomposed propane or butane passes off thus preventing the necessity of separating the aromatic from the undecomposed aliphatic, as is the case with higher boiling fractions.

The above reasons as well as the fact that this fraction constitutes mostly a waste product have led the writer to start a study of its decomposition products with a view to its possible utilization in other ways than as a lighting material.

A careful search of the literature has failed to furnish any work that has been published on the decomposition of propane or butane. Even Beilstein, that can usually furnish reference to the products obtained by passing vapors of almost any organic compound through "a red hot tube," furnishes no light on the subject.

The plan of the work consisted in:

- 1—The determination of the composition of the "cracked" gases with respect to "unsaturated" and hydrogen formation.
- 2—The determination of the amounts of tar formed (aromatics) and its composition.
- 3—The composition of the unsaturated.
- 4—The influence of catalyzers.

One difficulty arises with the investigation of the butane-propane fraction: being put up in a cylinder under pressure, on releasing it we have the reverse of ordinary distillation, the temperature being kept constant in this case, while the pressure changes. Under these circumstances the lower boiling fraction comes off first, the composition of the gas altering as the pressure drops. For this reason one must work within certain pressures in order not to change the composition of the gas between too wide limits. The pressure dropped 5 lbs. during the duration of these experiments and the percentage of butane rose, as one would expect. No appreciable difference could be noted either in the "unsaturated" or the hydrogen content, but the amount of tar increased somewhat with the increase of butane.

The apparatus employed<sup>1</sup> consisted merely of a heating chamber, the temperature of which could be accurately controlled, a coil to cool the gases and finally a device to settle the tar "fog." All who have worked with the decomposition of hydrocarbons at high temperature are familiar with the finely divided condition in which the liquid products deposit on cooling the gas, the so-called tar "fog." By far the largest proportion of the tar remains in suspension in this finely divided condition and requires considerable time for settling. On a large scale, as in gas manufacture, this "fog" is removed by various forms of scrubbers, but the writer is not aware of any device for use on a small scale.

<sup>1</sup> For full details see experimental part.

After many unsuccessful attempts to remove this "fog" by filtering the gases through numerous layers of glass wool the principle of a well-known patent<sup>1</sup> was finally adopted. This was the deposition of these finely divided particles passing the gases from the furnace between two conducting plates maintained at a high difference of potential. The results were very successful and whereas only a few drops of tar were obtained per cu. ft. of gas by relying solely on condensation, as much as 10 cc. per cu. ft. of gas were obtained by electrical deposition. There is, of course, no novelty in this device but it is surprising that it has not been employed before in small scale experimentation. The fact that almost all previous work on hydrocarbon decomposition on a small scale has failed to take into account this carrying off of most of the tar in finely divided form by the gas stream may necessitate some revision of earlier work. Thus Norton and Andrews,<sup>2</sup> without any tar depositing, passed the gases from the decomposition of hexane, iso-hexane and pentane through bromine for ab-

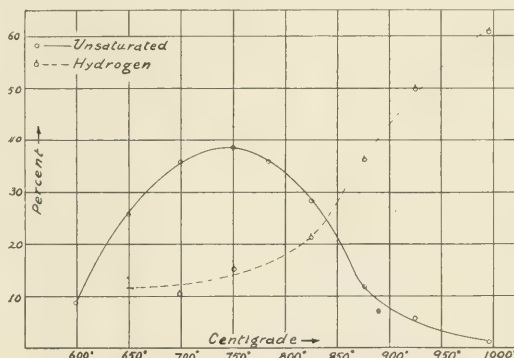


FIG. I—DECOMPOSITION OF PROPANE-BUTANE FRACTION  
NO CATALYZER

sorption of the unsaturated, and obtained only a qualitative test for benzol with no mention of higher aromatics; they obtained no benzol from pentane. Haber<sup>3</sup> obtained by the decomposition of hexane "a little benzene." In view of the writer's experience with and without a tar-settling device, and taking into consideration that the higher hydrocarbons of petroleum distillates yield considerable benzol as well as toluol and higher aromatic homologues,<sup>4</sup> as well as the additional fact that the lower hydrocarbons investigated also give the same aromatics, it seems very unlikely that these few intermediate hydrocarbons should not, and the question should remain an open one, at least until the deposition of the tar "fog" should prove it otherwise.

The results of the decomposition of the gas at various temperatures are plotted in Fig. I. The rate of flow through the heating apparatus was kept constant throughout all these experiments, being maintained at 0.45 cu. ft. per hr. This rate was chosen

<sup>1</sup> See F. G. Cottrell, *THIS JOURNAL*, 3 (1911), 542.

<sup>2</sup> *Am. Chem. J.*, 8, 1.

<sup>3</sup> *Ber.*, 29, 2691.

<sup>4</sup> For a very complete review of the literature on this subject see Egloff and Twomey, *Jour. Phys. Chem.*, 20 (1916), 121.



as being sufficiently slow to permit the gases to be heated to the high temperature. The per cent of "unsaturated" increases gradually till a maximum is reached in the neighborhood of  $750^{\circ}$ . Beyond  $750^{\circ}$ , when the aromatic formation begins, the "unsaturated" decrease and become practically nil near  $1000^{\circ}$ .

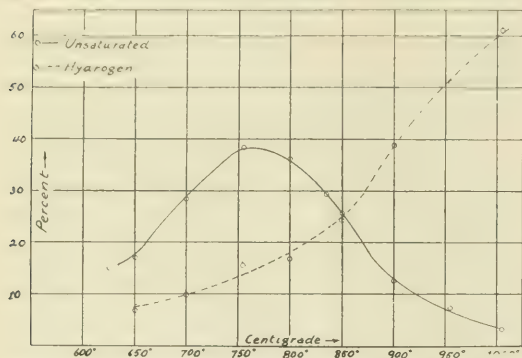


FIG. II—DECOMPOSITION OF PROPANE-BUTANE FRACTION, USING COPPER AS CATALYZER

The hydrogen curve rises slowly at first but more rapidly as the point of aromatic formation is reached.

The nature of the "unsaturated" was determined by passing the gases through bromine and fractionating the bromides. The "unsaturated" consisted of a mixture of hydrocarbons in which ethylene predominated; propylene was also doubtless present but owing to the small amount it could not be separated by fractional distillation of the bromides. Butenes, however, were present, as tetrabromobutane was isolated from the mixed bromides. The presence of butenes, whose identification is an easy matter owing to tetrabromobutane being a solid and readily purified by crystallization, has been reported before as a decomposition product of the lower hydrocarbons.<sup>1</sup>

Benzol, toluol, and naphthalene were shown to be present in the tar. In the intermediate fractions other homologues are doubtless present, but owing to the small amount of material could not be isolated.

It is interesting to note that aromatic formation has taken place here from hydrocarbons of lower carbon content than benzene and that the formation of aromatics is coincident with a lowering of the content of "unsaturated," the principal constituent of which is ethylene.

By using copper as a catalyzer a curve of the same nature is obtained as may be seen in Fig. II. The aromatic formation takes place at the same temperature and the amounts at the rate of 0.45 cu. ft. per hr. are the same.

The use of iron as catalyzer gives an altogether different result (Fig. III). The "unsaturated" content drops suddenly at about  $725^{\circ}$  and the hydrogen rises very rapidly. Coincident with these changes is the copious deposition of finely divided carbon. There is no tar formation noticeable beyond a very slight amount of bluish "fog." It is of interest to note the rapidity with which the reaction forming carbon and hydrogen is catalyzed above  $725^{\circ}$ . Below that temperature the decomposition of the gas proceeds in much the

same manner as in the two previous cases with the exception that the unsaturated content is slightly lower and that the maximum is reached at about  $725^{\circ}$  instead of  $750^{\circ}$ . There can be no question of simple surface action. Copper and iron gauzes of the same mesh, cut into equal sizes, were used in both cases and the results are so widely different as to leave no doubt that we are dealing here with a specific catalytic action.

With nickel as catalyzer the results were even more divergent from the decomposition curve of the gas without catalyzer. Here there was practically no "unsaturated" formed, the highest per cent being 4.9 at  $630^{\circ}$  whereas the hydrogen per cent rose suddenly between  $540$  and  $580^{\circ}$  till a maximum of 83.2 per cent was reached at  $700^{\circ}$ ; above that temperature no readings could be taken as the carbon deposited plugged up the tube in a few minutes. No curve is plotted for the decomposition with nickel as catalyzer but the results are given in Table II. The formation of hydrogen increases so rapidly and is so much affected by such slight changes as a slight diminution or increase in temperature as well as the deposition of carbon on the catalyzer that no curve could be drawn through the points obtained though they indicate a rapid decomposition rate. The results obtained are similar to those of Buganadse<sup>1</sup> who by passing crude Russian petroleum over nickel obtained a gas analyzing 72 to 75 per cent hydrogen.

#### EXPERIMENTAL

**MATERIAL**—The material used was so-called "liquid gas" bought in the market in a steel cylinder under 100 lbs. pressure. It was obtained by condensation from natural gas. The pressure quickly dropped to 42 lbs. where it maintained itself for a considerable time, falling to 37 towards the end of the experiments presented. At the beginning of this work the analysis of the gas by explosion with about nine volumes of oxygen gave results that indicated it to be composed

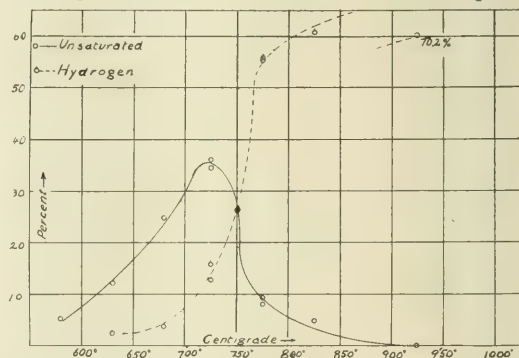


FIG. III—DECOMPOSITION OF PROPANE-BUTANE FRACTION, USING IRON AS CATALYZER

of propane with 3 per cent butane. Towards the end the proportion of butane increased considerably as would be expected from the decrease in pressure. The results of the analyses are shown in Table I. It is to be noted that the proportion of  $\text{CO}_2$  increases with time, being always higher than that required for

<sup>1</sup> J. Russ. Phys. Chem. Soc., **1910**, 198, see also Brooks, Bacon, Padgett and Humphrey, *THIS JOURNAL*, **7** (1915), 182.

<sup>1</sup> Norton and Andrews, *Loc. cit.*, p. 8.

pure propane, but never reaching that required by a mixture that would contain more than 20 per cent butane.

TABLE I—ANALYSES OF GAS DURING COURSE OF EXPERIMENTS

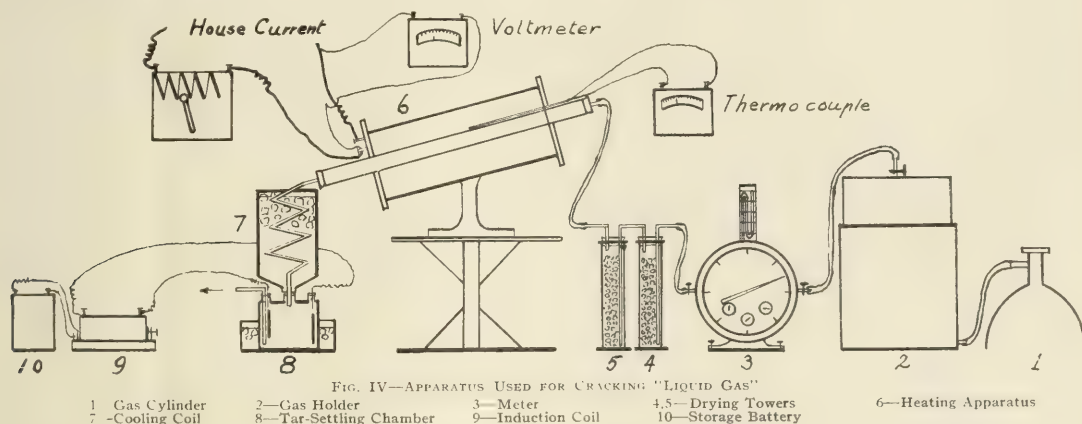
TIME SAMPLED:	FIRST WEEK			EIGHTH WEEK		
SAMPLE NO.	I	II	III	I	II	III
Gas Sample, cc.	9.0	9.3	9.4	10.1	10.2	9.8
Contraction, cc.	30.7	30.7	31.0	33.2	32.6	31.3
Volume CO <sub>2</sub> , cc.	30.2	30.6	30.7	34.0	33.4	32.1

The gas showed no "unsaturated" when these were determined by shaking with bromine water. When shaken with fuming sulfuric in a gas pipette for the customary 3 min. a decrease in volume of 3 to 4 per cent took place. As it was shown later that this difference between the absorption by bromine and by fuming sulfuric decreased as gases that came from a higher and higher temperature were analyzed, it was evident that this absorption was due to the direct absorption of the propane and butane by the fuming acid. The gas showed no CO<sub>2</sub> or hydrogen.

APPARATUS—The apparatus used is shown diagrammatically in Fig. IV. Since the pressure used was atmospheric, the gas was released from the cylinder into a gas holder and then passed through a meter graduated to 1/1000 of a cu. ft. and provided with a water gauge. The gas passed through two tall drying towers filled with granulated calcium chloride and then into the heating chamber, which consisted of a quartz tube

were led in through the middle openings, the end of the copper coil reaching just below the rubber stopper: they passed out through one of the side openings, the exit tube reaching to within 1/4 in. of the bottom of the bottle. In front of this exit tube was a copper plate connected by means of a fine wire to one pole of an induction coil. Through the opposite opening passed a carefully insulated wire attached to another copper plate or a piece of copper gauze and connected to the other pole of the induction coil. The gases coming from the cooling coil had then to pass between the two plates before passing out, and if a sufficient difference of potential was maintained between the two plates the "fog" completely settled in the bottle, the gases passing out perfectly clean. The difference of potential sufficient for these experiments was furnished by an induction coil powerful enough to give a 2-in. spark, the current being supplied by a set of six storage cells. This tar separator was also kept immersed in ice water throughout the duration of a determination, the object being to keep the vapor pressure of the tar as low as possible.

The samples for analysis were taken at the exit of the tar separator. When samples were not being taken, a water trap was placed at this exit to prevent air



30 in. long, 3/4 in. internal diameter, glazed on the inside, heated in an electric furnace capable of giving a temperature of 1200° C. The current was controlled by means of a rheostat and the temperature determined by means of a platinum-platinum-iridium thermocouple attached to a millivoltmeter carefully standardized. By means of the rheostat the temperature could be controlled within 5°. Corrections were made from the temperature read off on the millivoltmeter by reference to a correction curve. These varied from 20 to 26° in the range of temperatures employed.

After passing through the heating chamber the gases were led through a copper coil made of 3 ft. of 1/8-in. copper pipe. This coil was kept immersed in ice water throughout the duration of a determination. But little tar condensed in the coil, most of it passing along with the gases in the form of a fine "fog." To remove this "fog" the gases were passed into a 250 cc. Woulfe bottle provided with three openings. The gases

from passing into the apparatus. When the gases were being absorbed in bromine for the determination of the nature of the "unsaturated," a gas-washing bottle with bromine and water was placed beyond the water trap.

The catalysts were copper, iron and nickel, 40-mesh wire gauzes cut into uniform sizes 12 in. X 4 in. and rolled so as to fit the quartz tube snugly. These rolls were pushed into the tube far enough so that they would be entirely within the heated area. Copper wool, copper and iron filings were also used, but for the sake of uniformity only the gauzes were used in the experiments presented.

PROCEDURE—The *modus operandi* was as follows: The gas was led through the meter at a measured rate, in the case of these experiments the rate being 0.45 cu. ft. per hr. The rate was determined with a stop watch, the flow of gas being adjusted by slightly opening or shutting the intake cock of the meter. The gas was passed through the cold apparatus to remove



TABLE II.—ANALYSIS OF GASEOUS PRODUCTS OBTAINED WITH AND WITHOUT CATALYZERS

No CATALYZER			COPPER AS CATALYZER			IRON AS CATALYZER			NICKEL AS CATALYZER		
Temp	Unsat-	Hy-	Temp	Unsat-	Hy-	Temp	Unsat-	Hy-	Temp	Unsat-	Hy-
° C.	Per cent	Per cent	° C.	Per cent	Per cent	° C.	Per cent	Per cent	° C.	Per cent	Per cent
600	8.9	...	625	15.0	...	580	5.3	...	510	0.0	0.4
650	25.7	13.0	650	16.9	6.8	630	12.2	2.3	540	2.1	4.6
700	35.9	10.9	700	28.4	9.9	675	24.8	3.8	580	3.0	45.8
750	38.5	15.2	755	38.4	15.5	725	34.5	12.5	630	4.9	54.0
785	35.8	...	800	36.3	16.7	735	36.1	15.8	640	3.9	75.1
825	28.4	21.4	835	29.4	...	750	26.8	27.1	680	2.6	68.4
875	11.8	37.0	850	25.8	24.3	775	9.4	54.8	700	1.9	83.2
925	5.7	50.5	900	12.6	38.9	775	8.1	55.6	...	...	...
995	1.3	62.9	955	7.4	51.0	825	4.8	60.7	...	...	...
...	...	...	1010	3.2	61.0	975	0.0	70.2	...	...	...

the air and the furnace quickly brought up to the desired temperature by putting the full current through it. As the temperature was reached the current was regulated so that the reading of the voltmeter corresponded with the desired temperature. The temperature was closely watched during the experiment and regulated by means of the rheostat. Once adjusted it kept fairly constant within 5°. The gas was then passed through the heated tube for half an hour before a sample was taken for analysis. This time was found to be the minimum necessary to insure concordant results. After the sample of gas had been taken and while it was being analyzed, the temperature was quickly brought up to the next point and the gas passed through for another half hour before the next sample was taken.

When catalyzers were being used it was found that they rapidly became coated with carbon. This was especially the case with nickel and iron; copper was not so much affected. With iron the gauze could not be used for more than an hour at temperatures below 700° or for much more than half an hour at higher temperatures. Each point on the iron curve above 700° had then to be determined with a fresh piece of gauze, otherwise no concordant results could be obtained. With nickel the deposition of carbon was so rapid above 700° that no determination could be made, as a wad of carbon formed in a few minutes within one inch of the heated gauze and effectively plugged up the tube.

**GAS ANALYSIS**—The gases were collected and analyzed over water. For the absorption of the "unsaturated", bromine water was used, since, as mentioned above, fuming sulfuric absorbed some of the propane and butane. The following are typical results:

Temperature.....	Room	650°	700°	750°	800° C.
Per cent absorbed by bromine.....	0.0	14.2	23.4	36.6	34.5
Additional per cent absorbed by sulfuric acid.....	4.0	4.0	2.1	0.3	0.1

These showed that as long as any undecomposed propane or butane was present some was absorbed by the fuming sulfuric acid, and as the amount of these decreased with increasing temperature, the amount absorbed by the sulfuric acid decreased also. The hydrogen was determined by combustion over copper oxide at 275° C. The results of the analyses are shown in Table II.

**THE UNSATURATED**—The gases coming between 800 and 850° were passed through bromine till the latter became colorless. After drying, 40 cc. were distilled fractionally in a small distilling flask. After four fractionations the following fractions were obtained: 125–129°, 5 cc.; 129–131°, 12 cc.; 132–142°, 6 cc.; 143–144°, 2 cc. Thick fumes of HBr came over above 145° so that the distillation was stopped. On standing,

the residue in the flask solidified into a mass of dark colored crystals. Drained from about 3 cc. of mother liquor and crystallizing three times from alcohol they crystallized in small, colorless prismatic needles melting at 116°.

The fraction 129–131° gave a specific gravity of 2.30 at 20°.

**AROMATICS**—No aromatic formation was observed below 700°. At that temperature the "fog" began to make its appearance, at first of a bluish tinge, growing darker with increasing temperature till it became dark brown at about 850°. The tar deposited between 800 and 900°, was dark in color and quite fluid. It showed a specific gravity of 0.985 to 1.000. Above 900° the tar became quite thick and on standing solidified.

The amount formed varied with the rate. If the latter was 1 to 1½ cu. ft. per hr. the amount varied around 5 cc. per cu. ft. of gas. At the rate of 0.45 cu. ft. per hr. as much as 10 cc. per cu. ft. were obtained.

No tar formation was observed in the cases where iron and nickel were used as catalyzers, whereas good yields were obtained with copper.

Thirty cc. of tar were distilled in a small flask and the following fractions collected: 80–125°, 9.5 cc.; 125–173°, 5.5 cc.; 175–200°, 3 cc. At 200° naphthalene began to come over and solidified in the condenser. On further fractionation 6 cc. were obtained below 100° and about 3 cc. between 105 and 110°. These fractions on nitration yielded nitrobenzol and 2,4-dinitrotoluol, m. p. 69° C.

#### SUMMARY

I—It has been shown that mixtures of propane and butane are decomposed at high temperatures, giving ethylene, butene and other lower unsaturated compounds, hydrogen and aromatics.

II—The percentage of "unsaturated" increases with increasing temperatures to a maximum in the neighborhood of 750° C., then decreases with increasing temperatures. The percentage of hydrogen increases with increasing temperatures. The aromatic formation begins at about 750 and is coincident with an increase of the rate of hydrogen formation.

III—The action of copper, iron and nickel as catalyzers has been studied. Iron and nickel prevent aromatic formation and favor the decomposition of the hydrocarbons to free carbon and hydrogen.

IV—The electrical deposition of tar "fog" in gases from high temperature decomposition has been found to work very satisfactorily for small scale experiments.

Further work upon these topics is now in progress in this laboratory.

DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY  
NEW YORK CITY

AN INVESTIGATION OF COMPOSITION FLOORING<sup>1</sup>By R. R. SHIVELY<sup>2</sup>

Received April 17, 1916

In 1867, Sorel<sup>3</sup> found that a very hard material might be produced by mixing magnesia and a solution of magnesium chloride and then allowing the mixture to stand for some time. Sorel concluded that the compound which was formed possessed the following formula:  $\text{MgCl}_2 \cdot 5\text{MgO} \cdot 12\text{H}_2\text{O}$ , or  $\text{MgCl} \cdot \text{OH} \cdot 4\text{Mg}(\text{OH})_2 \cdot 12\text{H}_2\text{O}$ . The investigations of Sorel initiated considerable inquiry, mostly by French and German chemists, but there has been a diversity of opinion regarding the exact composition of the product.<sup>4</sup>

During the past twenty-five years Sorel cement has been extensively employed with success as a cementing material for so-called "composition flooring." According to European practice, the magnesia, mixed with various "fillers," such as sawdust, sand, terra alba, infusorial earth or asbestos, and colored with different inorganic colors, is made into a "mortar" by the addition of a solution of magnesium chloride; the material is then applied to the floor and leveled, and, after standing several hours, it is carefully troweled. After 8 or 10 hrs. the cement sets and the surface of the flooring is then usually treated with a coat of oil, after which the composition is ready for use.

It has been found that suitable preparations of this type make ideal compositions for floor, base, wainscot and stairs. When carefully prepared, the composition is permanent, fireproof and waterproof, and it can be applied upon wood, concrete or iron base in a plastic form, giving a smooth, continuous surface. The wainscot may also be made from the same material, thus forming a perfect seal between the base and wainscot and giving a floor devoid of cracks. Any color shade may be produced with the exception of pure white, and very attractive effects may be obtained by using borders of different colors, a mosaic design, or a narrow strip of another color around the floor a short distance from the wall. Moreover, the mixture is little affected by heat or cold, having a very low heat conductivity, and the floor produced therefrom does not impart a feeling of coldness to the feet; furthermore, its absorption of water is very small and it is accepted by insurance companies as fireproof.

The composition is usually applied in two coats: an under fibrous coat, about  $5/16$  in. thick, and an upper coat containing less fiber, from  $5/16$  to  $1/2$  in. thick. The under fibrous coat imparts elasticity to the material and renders the floor noiseless and pleasant to the tread. In fact, this composition does not give rise to the fatigue experienced from the use of stone, cement, terrazzo or other hard floors. Furthermore, even when troweled to a very smooth surface, this composition does not produce a slippery floor.

These advantages, along with the facts that the composition costs less than tile, marble, etc., and that it will outwear eight or ten applications of linoleum, have made it a very popular floor material in Europe, especially in Germany and England.

Composition flooring of the general type described above was introduced into the United States a short time after it came into favor abroad. American manufacturers have, however, experienced considerable difficulty in the use of Sorel cement. Some have attributed this to the differences in the climatic conditions of Europe and America, the contention being that the sudden changes of temperature encountered in the United States are not experienced abroad, particularly in England and Germany. Others have expressed the opinion that the principal cause of the failure in this country is attributable to the mixtures employed: the assertion has been made that the mixtures in use here have been neither scientifically nor even carefully prepared. Inasmuch as many of the floors examined by the author are as perfect as could be desired, he is inclined to favor the latter explanation. If the trouble is due to the sudden climatic changes, why should one floor be affected and not another in the same locality?

In 1911—that is, at the time when the author became interested in this field—in New York City alone there were at least twenty firms engaged in the composition-flooring business, and the competition was very keen indeed. All of the companies were cutting prices in order to secure business and many of the firms were putting down the cheapest mixtures which they could conceive. In fact, everything possible was being done to minimize the cost of the product, without much regard for the requirements of a correctly made mixture. The components of the mixtures were weighed and mixed by ordinary laborers, so that it was quite impossible for the mixtures to be of a definite consistent composition. Consequently, all of the manufacturers were experiencing decided trouble with their floors. To illustrate, the color frequently "went bad;" some floors would crack or bulge, and at no time could they be assured of a satisfactory floor. As a result, many floors had to be relaid. Then, too, the cost of magnesite was constantly increasing, labor costs were high, and the selling price was so low that it was impossible to make a reasonable profit out of the business.

At the time of this investigation, the red mixture in use by the donors of the Hydrolith Fellowship was supposed to contain:

INGREDIENTS:	Magnesite	Sawdust	Red color	Clay	Terra alba	Infusoria earth
Percentages	50	9	10	11	10	10

Some very good floors were made from this composition and again some could not have been worse. In some cases the floors expanded, while in other cases they contracted and cracked badly. Then, in certain of the floors, the color faded decidedly, so that in a short time the appearance became very unattractive.

## EXPERIMENTAL

The investigation conducted by the author at the Mellon Institute of Industrial Research included

<sup>1</sup> Presented at the Urbana Meeting of the A. C. S., April 19, 1916.

<sup>2</sup> This report presents the results of a part of the work done during the author's tenure of the "Hydrolith Fellowship" (September 21, 1911, to March 1, 1913), Industrial Fellowship No. 8, at the Mellon Institute of Industrial Research of the University of Pittsburgh. The investigation was carried out under the direction of Dr. Raymond F. Bacon.

<sup>3</sup> *Compt. rend.*, **65** (1867), 102.

<sup>4</sup> Bender (*Z. anorg. Chem.*, **4**, 644) assigned the formula  $\text{MgCl} \cdot 5\text{MgO} \cdot 14\text{H}_2\text{O}$ , or  $\text{MgCl}_2 \cdot 9\text{MgO} \cdot 24\text{H}_2\text{O}$ ; Davis (*Chem. News*, **25**, 258) reported  $\text{MgCl}_2 \cdot 5\text{MgO} \cdot 13\text{H}_2\text{O}$ , while Krause (*Ann.*, **165**, 38) decided upon  $\text{MgCl}_2 \cdot 5\text{MgO} \cdot 18\text{H}_2\text{O}$  as the correct formula.



overcoming the change in color, obviating the expansion and contraction, and reducing the cost in any legitimate way.

The first experiments carried out were for the determination of the correct amount of magnesite and magnesium chloride to be used, the effect of different fillers, and the results of working samples in various ways. Red colored mixtures were used in this series, which consisted of 1000 samples. All of the materials entering into the compositions were carefully weighed, made up into 500-g. samples and thoroughly mixed before the addition of the magnesium chloride solution, the strength and amount of which were also very accurately determined.

The results of this series of experiments showed that with the fillers employed it was necessary to have present not less than 8 or 9 per cent of magnesium chloride and from 20 to 30 per cent of commercial magnesia. When an extremely hard and durable flooring composition was desired, still larger amounts were required. In samples where more than 1 part of magnesium chloride was employed to 3 parts of magnesia, there was always a tendency for the excess of magnesium chloride to come to the surface.

In a number of experiments, terra alba was the only filler employed with the exception of sawdust; in others infusorial earth was used, while in still others clay was the only filler besides sawdust. These tests were carried out in parallel, *i. e.*, each day samples were made containing the same percentage of magnesium chloride and magnesite with the same percentage of each of the different fillers. This was done for the purpose of studying the relative effect of each filler and to ascertain whether all acted in the same manner. The only noticeable differences were in the samples in which clay and infusorial earth were employed. Since these substances are lighter than terra alba, it was found that the samples covered more space than those in which terra alba alone was used. It was also learned that, on account of the greater bulk of these substances, they hardened more slowly and invariably gave less hard samples than those in which terra alba alone was employed. The terra alba samples hardened first, those containing infusorial earth next, and the ones with clay last. Clay quite appreciably retarded the setting of the cement.

Determinations were made of the least amount of color which could be used to obtain the desired shade. Varying amounts of Venetian red were employed, and it was ascertained that 10 to 12 per cent were necessary. Determinations were also made of the greatest amount of sawdust which could be used to obtain a floor which would not be liable to expand or contract and would yet be of sufficient hardness. It was found that samples containing 6 to 8 per cent of sawdust were very hard and did not impart the proper resistance or elasticity to the floor; but that samples with 10 to 12 per cent, according to the other fillers used, were very satisfactory. Samples containing a higher percentage of sawdust hardened very slowly and those with from 16 to 20 per cent of this material were always quite soft after drying. It was

found, however, that this large amount of sawdust could be used with advantage in the under fibrous coat.

Following the completion of this preliminary work, the author superintended the laying of a floor of 550 sq. ft., following the formula which had given the best results in the laboratory experiments, the composition being:

Ingredients	Magnesium chloride	Magnesite	Sawdust	Red color	Clay	Terra alba
Percentages	10	40	10	12	20	8

The materials were carefully weighed and thoroughly mixed, the dry mixture was then incorporated with the calculated amount of magnesium chloride solution and water was added until the proper consistency was attained. The mixing was continued until all lumps had disappeared and the mixture was then applied over metallic laths. It hardened slowly, but, when hard, it gave a perfect floor which exhibited no physical changes after the expiration of 6 months.

A second series of experiments was taken up in order to determine the effect of different fillers upon the hardness, color and surface of the floor and the effect of various combinations of fillers. It was thought that such an investigation would supply information which would enable one to select the materials giving best results, and that if there was no difference in the results obtained by the employment of various fillers, the cheapest thereof could be selected.

It was found that in samples containing small percentages of magnesium chloride and oxide, the hardening occurred much more slowly than when a greater percentage of the actual cementing material was used. In samples containing high percentages of terra alba, infusorial earth or clay, the difference in the time of setting was quite noticeable: without exception, the samples containing terra alba hardened first, those containing infusorial earth next, and those filled with clay last. In samples with higher percentages of cement, this difference was not so pronounced, but still it could be observed. In all experiments wherein these ingredients were added as the only mineral filler, the terra alba samples were hardest, and there was little, if any, difference between the clay and the infusorial earth samples. It is, of course, a question as to whether this hardness will cause a floor to wear longer than a floor with more resilience which gives, rather than wears. If, however, such hardness is desirable, it can be attained by using greater percentages of cement with the clay and infusorial earth. In none of the samples could any apparent objection be found to any of the fillers in reference to their effect on the surface. All samples, whether containing but one filler or all three, appeared to give the same finish. It was found, however, that when the samples contained a large percentage of clay or infusorial earth, it was necessary to use more color.

Regarding the amount of magnesite and magnesium chloride necessary, the results of this series of experiments showed clearly that never more than 40 per cent of magnesite or 12 per cent of magnesium chloride could be employed. In tests where more than these percentages were used, a very hard floor was obtained, whereas the smaller amount gave a sufficiently hard

composition. The only samples in this series of experiments which showed a tendency to develop physical defects were those which contained high percentages of magnesite and magnesium chloride. In every case when the percentage of magnesium chloride was more than one-third that of the magnesite, there was a tendency for the excess chloride to come to the surface.

In a third series of experiments an effort was made to study the relation of the mass of composition to the volume of magnesium chloride solution sufficient to make a mixture of the proper consistency for laying. This was considered important, since, in preparing the mixture, the workmen invariably used a sufficient amount of magnesium chloride solution of a certain degree Baumé regardless of the actual magnesium chloride contained therein. For example, it was customary to use a 21° Bé. solution in summer and an 18° Bé. solution in winter. Accordingly, solutions of these strengths were used in the experiments. The solid constituents of the mixture were made up to 250 g. and to these samples enough magnesium chloride solution was added to obtain the proper consistency for laying. From the amount of solution required, the actual weight of the magnesium chloride used was calculated, and from this the percentage of magnesium chloride in the finished product was computed.

The average amount of magnesium chloride solution required for 32 samples of this composition was 178 cc. with a maximum of 225 cc. and a minimum of 160 cc. The average amount of magnesium chloride added in per cent was 11.1 for the 18° Bé. solution and 13.3 for the 21° Bé. solution. The maximum percentage required for the 18° Bé. solution was 13.8 and the minimum 10.2. It was found that mixtures containing a large amount of clay or sawdust required enough of the magnesium chloride solution in mixing to bring the percentage of magnesium chloride above the 1:3 limit; in such samples it was found that there was always a tendency of the floor to warp on standing.

These experiments demonstrated that, in order to obtain the best results, the strength of the magnesium chloride solution should be known and just sufficient of it should be added to secure the correct percentage of magnesium chloride with enough additional water to obtain the proper consistency.

In connection with the third series of experiments, slate was used as the coloring material, but it was found to give very uncertain results. Talc was also tried as a filler and it was found that, when used in moderate amounts, it aided greatly in giving the floor a luster when properly troweled; moreover, the tests showed that it slightly decreased the absorption of the material. When too much talc is used, however, it constantly comes to the surface, especially after the sample is washed and allowed to dry slowly. Some experiments which were made to determine the largest amount of sawdust that could be used, showed that the greatest that could be safely and successfully employed was 15 per cent. In these samples, it was necessary not to have an excess of magnesium chloride,

for bad warping occurred when too much was used. Sand was also experimented with as a filler and it was found that a very hard composition resulted with a large percentage of sand. While it is difficult to obtain sand of such fineness as to permit of the production of a very smooth surface, it aids in producing a hard durable floor.

The results of ten other experimental series may be briefly noted. Efforts to find a substitute for Venetian red established the fact that while hematite of desired color would cost, when using 25 per cent of color, at least two-thirds as much as Venetian red, the color obtained was one that did not meet with general approval and twice as much was required to produce the same color intensity as that imparted by the prepared color. In connection with reducing the cost of the color, about 30 samples were made in which aniline dyes were used: none of these retained their color for any length of time.

In one series in which varying amounts of sawdust and asbestos were used, it was found that when used in too great quantities, asbestos interfered somewhat with the troweling; the results obtained indicated that not more than 5 per cent of asbestos should be employed, since greater amounts interfered with the production of a good surface.

A series of experiments was carried out for the purpose of studying the effect of adding oil to the composition and then comparing the absorption of samples made from different fillers. The samples were all made on the same day and an attempt was made to trowel each sample in the same manner. In the samples in which oil was used, the oil was thoroughly mixed therewith, and then these samples were brought to the proper consistency by the use of a calculated amount of concentrated magnesium chloride solution and water. The samples were allowed to stand one week and then a part of each sample was used for an absorption test. The samples were weighed, immersed in water for 24 hrs., and reweighed. These samples were then placed aside for 4 mos., weighed, immersed in water, and then reweighed. The absorption was not proportional to the amount of oil used, but, after the samples had stood for some time, they all absorbed more water, with the exception of those in which linseed oil was used. These showed no indication of oil on the surface, while those in which hard mineral oil was used possessed an oily appearance. The results indicated that the magnesium linoleate acted as a binder between the particles, thus lowering the absorption. The samples in which a small amount of oil was used were sufficiently hard; but, when a large amount of oil was employed, several months of standing were necessary for the samples to become satisfactory in this respect. The samples without oil faded badly after the absorption test, while little change could be observed in the color of the samples which contained oil. Invariably, the samples containing oil set more slowly.

Experiments were conducted with the object of reducing the cost of the composition by employing other materials with reduced amounts of magnesite.



Portland cement magnesite mixtures had a bad color, absorbed a large amount of water and shrank on drying; in general, they resembled more closely the cement than the composition floors. Plaster of Paris gave compositions which dusted badly, lacked hardness, and set too quickly. Likewise, gypsum which had been heated to 400° C. gave samples which set too quickly and were no harder than the samples made from ordinary plaster of Paris. Samples prepared with the addition of a cement made of molecular quantities of magnesia, magnesium sulfate and plaster of Paris, said to form a white, quick-setting strong cement, also set quite quickly and were very hard, but the material rubbed off easily.

In the effort to find the material which would be a suitable binder for fillers or one that could well be used as a surface material, a number of experiments were made with asphalt, "Redmanite," gelatin-glycerol mixtures, "Galalith," viscose and vegetable resins. No results of commercial importance were obtained.

Finally, it may be mentioned that in 1912 a section of a floor, 12 ft. by 16 ft., was laid in a factory room which was in constant use; this floor was put down in the center of the room and was subjected to a great deal of wear. It was scrubbed every day with alkaline cleansing material and hot water. At the end of 7 mos. the floor was reported to be entirely set and as good as terrazo. Further experience warranted the conclusion that the flooring, the composition of which was identical with that laid in 1911, noted above, was more desirable than a floor constructed from a hard, nonpliable, highly conductive substance like terrazo.

#### PRACTICAL CONCLUSIONS

The successful working of composition flooring of the type considered does not depend entirely upon the chemical composition, but also upon the mechanical manipulation. The exercise of constant care is necessary in laying the floor and consequently only skilled workmen should be employed in practice; in particular, composition flooring should not be over-troweled, and the necessary precautions should always be taken in laying floors over surfaces which are subjected to heat. The composition should be dependent upon the uses to which the floor is to be put; but a formula is given which, when suitably modified along the lines indicated and expertly used, will comply with the conditions usually encountered in practice.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH  
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#### EMULSIFIED OR CUT PETROLEUM

By CHARLES K. FRANCIS  
Received April 25, 1916

A large quantity of emulsified or "cut" oil is produced from many wells in the Cushing pool of Oklahoma. Some of the pipe lines have refused to accept this oil claiming that it contains too much sediment which does not separate well on standing, and the refineries complain that it has a bad action on the stills.

It is the author's intention to present part of the details of an investigation which was undertaken

for the purpose of determining the nature of these emulsified oils and to suggest methods for properly treating them.

The oil selected for special study was produced from the Bartlesville sand and had a specific gravity of 0.8279 (30.1° B<sub>60</sub>). After 10 min. in the centrifuge, which made 1450 r. p. m., the total residue appeared to be 1.6 per cent. Subsequent examinations proved that this residue contained but a very small amount of solid matter, the larger part being water. The solid substance consisted of minute particles which, when measured under the microscope, were found to vary from 1/400 mm. to 1/20 mm. in diameter, or from 98 millionths to 19 ten-thousandths of an inch.

A portion of the oil was filtered and washed with casing head gasoline, gravity 84° B<sub>60</sub>. This treatment left an insoluble residue, equivalent to 0.505 per cent, consisting of 0.277 per cent nonvolatile mineral matter and 0.228 per cent organic and volatile substances.

ANALYSIS OF RESIDUE FROM CUT OIL FROM THE BARTLESVILLE SAND		
SUBSTANCE	Per cent Based on	
	Residue	Oil
Sand.....	2.69	0.007
Gypsum.....	13.35	0.037
Calcium chloride.....	7.60	0.019
Magnesium chloride.....	0.91	0.002
Salt.....	75.45	0.209
Total.....	100.00	0.274

There is but a trace, less than 0.5 per cent, of water in this oil, so the quantity of salts present is more than sufficient to saturate it.

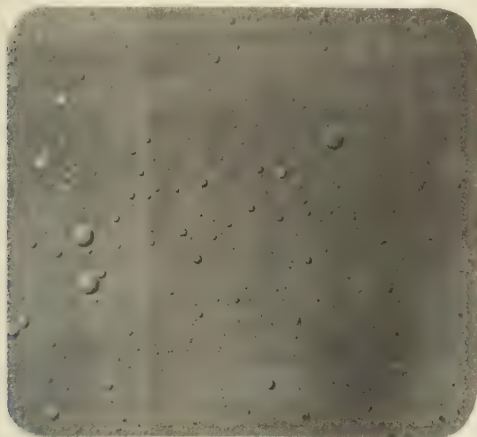
The common method for testing an oil for suspended matter, at the well or while in the stock tank, is to place some of it on a piece of glass and then look through it while holding it to the light. An experienced gauger can by means of this simple method quite accurately estimate the quality of an ordinary oil, but the test gives no positive information concerning the nature of any sediment which may be detected. Sometimes particles of water and gas may be thought to be mineral matter; indeed, such mixtures often have the appearance of suspended mineral matter. Oils holding water and gas in suspension soon settle, whereas oils truly cut or emulsified have been allowed to stand for weeks without clearing satisfactorily.

The nature of any substance held in suspension in petroleum may be quickly determined by means of a microscope. Good oils are represented in Figs. I and II—the predominating objects are water and gas; but, under the same magnification of the microscope, a cut oil, that is, emulsified, will appear as shown in Figs. III and IV. The mineral matter in these oils is chiefly common salt. In Fig. V several of the more prominent crystals of this substance are indicated by an X beneath. This photograph illustrates how the material shown in Fig. III changed through evaporation while exposed to the air for a few minutes, and brings out the character of the mineral matter. In the lower right-hand corner of the photograph a crystal of salt may be seen encased in a globule of water.

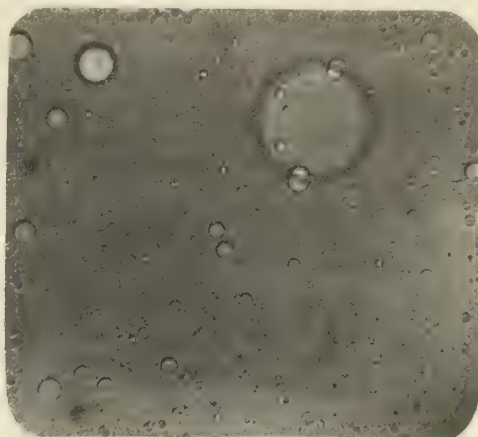
The analysis and the microscopical examination confirm each other as to the nature of the solid material present in this oil. The amount of mineral residue,

0.2 per cent, is surprisingly small when compared with the 1.6 per cent found by means of the centrifuge, which is so extensively used for making this test. A residue of 0.2 per cent would not be sufficient to cause the oil to be rejected by the average gauger representing the pipe line, but the chemical properties of the salts are very serious if their behavior when

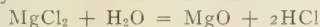
Many experiments have been made to devise a method which will cause emulsified petroleum to separate. A patented process has been described<sup>1</sup> by A. T. Beasley which is being used in California, consisting of a combination of electricity and hot water. "The action of the electricity is to create a very strong electrostatic field in which the infinitely small particles

FIG. I  $\times 83$ 

GOOD OIL—SHOWING WATER AND GAS

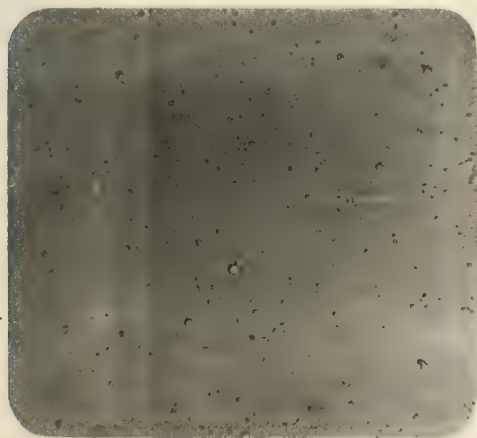
FIG. II  $\times 372$ 

heated is considered. The well-known action of chlorides, especially magnesium chloride, in boiler waters may be used to illustrate this:

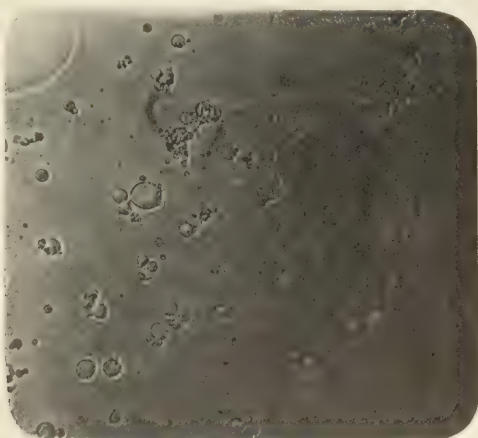


Hydrochloric acid (HCl) may be formed in the same way, certainly to some extent, when calcium chloride is heated. The scale forming and corrosive action

of water will be formed into chains from electrode to electrode. If the voltage be sufficiently high the fine films of nonconducting oil between the water particles will be punctured, bringing the entire chain together in the form of one comparatively large drop. This drop is now free water and is deposited." The system is composed of three units—a water trap,

FIG. III  $\times 83$ 

EMULSIFIED OIL—SHOWING WATER AND MINERAL MATTER

FIG. IV  $\times 372$ 

of the group of salts reported in the analysis has often been a grave matter in steam boilers; so then, oils containing them would in a short time seriously injure the condensing tubes and the stills in the refinery. On a basis of 4000 bbls. of oil treated each day, the amount of salt accumulating daily would be 2400 lbs., about 240 lbs. of calcium chloride and 24 lbs. of magnesium chloride.

an electrical treater, and an automatic oil and water separator. The oil in the treater is maintained at a temperature which may vary with the viscosity of the oil and the weather conditions, by means of a steam coil. No doubt the heat has much to do with the breaking down of the oil globule when this method is used.

<sup>1</sup> *Oil Age*, April, 1911; see Redwood, 1, 318.



In the Oklahoma fields it is the common practice to treat the emulsified oils with water, the temperature of which is maintained at 80 to 125° F., depending upon the quality of the oil and the weather conditions. This treatment is conducted in a tank (Fig. VI), placed between the flow tank and the stock tanks. It is simply one unit in addition to the usual



FIG. V X 83  
SALT IN EMULSIFIED OIL

equipment on a lease. The illustration indicates all the essential features of this method. The flow of oil is continuous, being controlled so that a constant stream is distributed upward through the warm water, passing out to the stock tanks.

Many samples of crude oil from the Cushing field, which have been examined here, have had an initial boiling point of 130° F.; hence this treatment, even

pansion causes the breaking of the oil film; then the fine particles of salt are dissolved by the extra water present and carried to the bottom of the stock tank within a short time after the treated oil is delivered there. Some salt is removed by the water during the treatment, consequently the water in the treating tank should be renewed occasionally or it may become saturated with the salt and have no action on the oil being passed through it.

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## THE DECOMPOSITION OF HYDROCARBONS AND THE INFLUENCE OF HYDROGEN IN CARBURETED WATER GAS MANUFACTURE

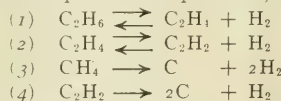
By M. C. WHITAKER AND E. H. LESLIE

Received June 1, 1916

(Concluded from our previous issue)

### THE DECOMPOSITION OF PARAFFIN HYDROCARBONS

Figs. 9 to 14 indicate the proportions of the various components obtained when the oil was decomposed alone. Fig. 9 shows that at 621° C. the gases are composed of about 10 per cent hydrogen at all oil rates above 5 cc. per minute. The reactions which contribute to the formation of this hydrogen, named in order of their probable importance, are:



The conditions are those which are known to be favorable to the condensation of acetylene. The methods for the determination of acetylene are so unsatisfactory that no effort was made to determine the proportion of acetylene in the gases formed. Other investigators have found the amount small in similar experiments.

The rapid increase in the proportion of hydrogen with decreasing oil rates below 5 cc. per minute is thought to be due to a marked increase in the extent to which reactions (3) and (4) take place. At 723° C. only a slightly larger proportion of hydrogen is formed than at 621° C., indicating that reactions (3) and (4) do not become rapid up to this temperature. A very marked increase in the hydrogen production takes place when the temperature is elevated to 825° C., chiefly due to an increase in reactions (3) and (4), as is evidenced by the very large amount of free carbon which was liberated and which tended to stop the furnace tube. No trouble was occasioned by this carbon deposition at 621 or 723° C.

Fig. 11 shows the proportion of illuminants, or components removed by 20 per cent fuming sulfuric acid, in the oil gases made at the three temperatures. The percentage of illuminants is highest in the gases made at 621° C. at all oil rates, and remains practically constant at 52 per cent at all oil rates above 10 cc. per minute. The proportion of illuminants formed at 723° C. is higher than at 825° C. except possibly at high oil rates. It is thought, however, that the proportion of illuminants at high oil rates would not be greatly different at any of these temperatures.

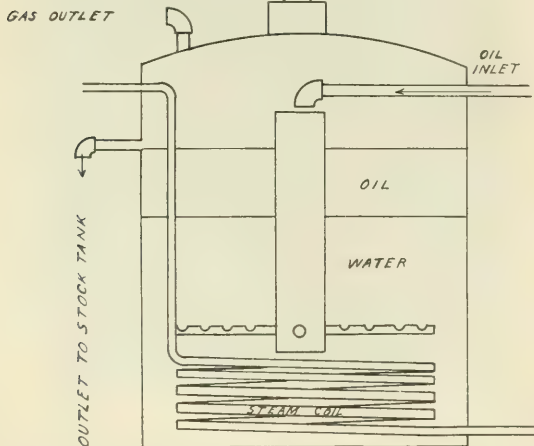
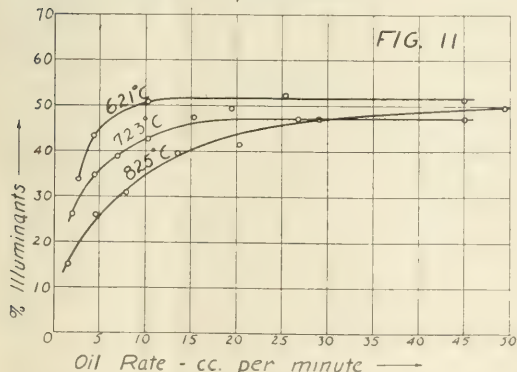
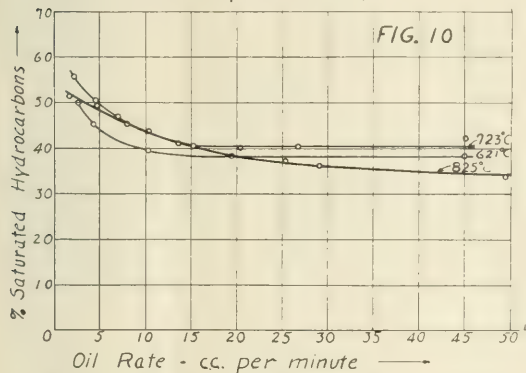
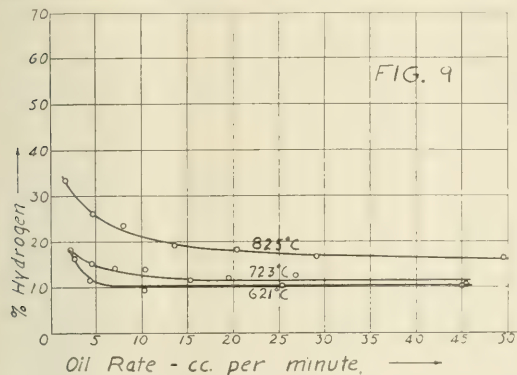


FIG. VI—TREATING TANK FOR EMULSIFIED OIL

when conducted at the higher temperature, should not seriously affect the gravity of the oil.

There is a large quantity of salt in some wells in the Cushing pool, and it is this substance, as noted above, which is mainly the cause of the emulsified oils. In the warm water treatment, the slight ex-

The fact that the proportion of illuminants is lower, the higher the temperature at moderate to low oil rates, is due to the secondary reactions of these hydrocarbons. Ethylene is decomposed into carbon and methane to some extent. Condensation to naphthenes takes place. At these low oil rates the proportion of hydrogen present is considerable, and the higher the temperature the higher this percentage. Hence it

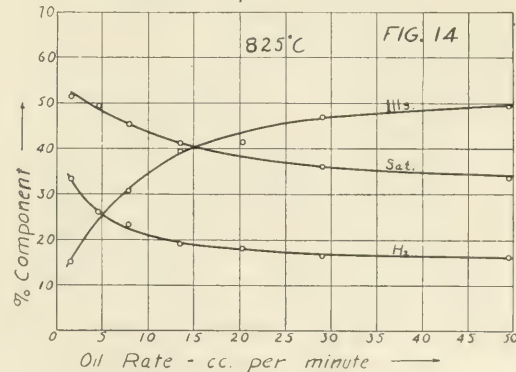
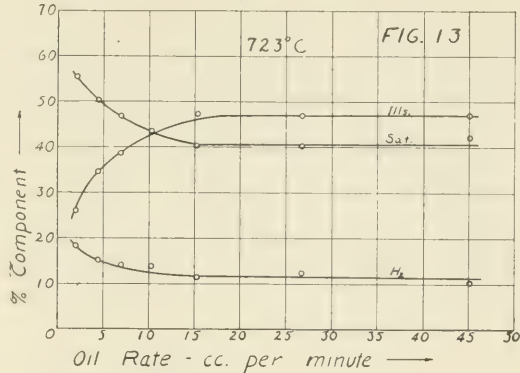
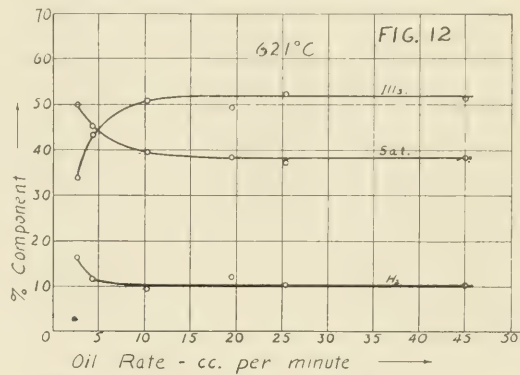


would be expected that hydrogenation reactions such as  $C_2H_4 + H_2 \rightleftharpoons C_2H_6$  and  $C_2H_2 + 2H \rightleftharpoons 2CH_4$  would take place.

The relation between the proportions of saturated hydrocarbons formed at different temperatures is shown in Fig. 10. It can be seen that the proportion of saturateds in the gas is higher at 723° C. than at 621° C. at all oil rates. This no doubt is due to the

faster speeds of such reactions as  $C_2H_4 \rightarrow C + CH_4$  and  $C_2H_6 + H_2 \rightleftharpoons 2CH_4$ .

It might reasonably be expected that the percentage of saturateds in the gases would be greater at 825° C. than at 723° C., but it can be seen from Fig. 10 that this is not the case. At low oil rates the proportion of saturateds is lower at 825° C. than at 723° C. This is chiefly due to the fact that the reaction

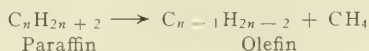


$CH_4 \rightarrow C + 2H_2$  has an appreciable velocity at this temperature. As the oil rate increases it would be reasonable to expect that the effect of this reaction would be less and less. However, the divergence between the 825° C. curve and the 723° C. curve becomes greater the faster the oil rate. This state of affairs is apparently due to the superimposed effect of another reaction. When the high paraffin hydro-



carbons first break down under these conditions the chief products are low molecular weight paraffin hydrocarbons and high molecular weight olefins. At 621 and 723° C. a considerable proportion of the high molecular weight olefins formed pass on through the tube into the tar. The tars were larger in amount the lower the temperature, and when the tar curves are studied it will be seen that there is not a marked difference between the tar formation at 621 and 723° C. but that a considerable difference is found at 825° C. These low temperature tars were treated with concentrated sulfuric acid in the cold, and it was found that 20 to 25 per cent by volume was removable in this fashion, the greater portion of which was doubtless olefins of high molecular weight. At 825° C. the effect of the heat is sufficient to break down these higher olefins almost completely. In the process ethylene and propylene are formed in large quantity with the result that the percentage of saturated hydrocarbons drops. The proportion of illuminants and saturated hydrocarbons present in the gases at 825° C. is greatly lowered on account of the high percentage of hydrogen present in these gases.

Figs. 12, 13 and 14 show the relations between the component illuminants, saturateds, and hydrogen at the temperatures 621, 723 and 825° C., respectively. Of all the proportions of these components those at the high oil rates at 621° C. most nearly represent the products of the primary decomposition of the oil. The hydrogen is largely the result of secondary reactions. If the illuminants and saturateds are calculated to a 100 per cent basis the proportion is 58 per cent illuminants and 42 per cent saturateds. Such a ratio as this would be expected in the reaction if the primary decomposition of the paraffin was:



and if then, the high molecular weight olefins in part broke down to lower olefins.

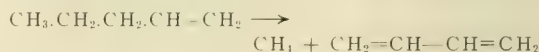
The mechanism of the reactions at work can be judged somewhat from a consideration of the relations between the curves for the percentages of illuminants, saturateds, and hydrogen. Thus, in Fig. 12, if it is assumed that the illuminants are chiefly ethylene and the saturateds largely methane, it can be seen that the normal formation of ethylene is 52, that of methane 39, and that of hydrogen 10 per cent.

Consider the proportions in the gas at an oil rate of 2.5 cc. per minute. They are ethylene 34, methane 50, and hydrogen 16 per cent. The decrease in ethylene has been 18 per cent on the basis of the total gas. If this had been due to the reaction  $C_2H_4 \longrightarrow C + 2H_2$  the methane should have increased 18 per cent on the basis of the total gas. In fact it increases only 11 per cent.

The hydrogen increases 6 per cent on the total gas basis. If this were due to the reaction  $CH_4 \longrightarrow C + 2H_2$  a 3 per cent decrease in the methane should have taken place. But as has been seen, other reactions also give rise to hydrogen. Assuming, however, that the above reaction was the sole change of this sort, only 14 per

cent out of the 18 per cent increase in methane which should have been found, had the ethylene reacted entirely with formation of carbon and methane, would be accounted for. Hence the ethylene must be removed in other ways, for example, by the condensation to naphthenes.

It is not probable that the 6 per cent increase in the hydrogen is entirely due to the decomposition of methane. Dehydrogenation of naphthenes, dissociation of ethylene and ethane, etc., may give rise to hydrogen. Then, too, not all the methane formed comes from the decomposition of ethylene. Decomposition of higher olefins in such a manner as



and hydrogenation of olefins,  $C_2H_4 + 2H_2 \rightleftharpoons 2CH_4$ , may contribute.

A similar argument may be worked out for the relation between the illuminants, saturateds, and hydrogen at 723 and 825° C.

The marked decrease in illuminants with decreasing oil rates at 825° C. is notable. No corresponding increase in saturateds takes place. It is apparent from the high percentage of hydrogen that methane is decomposing extensively into carbon and hydrogen.

#### PROPORTION OF ILLUMINANTS AND SATURATED HYDROCARBONS

In order that the effect of hydrogen on the composition of the gases as regards illuminants and saturated hydrocarbons may be seen, Figs. 15, 16, 17, 18 and 19 are shown. These curves were drawn by calculating the illuminants and saturated hydrocarbons to a basis of 100 per cent. In this manner the proportions of the two classes of compounds can be seen.

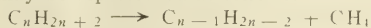
It might be expected that hydrogenation reactions would play an important part and that the proportion of saturated hydrocarbons would be higher in the oil-gas-hydrogen runs than in the straight oil-gas runs. It will be shown later in this paper that hydrogenation does take place to a considerable extent.

It should be noticed that at low temperatures the presence of the hydrogen has no influence on the relative amounts of illuminants and saturated hydrocarbons at high oil rates; *i. e.*, its presence has little effect on the mechanism of the primary decomposition and the early stages of the secondary decomposition. But at low oil rates where the gases are exposed to the effect of heat for a longer time, and where extensive secondary and tertiary changes take place, the hydrogen has a considerable influence at temperatures of 723 and 825° C. At 621° C. the influence of the hydrogen is not marked.

It will be remembered that the first reaction undergone by a paraffin hydrocarbon when it is thermally decomposed is that which gives rise to a high molecular weight olefin and a low molecular weight paraffin. It is probable that the higher the molecular weight of an olefin the more readily it is hydrogenated.

If the high molecular weight olefins are hydrogenated, paraffins would be formed. These would

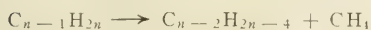
again decompose into long chain olefins and low molecular weight paraffins. This sequence of reactions may be represented as follows:



Paraffin Olefin



Olefin Paraffin



Paraffin Olefin

The net result of such a sequence of reactions would be an increase in the proportion of paraffins in the

$2H_2 : 1$  Gas (Figs. 17 and 19), the proportion of saturated hydrocarbons is greater in the hydrogen-oil-gas runs. It is probable, therefore, that the above reactions take place in all cases but that the effect of the hydrogen at low oil rates on the extensive secondary changes is so great that the result of the hydrogenation is masked.

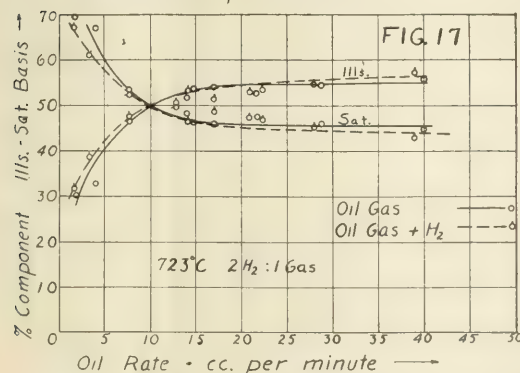
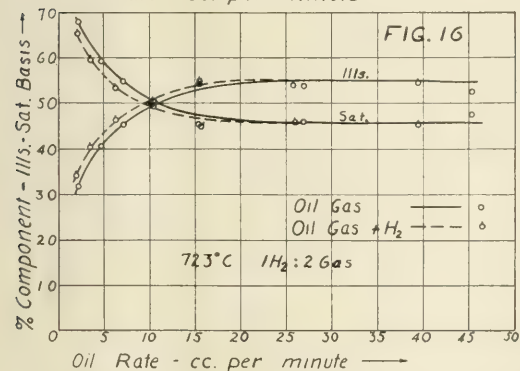
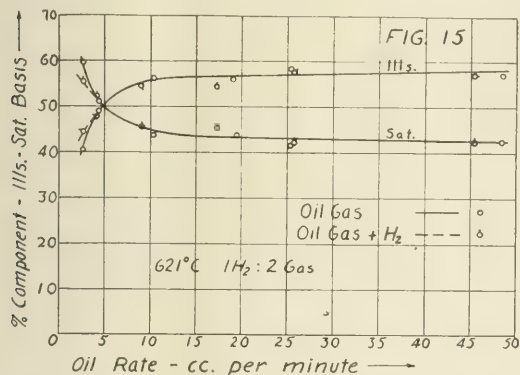
Apparently the low molecular weight olefins are not hydrogenated to a large extent, for were this the case the proportion of saturated hydrocarbons present would be greatly increased. This is not the case.

The increase in the proportion of olefins in the hydrogen-oil-gas runs at low rates of oil feed may be accounted for in two ways:

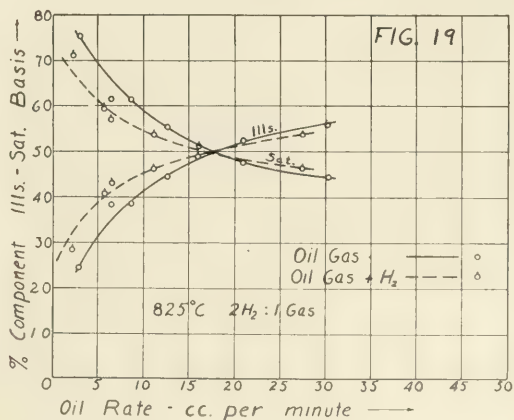
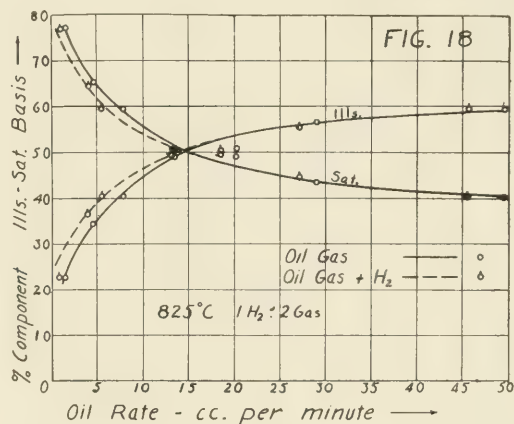
(1)—The effect of the hydrogen may be to increase those reactions which give rise to olefins.

(2)—The effect of the hydrogen may be to retard those reactions which tend to remove or destroy the olefins.

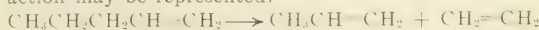
The largest proportion of the ethylene and propylene present comes from the direct splitting up of high



gas. But as can be seen in the figures, the proportion of paraffins is less in the cases of the hydrogen-oil-gases. However, at high oil rates where secondary reactions are not so important, and in the series of runs at 825° C. where the concentration ratio was



molecular weight olefins. If an olefin of fairly high molecular weight may be used to illustrate, this reaction may be represented:



It will be noticed that the result is an increase in



volume. The equilibrium point of the reaction would therefore be shifted by a diminution of pressure in such direction as to favor the production of ethylene and propylene. The introduction of hydrogen has the same effect as a reduction in pressure, and would therefore have a similar effect on the equilibrium.

Chief among the reactions which remove olefins

as the influence of volume relationships on the equilibrium point is concerned, would not be affected.

Whether the displacement of the equilibrium points in any of these reactions is sufficient to be worthy of mention can not be said. In no case is the equilibrium condition attained, but the speeds of the various reactions would depend on the difference between the actual condition of the system and the equilibrium condition; hence any displacement of the equilibrium point would be important.

The increase in the proportion of olefins may be looked upon from another angle. When hydrogen is introduced along with the gas the time of contact of the gas with the heated tube is diminished, due to the increase in the total volume passing in unit time. If it is the case that the reactions which give rise to the olefins ethylene and propylene are fairly rapid, while those which destroy them are slower, the summational effect of an increased gas rate would be an increased proportion of olefins. That the speed of the reactions which produce olefins is fairly great can be seen by reference to Fig. 22, which shows the mean molecular weight of the olefins formed at 825° C. The mean molecular weight lies between 30 and 34. The molecular weight of ethylene is 28, while that of propylene is 42. The proportion of olefins higher than propylene cannot be great, therefore, and it would seem that they break down largely to ethylene and propylene. That the reactions which cause a removal or destruction of ethylene are only moderate in speed has been seen under the discussion of the reactions of ethylene in the first part of this paper.

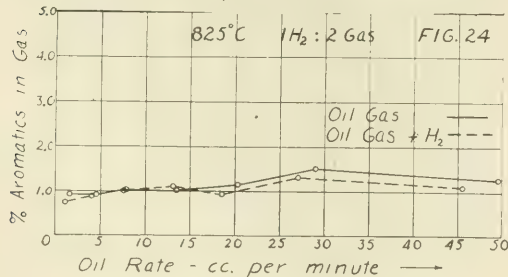
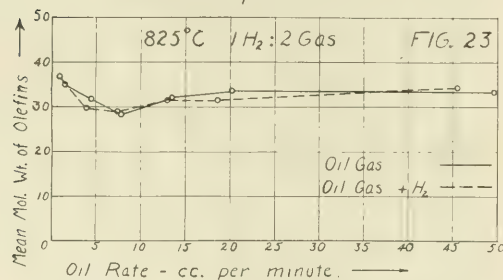
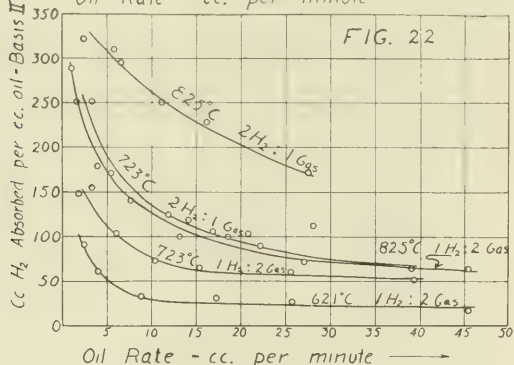
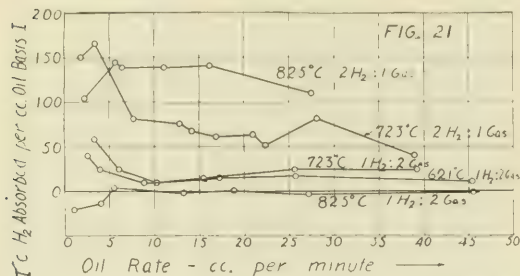
This latter explanation appears more probable than the one concerning the displacement of the equilibrium points of reactions; however, both of these effects may be concerned in the production of the results observed.

It will be noticed that the two different hydrogen concentrations produce similar results at 723° C. but that at 825° C. the proportion of olefins is much higher when the concentration ratio is  $2H_2 : 1 \text{ Gas}$ . The rather large difference in this last case indicates that the chief effect of the hydrogen is due to its cutting down the time of heating, for at 825° C. the decomposition of the higher olefins to ethylene is doubtless very rapid, and takes place extensively in spite of the reduced time of heating in the hydrogen-oil-gas runs.

#### THE ABSORPTION OF HYDROGEN

Calculations from the analytical data show that a considerable absorption of hydrogen takes place when the oil is cracked in an atmosphere of this gas. Haber was of the opinion that the oil produced no hydrogen by its own decomposition when it was cracked in an atmosphere of hydrogen. On the other hand, it might be assumed that there would be as much hydrogen produced under these conditions as when the oil was cracked alone. These two assumptions offer two bases on which the absorption of hydrogen may be calculated.

(I)—If no hydrogen is produced by the cracking of the oil, the hydrogen absorption per cc. of oil would



such as ethylene and propylene are condensation and decomposition. These reactions may be represented as  $3C_2H_4 \rightarrow C_6H_{12}$  and  $C_3H_4 \rightarrow C + CH_4$ .

The presence of the hydrogen would displace the equilibrium point of the first of these reactions in favor of the ethylene. The latter reaction, in so far

be equal to the difference between the hydrogen added and that present in the final gas divided by the total number of cc. of oil.

(II)—If the oil produces as much hydrogen as when cracked alone, the difference between the hydrogen added plus that normally produced from the oil at the particular oil rate and the hydrogen in the final gas represents the absorption. This divided by the total number of cc. of oil gives the absorption in cc. per cc. of oil.

Fig. 21 shows the absorption per cc. of oil calculated on basis (I) for the several temperatures and concentrations. Fig. 22 shows these absorptions calculated on basis (II).

It will be seen that the curves of Fig. 22 are much smoother and more regular than those of Fig. 21, not because they are drawn more smoothly, but because the points fall on smoother curves. The general form of the curves, too, in Fig. 22 is that which would be expected from a consideration of the curves for the hydrocarbon components formed per cc. of oil. The curves of Fig. 21 show no general similarity to each other, while those of Fig. 22 show similar general characteristics. The curves representing the formation of all the other components of the gases show regular variations, and it would be expected that this regularity would extend to the curves for hydrogen absorption.

In general, therefore, it seems that the basis on which the curves of Fig. 22 are calculated is more nearly correct than the basis which assumes that no hydrogen is produced from the oil when it is decomposed in hydrogen. This view is strengthened by the fact that in the case of the 825° C. gases with hydrogen concentrates  $1H_2 : 2$  Gas, the absorption curve in Fig. 21 falls below the 0.0 line, *i. e.*, hydrogen must have been formed from the oil since there was more hydrogen in the final gas than was added through the meter.

It is probable that the true value for the hydrogen absorptions for any set of conditions falls between the two values as calculated from the two limiting assumptions. It is thought that the true values are slightly less than the values of the absorptions as they would be read from the curves in Fig. 22.

The curves of Fig. 22 show the interesting fact that at any particular temperature the hydrogen absorption per cc. of oil decreases with increasing oil rate. The great importance of the time factor is well brought out here. At constant oil rate, and approximately the same hydrogen concentration the absorption per cc. of oil is greater the higher the temperature. There would, however, be an upper limit to this on account of the excessive decomposition of all hydrocarbons at elevated temperatures.

The effect of increasing the concentration of hydrogen is clearly shown in Fig. 22 for the curve for the  $2H_2 : 1$  Gas runs is above the curve for the  $1H_2 : 2$  Gas runs at both 723 and 825° C. The speed of hydrogenation reactions is greater the higher the concentration of hydrogen.

It is interesting to note that the curve for the

$1H_2 : 2$  Gas runs at 825° C. falls below the curve for the  $2H_2 : 1$  Gas runs at 723° C. This shows that the increasing temperature is tending to cause dehydrogenation reactions or hydrocarbon dissociations to a marked degree at 825° C. The effect of hydrogen in greater concentration in reversing these dissociations is clearly brought out when the position of the  $2H_2 : 1$  Gas curve for 825° C. is considered in its relation to the  $1H_2 : 2$  Gas curve at this same temperature.

#### MEAN MOLECULAR WEIGHT OF THE OLEFINS

In Fig. 23 the mean molecular weight of the olefin hydrocarbons in gases made at 825° C. in oil-gas runs and in hydrogen-oil-gas runs with the concentration ratio  $1H_2 : 2$  Gas can be seen.

It should be kept in mind that the molecular weight of ethylene is 28 and that of propylene is 42. From the position of the curves it can be seen that approximately one-third of the olefins is propylene. The curves lie very close together, and it is impossible to say just what the influence of the hydrogen is on the formation of the olefins.

If the method of calculation of the molecular weight of the olefins, as explained under the discussion of the analytical methods, is considered, it is apparent that all the analytical errors pile up and are brought out in this calculation. This no doubt accounts for the irregularity in the curve, and also for the fact that there is no consistent difference in the position for the oil-gas runs and the hydrogen-oil-gas runs.

It was thought that certain differences might be brought to light by the curves for the mean molecular weights of the olefins. If the higher olefins were more easily hydrogenated than ethylene the curve for the mean molecular weight of the olefins in the hydrogen-oil-gas runs would fall below that of the oil runs. If, on the other hand, the presence of the hydrogen, on account of its causing a more rapid passage of the gas through the tube, resulted in a less extensive decomposition of the higher olefins, the curve for the hydrogen-oil-gas runs would lie above that for the oil-gas runs.

It may be thought that these two effects are balancing each other with the result that the curves are practically the same. It would have been desirable to have carried out a similar series of runs with a high concentration of hydrogen, but the calculation of the mean molecular weight of the olefins can be made only when the per cent of benzene in the gas is known, and, as has been noted, the method for the determination of benzene was found only as this experimental work was drawing to a close.

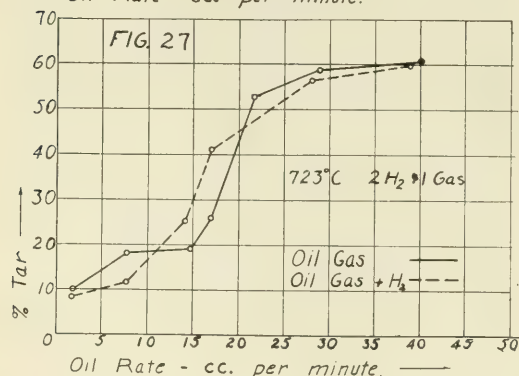
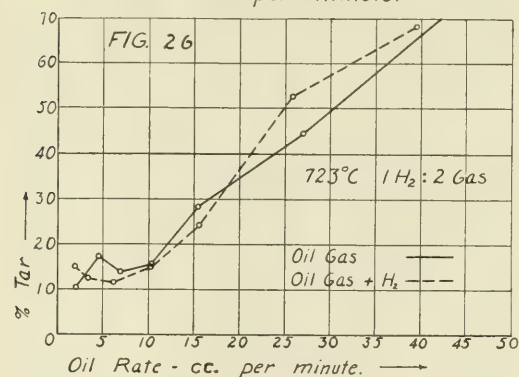
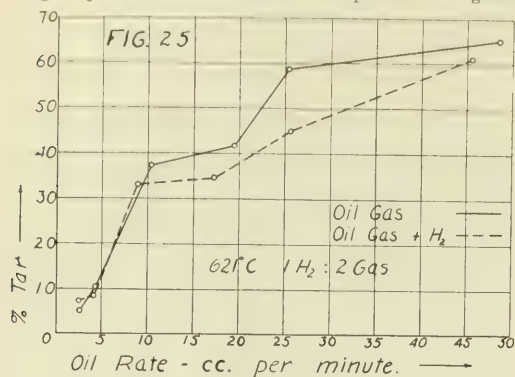
#### THE FORMATION OF AROMATIC HYDROCARBONS

Fig. 24 shows the percentage of aromatic hydrocarbons present in the gases made at 825° C. when oil is cracked alone or in hydrogen when the concentration ratio is  $1H_2 : 2$  (Oil Gas + Tar Gas). The method of determining these percentages has been described under the analytical methods.

The percentage of aromatics appears to increase slightly with increase in oil rate. Whether this is



actually the case or not cannot be definitely stated. The exact opposite would be expected. It is thought that the apparent increase may be due to the freezing out of high molecular weight hydrocarbons of other types than the aromatic compounds. High molecular weight paraffins and olefins are present in greater



proportion in the gases made at high oil rates than in those made at low oil rates.

The smaller proportion of aromatic hydrocarbons present in the gases made at low oil rates may possibly be due to the removal of benzene to form compounds such as diphenyl, naphthalene and anthracene, which pass largely into the tars.

The hydrogen apparently has little effect on the formation of aromatics at low oil rates, but decreases the aromatic formation somewhat at higher oil rates.

This is possibly due to the retarding effect which the presence of hydrogen would have on the formation of aromatics or hydroaromatics by condensation reactions. Less gas is formed from the oil at high oil rates than at low oil rates, and as a consequence the concentration of hydrogen is greater at high oil rates than at low oil rates.

#### TARS

The tars were collected from the tar drip and the volume measured. This volume divided by the volume of the total oil used and multiplied by 100 gives the percentages of tar formed. Figs. 25 to 29 show these tar percentages for both oil-gas and hydrogen-oil-gas runs plotted against the oil rate at the temperatures indicated. It should be mentioned that at low oil rates these percentages are not accurate. The low-oil-rate tars are heavy and viscous, and as a result do not run down through the condenser as easily as the lighter high-oil-rate tars.

As far as can be judged from the curves in Figs. 25, 26, and 27, for temperatures of 621 and 723° C., there is no marked regular difference between the tar formation in the oil-gas runs and the hydrogen-oil-gas runs.

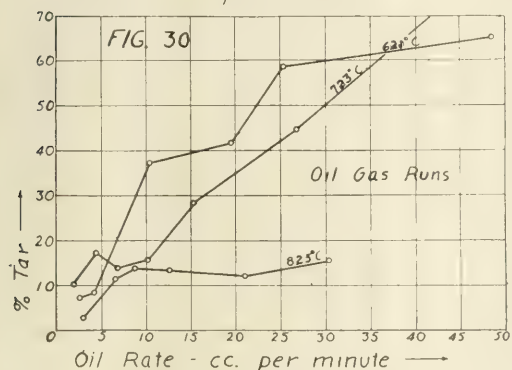
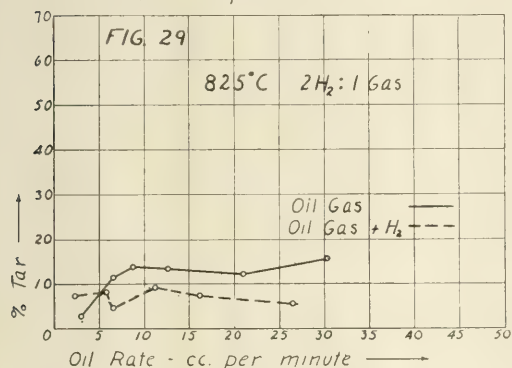
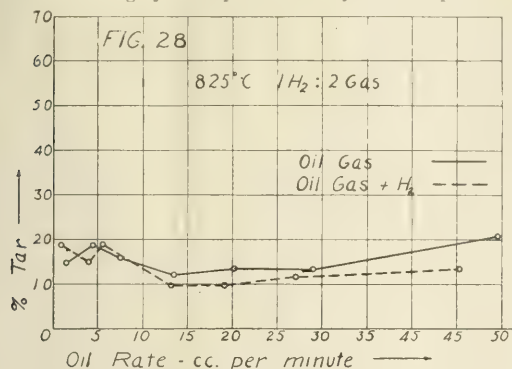
At 825° C. the percentage of tar in the oil-hydrogen runs is consistently less than in the oil runs except at low oil rates where, as has been mentioned, the tar percentages as shown mean little. This difference is more marked in the curves of Fig. 27 where the concentration ratio was 2 Hydrogen : 1 (Oil Gas + Tar Gas) than in the curves of Fig. 28.

In general, two classes of compounds are contained in the tar: (1) unchanged or partially changed oil; (2) synthetic hydrocarbons which are the products of extensive change. It may be thought that hydrogen, on account of its decreasing the time of contact of the hydrocarbon vapors with the heated tube, would tend to increase the proportion of tar since the decrease in the time of heating would cause a less extensive decomposition of the oil vapors. On the other hand, this decrease in the time of heating would also diminish the extent to which synthetic reactions resulting in the formation of tarry products would take place. Also the percentages of the hydrogen would retard these reactions, since they are all reactions which result in decrease of volume. Apparently these effects are balanced at temperatures of 723° C. or below. At 825° C., however, the percentage of tar is less. This leads to the belief that synthetic reactions are responsible for a considerable proportion of the tars at temperatures in the neighborhood of 825° C.

Fig. 30 shows clearly the effect of temperature on tar formation, and also the effect of increase of oil rate at constant temperature. The proportion of tar increases with increasing oil rate and most markedly so, at temperatures of 621 and 723° C. The largest proportion of these tars at moderate to high oil rates is undecomposed oil, as shown by distillation and treatment with concentrated sulfuric acid. This is also indicated by the fact that a temperature change from 621 to 723° C. produces no great difference

in tar formation, and also by the fact of the very rapid increase in the percentage of tar with increasing oil rate.

At 825° C. the proportion of tar does not increase greatly with increasing oil rate, indicating that these tars are largely composed of synthetic products,



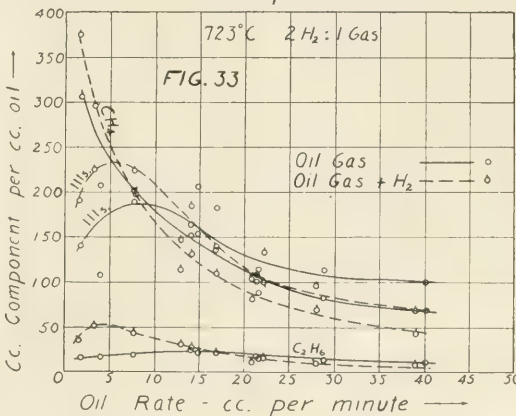
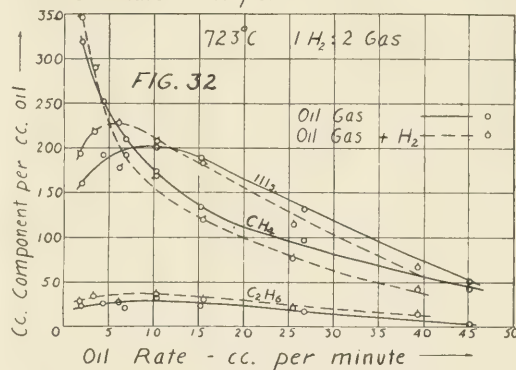
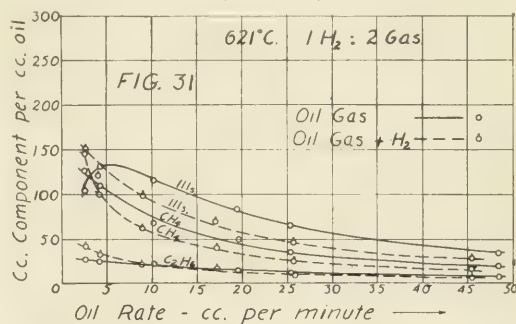
which is further substantiated by other physical characteristics, such as distinct aromatic odor and their reactions with concentrated sulfuric acid.

All the tars were strongly fluorescent.

FORMATION OF ILLUMINANTS, METHANE, AND ETHANE, AND THE OBTAINING OF PARTICULAR END-PRODUCTS FROM A PARAFFIN HYDROCARBON OIL

In Figs. 31 to 35 the cc. of illuminants, methane and ethane formed from 1 cc. of oil are shown plotted against the oil rate at the temperatures and hydrogen-

gas concentration ratios indicated. It can be seen from Fig. 31 that at 621° C., with the exception of the illuminants in the case of the straight oil-gas runs, the number of cc. of all these hydrocarbons formed from 1 cc. of oil increases with decreasing oil rate. There would be a limit to this, however, for, were the oil rate



made low enough, a very extensive decomposition of the hydrocarbons would set in.

Fig. 31 shows that the illuminants are the most easily decomposed of the gaseous hydrocarbons. The curve for the illuminants in the straight oil-gas runs has a maximum due to the fact that though the longer time of contact of the oil vapors with the heated tube at low oil rates causes a more extensive formation of ethylene and other illuminants, an oil rate is reached where extensive decomposition of these



hydrocarbons takes place, which more than overcomes the more rapid illuminants formation at low oil rates. Condensation and hydrogenation, which are more extensive at low oil rates, are important in this connection also.

No maximum is observed in the illuminants curve for the hydrogen runs, doubtless because the time of contact of the oil vapors with the heated tube is less at any particular oil rate than in the case of the oil-gas runs. The curve for the illuminants in the hydrogen-oil-gas runs, for this reason also, is always below that for the illuminants in the oil-gas runs, except at low oil rates.

Less methane is formed per cc. of oil in the hydrogen-oil-gas runs than in the straight oil-gas runs except at low oil rates. That the time of contact here is sufficient so that extensive hydrogenation takes place is clearly brought out from a consideration of Fig. 22 in connection with Fig. 31. At all oil rates the decreased time of contact of the gases with the heated furnace tube, on account of the absorption of hydrogen, results in a lower formation of methane.

The relationships for ethane are much the same as for methane, and for the same reasons.

Figs. 32 and 33 show the relationships between the hydrocarbons at  $723^{\circ}\text{C}$ . at hydrogen concentration ratios of  $1\text{H}_2 : 2\text{Gas}$  and  $2\text{H}_2 : 1\text{Gas}$ , respectively. More of each of the components is formed per cc. of oil at  $723^{\circ}\text{C}$ . than at  $621^{\circ}\text{C}$ . The maximum in the illuminants curve falls at a higher oil rate than at  $621^{\circ}\text{C}$ . as would be expected, since the higher temperature would cause a more rapid decomposition, condensation, and hydrogenation of the illuminants to take place. At  $723^{\circ}\text{C}$ . the maximum on the illuminants curve for the hydrogen runs can be seen clearly. It is interesting to note that this falls to the left of the maximum on the curve for the oil-gas runs. The decreased time of heating on account of the hydrogenation admixture is responsible for this.

The effect on the illuminants of increasing the concentration of hydrogen is clearly brought out in Figs. 32 and 33. The maximum on the curve for the illuminants in the hydrogen-oil-gas runs at the higher hydrogen concentration falls at a slightly lower oil rate than the maximum on the curve for the lower hydrogen concentration. The divergence between the illuminants curves for the oil-gas runs and the hydrogen-oil-gas runs is greater both at low and high oil rates at the higher hydrogen concentration than at the lower hydrogen concentration on the time of contact of the gases with the heated tube surfaces.

The relationships in the case of the methane and ethane are exceedingly interesting. The formation of methane is less in the hydrogen-oil-gas runs than in the oil-gas runs at moderate to high oil rates, due to the decreased time of contact of the gases with the heated surfaces, and this effect is more pronounced at the higher hydrogen concentrations, as would be expected. As the oil rate decreases the hydrogenation effect becomes important and the proportion of methane formed from 1 cc. of oil is greatest in the case of the hydrogen-oil-gas runs. The curve for

methane in the hydrogen-oil-gas runs crosses the methane curve for the oil-gas runs. This crossing is at a higher oil rate with the higher hydrogen concentration, showing clearly the effect of the increase of concentration of hydrogen on the hydrogenation reactions. The formation of methane is slightly greater in the hydrogen-oil-gas runs than in the straight oil-gas runs when the hydrogen concentration ratio is  $1\text{H}_2 : 2\text{Gas}$ . This difference is slightly greater at low oil rates than at high oil rates.

When the hydrogen concentration ratio is  $2\text{H}_2 : 1\text{Gas}$  the ethane formation per cc. of oil is less in the hydrogen-oil-gas runs than in the oil-gas runs at high oil rates. This is the effect of the decreased time of contact due to the admixture of a larger volume of hydrogen. But at low oil rates the formation of ethane is much greater in the hydrogen-oil-gas runs as can be seen in Fig. 33. The ethane curve has a maximum, too, which is interesting because it shows that at low oil rates the reactions of the hydrocarbon ethane itself have an important part to play.

Figs. 34 and 35 show the relationships between these hydrocarbons at  $825^{\circ}\text{C}$ . A much less pronounced decrease in the formation of illuminants with increasing oil rate is due to the fact that the temperature of  $825^{\circ}\text{C}$ . is sufficient to promote actively the formation of illuminants. The maxima on the illuminants curves for the oil-gas runs fall at the higher oil rates, as would be expected when the higher temperature is taken into consideration. The illuminants curves for the hydrogen-oil-gas runs are entirely above the illuminants curves for the oil-gas runs. This is again a result of the decreased time of heating when hydrogen is admixed. The effect is most marked when the higher concentration of hydrogen is used.

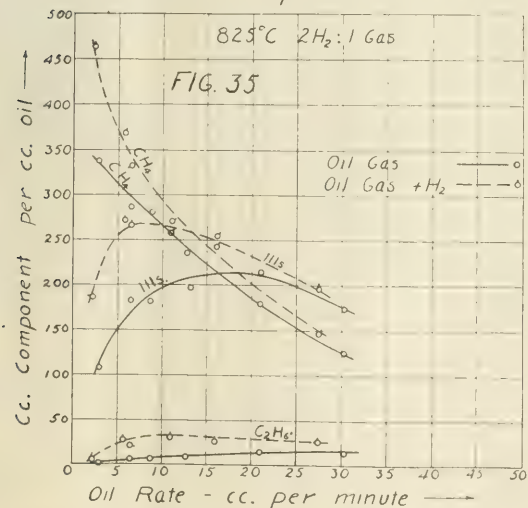
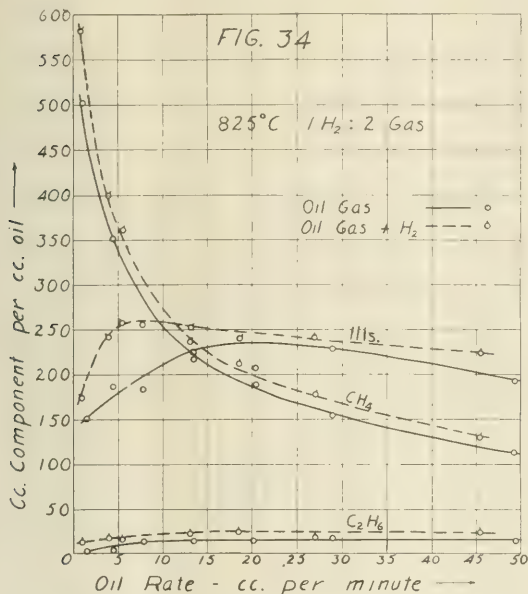
The curves for methane in the hydrogen-oil-gas runs fall above the curves for methane in the oil-gas runs at all oil rates at  $825^{\circ}\text{C}$ . This is due to two effects: *first*, the less extensive decomposition of the methane into carbon and hydrogen due to the decreased time of heating in the hydrogen-oil-gas runs; *second*, the increased rate of hydrogenation reactions such as  $\text{C}_2\text{H}_4 + 2\text{H}_2 \rightleftharpoons 2\text{CH}_4$ . The effect of hydrogen in reversing the reaction  $\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$  is probably not important, as has been brought out in the discussion of the methane equilibrium and the reactions of methane in the first part of this paper.

The effect of the greater concentration of hydrogen on methane production can be seen clearly by comparing Figs. 34 and 35. The divergence between the hydrogen-oil-gas and the oil-gas methane curves is greatest when the hydrogen concentration ratio is  $2\text{H}_2 : 1\text{Gas}$ , and this is practically true at low oil rates where hydrogenation reactions are most important.

More ethane is formed when hydrogen is mixed with the vapors of the oil than when it is not added. This is doubtless due to the combined influence of the hydrogen in diminishing the decomposition of the ethane and to its effect in hydrogenating the olefins. These effects are particularly marked when the concentration ratio is  $2\text{H}_2 : 1\text{Gas}$ .

It may have been noticed that the curves for the oil-gas runs made at the same temperature do not coincide exactly, since the carbon tube used carbonizes somewhat and becomes of smaller internal diameter, thus decreasing the time of contact of the gas with the tube and consequently altering the composition somewhat.

The effect of temperature on the hydrocarbon products of decomposition of an oil can be seen very

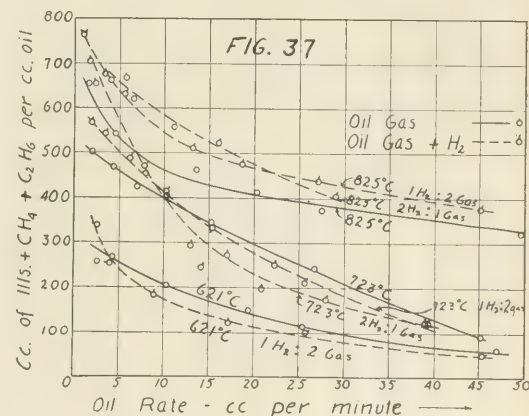
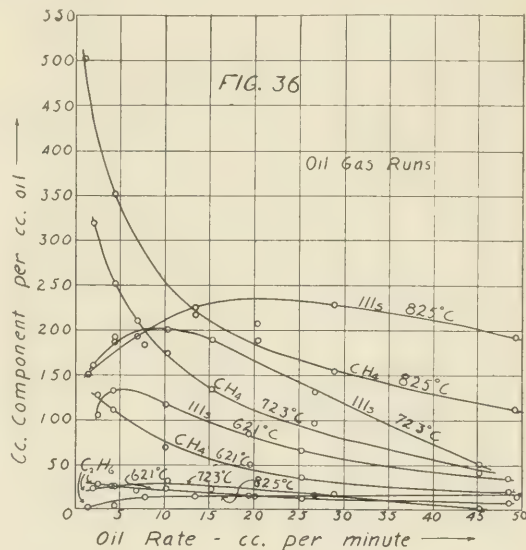


clearly from Fig. 36. Within the temperature range studied, the cc. of illuminants per cc. of oil increases with temperature, with one exception. At low oil rates there are more illuminants formed at 723° C. than at 825° C. The effect of the higher temperature in increasing the speed of the reactions which decompose ethylene more than overcomes the effect of the

higher temperatures in promoting the decomposition of the long chain olefins to ethylene and propylene.

It is interesting to note the position of the maxima of the curves for the illuminants at the several temperatures. These maxima indicate where the balance between the reactions of formation and the reactions of decomposition falls.

Within the temperature range studied, the formation of methane is greater the higher the temperature. At low oil rates the difference in the methane produced by a 100°-temperature rise is greater in the range from 621 to 723° C. than from 723 to 825° C., since at low oil rates 723° C. is a sufficiently high temperature to break down the original oil extensively.



The methane increase between 723 and 825° C. is largely due to the decomposition and hydrogenation of olefins  $C_2H_4 \rightarrow C + CH_4$  and  $C_3H_6 + 2H_2 \rightleftharpoons 2CH_4$ , as can be seen from a consideration of the illuminants curve for 825° C.

At high oil rates a temperature of 825° C. is necessary to form methane largely, as can be seen from the



position of the curve for methane at 621, 723 and 825° C.

The formation of ethane per cc. of oil is not large at any temperature studied, as shown in Fig. 36. The primary decomposition of the oil therefore involves chiefly a splitting off of methane rather than ethane or higher paraffin. The decomposition and dissociation of ethane are clearly shown by the falling off of the ethane curve as the oil rate decreases at a temperature of 825° C. On the other hand, a temperature of 825° C. is necessary to cause an extensive formation of methane and ethane per cc. of oil at high oil rates.

#### TOTAL HYDROCARBONS OBTAINABLE FROM THE OIL

The greater the proportion of the carbon of the oil which can be obtained in gaseous form the better the utilization of the oil for gas-making purposes.

Fig. 37 shows the *total cc. of illuminants + methane + ethane* obtainable from 1 cc. of oil under the varying conditions. At 621° C. more hydrocarbons are obtained per cc. of oil in the oil-gas runs than in the hydrogen-oil-gas runs, except at low oil rates where hydrogenation reactions become important. This is due to the lower time of contact of the oil vapors with the furnace tube in the case of the hydrogen-oil-gas runs. The same relations hold at 723° C. except that the hydrogen-oil-gas curves cross the oil-gas curve at a higher oil rate because of the greater effect of the higher temperature in hastening the hydrogenation reactions. The effect of the higher concentration of hydrogen is clearly shown. At 825° C. the hydrocarbons formed per cc. of oil are of greater volume in the hydrogen-oil-gas runs at all oil rates studied. The higher temperature promotes hydrogenation reactions at all oil rates. The effect of the greater concentration of hydrogen can be seen.

It is interesting to note that the slope of the curve for the hydrogen-oil-gas runs at 723° C. is much steeper than the slope of these curves at 825° C. at low oil rates, doubtless because at 825° C., and low oil rates, dehydrogenation reactions and reactions of decomposition of the hydrocarbons become of importance.

#### SUMMARY<sup>1</sup>

I—A critical review of the most important work on hydrocarbon decomposition and the influence of hydrogen on the reactions involved has been given. This has concerned itself with: *first*, the hydrocarbons of high molecular weight; *second*, the products of the primary decomposition; and *third*, the reactions of the simpler hydrocarbons. Summaries have been included which state concisely the probable course of the reactions of dissociation, decomposition, and condensation involved.

2—The subject of the mechanism of heat transfer in gas machines has been discussed.

3—Difficulties in the measurement of the true temperature of a gas have been pointed out.

4—In the experimental work a paraffin oil was thermally decomposed alone and in hydrogen at temperatures of 621, 723 and 825° C. Concentra-

tions of hydrogen approximating  $1H_2 : 2 \text{ Oil Gas}$  and  $2H_2 : 1 \text{ Oil Gas}$  were those studied. It has been shown what results may be expected in the decomposition of a hydrocarbon oil when temperature, rate of oil feed, and concentration of admixed hydrogen are carefully controlled.

5—The relationship between the rate of oil feed and the rate of gas generation has been brought out.

6—The proportions of illuminants, saturated hydrocarbons, and hydrogen resulting at varying rates of oil feed, and at temperatures of 621, 723 and 825° C. have been shown graphically and discussed.

7—The effects of hydrogen on the reactions which give rise to saturated hydrocarbons and illuminants have been shown graphically and discussed at some length. Besides its effect in hydrogenating olefins and other hydrocarbons, the hydrogen, since its addition causes an increase in the total volume of the gas passing through the heated zone of the furnace in a given time, decreases the time of contact of the gases with the heated walls of the resistor tube. The effects of this are discussed in connection with the curves showing the relationships between the components of the gas when the oil is cracked in hydrogen.

8—The mean molecular weight of the olefins in a series of gases made at 825° C. has been determined, and also the proportion of aromatic hydrocarbons in these gases.

9—The formation of tar was studied at the various oil rates, temperatures and concentrations of hydrogen.

10—Curves showing the number of cc. of illuminants, ethane and methane obtainable from 1 cc. of oil have been shown.

11—In general the manner of decomposition of a paraffin hydrocarbon oil has been mapped out over a considerable range of temperature, rate of oil feed, and concentration of hydrogen.

12—The results recorded in this paper may serve as a guide to the obtaining of more desirable results in commercial operations involving the decomposition of oil for gas-making purposes.

#### CONCLUSIONS

In addition to showing the proportions of products which are obtainable under a variety of conditions, which relationships have been fully set forth in the figures shown and which it is impossible to briefly summarize, it has been concluded as a result of this investigation:

I—That the importance of radiation insofar as it is concerned in the furnishing of the energy for the production of hydrocarbon reactions has been overestimated.

II—That effects often ascribed to catalysis are in reality due to effective heat transfer by conduction and convection from the large heated surfaces exposed to the gases.

III—That the equilibrium condition is not attained in a hydrocarbon system when an oil is decomposed by heat under conditions analogous to those of carbureted water-gas manufacture.

IV—That the course of the changes involved in the breaking down of a hydrocarbon oil may be roughly traced.

<sup>1</sup> Summaries 1, 2 and 3 refer to the printed dissertation

V—That hydrogen is produced from an oil even when the cracking takes place in hydrogen.

VI—That considerable absorptions of hydrogen take place when an oil is cracked in an atmosphere of hydrogen, and this absorption is greater the higher the concentration of hydrogen, the higher the temperature (within the range studied), and the lower the oil rate.

VII—That propylene and higher olefins constitute approximately one-third by volume of the illuminants of the gas.

VIII—That the proportion of tar increases with decrease in temperature, and with increasing oil rate, particularly at the lower temperatures.

IX—That no marked and consistent difference in the amount of tar formed when an oil is decomposed alone or in hydrogen at temperatures of  $723^{\circ}\text{C}$ . or below is noticeable. At  $825^{\circ}\text{C}$ . less tar is formed when the oil is cracked in hydrogen. The tars formed below  $723^{\circ}\text{C}$ . are in large part unchanged or partly changed oil, whereas those tars formed above  $800^{\circ}\text{C}$ . are essentially composed of synthetic products.

X—That the reactions which result in decreasing the proportion of illuminants are the most rapid.

XI—That the presence of hydrogen during the decomposition of an oil has the effect of increasing largely the proportion of the carbon of the oil appearing as hydrocarbons in the gas.

XII—That within the temperature range studied the volume of illuminants produced per volume of oil increases with the temperature with one slight exception. The formation of methane is greater the higher the temperature. The formation of ethane is not large at any temperature and therefore the primary decomposition of an oil involves chiefly a splitting off of methane rather than ethane or higher homologues.

XIII—That a temperature of  $823^{\circ}\text{C}$ . is desirable in decomposing an oil provided that too great opportunity for extensive secondary and tertiary change is not given.

XIV—That with correct design of apparatus, and proper adjustment of temperature, rate of oil feed, and concentration of hydrogen it is possible to obtain gases of widely varying compositions.

The authors wish to extend to Professor Floyd J. Metzger, Professor Samuel A. Tucker and Dr. Clive M. Alexander their thanks for valuable help and suggestions received.

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## STUDIES ON THE EXTRACTION OF ROSIN FROM WOOD. I—EXPERIMENTS USING A PETROLEUM SOLVENT

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### PURPOSE OF WORK

From a technical viewpoint, the process of extracting rosin from wood with chemicals offers a promising possibility for the utilization of "fat" stumps and

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<sup>2</sup> The data obtained in these experiments were submitted by this author in partial fulfillment of the requirements for the degree of B.S. in Ch.E. in the University of Wisconsin.

other waste resinous wood. In the simple steam distillation process only the volatile constituents of the wood are recovered and this method is no longer industrially feasible on this account. In the destructive distillation process, the products are charcoal, tar, and a turpentine more or less contaminated with products from the destructive distillation of the rosin and wood substance. This turpentine, at best, does not bring as high a market price as steam-distilled wood turpentine, although the recent introduction of temperature-controlled processes has removed this objection to a large extent. Compared with these two processes, the so-called solvent or extraction process affords the recovery of wood turpentine and pine oil comparable in quality and value with the oils from steam distillation and also a medium grade rosin whose market value, under normal conditions, is practically equal to the combined value of charcoal and tar from the destructive distillation process. However, the market value is less likely to fluctuate for tar and charcoal than for rosin. Strictly speaking, the extraction and distillation processes are not comparable, because the products are quite different. These processes represent the two types which taken together cover most of the possible products to be obtained from resinous wood.

Of the several different processes proposed for treating wood, the destructive distillation method, which is by far the oldest, is also at the present time apparently the best established from the standpoint of profitable commercial operation.<sup>1</sup> The principal difficulties that have been encountered in the extraction process have been: (1) an unstable market price for rosin, and (2) high cost of operation, due largely to an excessive loss of solvent. In attempting a solution of these difficulties, there are then at least two lines of attack which may give this process a better opportunity for commercial success: (1) obtaining another product which would not be subject to very great market variations, and (2) decreasing the operating cost. The use of the extracted wood as a raw material for paper pulp has been suggested several times as a possible solution of the problem of obtaining another product. Extraction by the usual method requires wood so finely divided (shredded wood) to yield a high proportion of the rosin that the extracted material is not suitable for pulp. If the wood is large enough for pulp, the yield of rosin is decreased. Considering the high operating costs as due largely to the loss of solvent, it would seem that the problem here is largely mechanical, and its solution should not offer very great difficulties.

With these ideas in mind, it was felt that a careful study should be made of some of the fundamental operating variables of the process.

The experiments were carried on at the Forest Products Laboratory, Madison, Wisconsin. The material consisted of longleaf pine stumps from Louisiana, donated by the Long-Bell Lumber Company of Kansas City, Missouri. Acknowledgment is made to Mr. S. D. Wells, Engineer in Forest Products, of the section

<sup>1</sup> This Journal, 6 (1914), 151.



of pulp and paper, for making the experiments on the suitability of extracted chips for pulp.

#### DESCRIPTION OF PROCESS

About fifteen patents have been granted in the United States for extraction processes and apparatus since 1909, and one or two plants were built and had been operated before that time. The different patents vary chiefly in the treatment of the wood before and after applying the solvent, in the manner of applying the solvent, and in the solvent itself. In general, the process, as carried out in the commercial plant, consists in first steaming the finely divided wood to recover the volatile constituents (turpentine and pine oil), followed in some cases by evaporating out of the wood as much of the condensed steam as possible. The solvent is then applied to the wood to dissolve out the rosin. After extraction, the wood is treated to recover the solvent adhering to, or absorbed by the chips. Evaporation of the solvent leaves the rosin as a residue, the solvent being recovered for subsequent extractions.

#### EXPERIMENTAL

**APPARATUS**—The apparatus used in the experiments was an extraction battery composed of three retorts, *A*, *B*, and *C*, shown in Fig. 1. The chips were placed in the perforated baskets, *D*, each retort holding from 30 to 35 lbs. of wood. The battery was so arranged that the solvent could be forced by means of a pump, *E*, to a storage tank, *F*, from which it flowed by gravity into any one of the retorts and from that retort to each one below it. Each unit was independent of the others so that different operations could be carried on at the same time. Each retort was also connected to a vacuum pump, *G*, through a condenser, *H*, and receiver, *I*, and equipped with an open coil for direct steam and closed coils for heating the solvent.

As it was desired to boil the solvent in contact with the chips the apparatus was so arranged that this could be done without decreasing the solvent by evaporation. This was accomplished by connecting the vapor outlet line of each unit to a condenser, *J*, and receiver or trap, *K*, placed above the battery. The trap was connected to the bottom of each retort and thus allowed the vaporized solvent, after it was condensed, to flow continuously back into the retort as in a reflux condensing apparatus. By connecting the top of each retort to the top of the trap, the vapor conditions were equalized and the solvent was prevented from backing up. With these "equalizers" open, the solvent in any retort could be boiled under pressure for any desired length of time with a constant reflux of the condensed vapors.

The simple still, *L*, was used for the evaporation of the saturated solvent to recover the rosin. The still was equipped with a steam jet and was connected through the receiver, *M*, to the vacuum pump to facilitate the removal of water and heavy oils from the rosin.

**SOLVENT**—Since a petroleum distillate has been most frequently used commercially as a solvent there was selected for the experimental work, a special gasoline furnished on a guarantee to boil between 70 and 150° C.

It was found, however, that the material contained at least 20 per cent boiling under 70°, a portion boiling as low as 30°. The solvent was, therefore, fractionated in a laboratory column (4 in. in diameter), the fraction below 70° C. being removed. By distillation in a Hempel column the solvent used gave 4 per cent boiling below 70° and 95 per cent boiling below 150°.

**EXTRACTION**—It was desired to make the laboratory study as comparable as possible with extraction in a continuous commercial extraction battery. In an extraction system of this type, all units receive exactly the same treatment and in no case is fresh solvent run on to fresh material, but the solvent most nearly saturated with the substance being extracted is run on to fresh material and the most nearly spent material

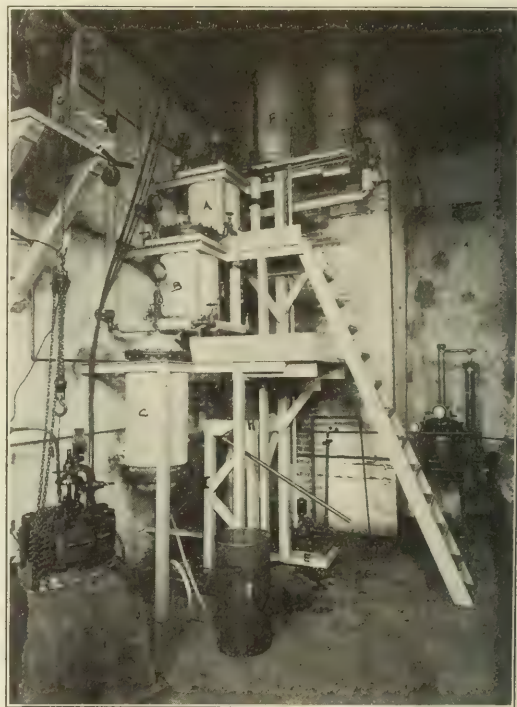
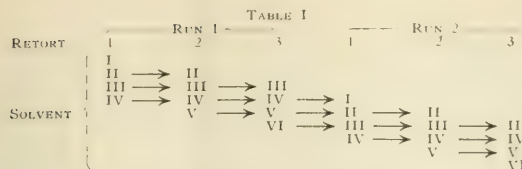


FIG. 1—EXTRACTION BATTERY

receives a final treatment with fresh solvent. This condition was approximated in a laboratory test, providing a system of four washes for each unit by employing six solvents. Three of these were distilled at the end of each run and three were used for the next run without recovering the rosin. The method may be better explained diagrammatically by referring to Table I.

Solvents I, II and III in each run were distilled for the recovery of rosin, having extracted the rosin from the wood in four retorts, while Solvents IV, V

<sup>1</sup> In purchasing solvents of this type commercially, the importance of contracts calling for extremely rigid specifications is indicated by this experience. With such a large proportion of a very low boiling fraction in the solvent it would be impossible to prevent a high solvent loss.



and VI become Solvents I, II and III, respectively, for the next run. Solvent I, in Retort 1; II, in Retort 2; and III, in Retort 3, represent the action of nearly saturated (theoretically) solvents on wood which has not been previously extracted. Solvent IV, in Retort 1; V, in Retort 2; and VI, in Retort 3, represent the final extraction of nearly spent chips with fresh solvent. Before beginning the first run, a preliminary run was necessary in order to secure Solvents I, II, and III, for the first test. After the retorts were charged in these tests, they were not opened until the dried extracted chips were removed.

The procedure used in conducting any test was briefly as follows: The chips were first steamed under 30 lbs. pressure<sup>1</sup> until no more turpentine and pine oil were obtained; the retorts were then connected to the vacuum pump from 30 to 60 min. to remove as much of the moisture as possible, steam being kept in the closed coils to facilitate evaporation. The solvent was then introduced until the chips were just covered and was then brought to boiling by means of the steam in the closed coils. The reflux system was open so that the vaporized solvent would condense, and flow back into the retort. In case the extraction was conducted under pressure the valves connecting the retort to the reflux were closed until the desired pressure in the retort was reached. The line connecting the retort with the reflux was then opened and the pressure controlled by the amount of steam passed into the closed coils. After extraction the solvent was transferred to the next retort, or in case it was the last extraction for that solvent, it was passed through a condenser which delivered it cold to the container. When the extraction was made under pressure, it was better to relieve the pressure before drawing out the solvent; this was readily done by turning off the steam and allowing condensation to continue in the reflux. When the solvent was drained out after the last extraction, that remaining in the chips was removed by steaming first at atmospheric pressure until no more solvent came off, and finally at 30 lbs. pressure for a few minutes. To insure that all the solvent was removed, the retort was then connected to the vacuum pump for about one hour. In only a few cases, however, was any more solvent recovered in this last step.

As soon as each solvent was removed after final extraction it was thoroughly stirred, and a sample taken. The weight of each solvent was taken before it was used in any run and after its final use in that run. The intermediate weights when a solvent passed from one retort to the next were not taken. In other words, the total amount of wood in the three units

of the battery was considered as the charge for the run rather than that in each retort as a separate unit. Since only three solvents were redistilled in any run and these contained some rosin from a previous run, it was not possible to determine the rosin yield from the actual rosin recovered by the redistillation of the solvent. The yields were determined by an analysis of the solvents. The total yields from several runs checked very well with the analyses.

#### ANALYSES

The efficiency of any extraction was based on a comparison of the amount of rosin in the solvents, as determined by an analysis, and the amount of rosin contained in the charge, as determined by an analysis of an average sample of the wood.

WOOD—A sample of the charge was taken by quartering the wood in each retort until the desired amount (about 1/2 lb.) was obtained. A portion of the sample from each retort was then ground to the fineness of sawdust and a moisture determination made by the xylol method,<sup>1</sup> generally employed in estimating moisture in wood which contains a volatile oil. An equal portion of the finely ground sample from each retort was extracted in a Soxhlet with chloroform. On drying the extracted sample to constant weight at 110° C. the weight of the wood free from moisture, rosin, and volatile oil was obtained. The extract from the Soxhlet was then evaporated in an oil bath kept at 150° C. After the chloroform had all distilled off a small jet of steam at slightly reduced pressure was passed through the rosin. This was continued for 1/2 hr. and the residue was then dried by using a much higher vacuum for 1/2-hr. intervals, without the steam, until the rosin showed a loss of less than 0.2 per cent for two successive treatments. Continued heating caused some decomposition, so that drying could not be carried to constant weight. The final residue was then taken as rosin. Since moisture and rosin and the extracted wood were determined the volatile oil was estimated by difference. The method is not entirely satisfactory, but since it is not practicable to determine volatile oil in so small a sample, and thus determine rosin by difference, it was felt that rosin could be determined as the non-volatile chloroform extract. Duplicates checked within 0.003 to 0.005 per cent and errors that were large enough to be of consequence to the experiment fell back on the sample itself. It is, furthermore, not strictly correct to compare the petroleum extraction with the chloroform control since there were probably small portions of the rosin that were insoluble in petroleum but were soluble in chloroform.<sup>2</sup> The extraction efficiencies were, therefore, lower than if based on the total petroleum soluble rosin present in the wood.

EXTRACTION—The yield of rosin in the tests was determined, as stated above, by an analysis of the different extracts. The amount of rosin in a weighed portion (about 200 g.) was determined in practically the same manner described for estimating the rosin

<sup>1</sup> THIS JOURNAL, 4 (1912), 789; also F. S. Bull 109, "Distillation of Resinous Wood with Saturated Steam."

<sup>2</sup> F. S. Circ. 134, "Estimation of Moisture in Creosoted Wood."

<sup>3</sup> Allen, "Commercial Organic Analysis," chapter on Colophony.



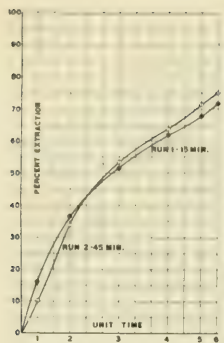


FIG. II—EFFECT OF TIME

Chip,  $\frac{3}{16}$  in.  
Pressure, 0 lbs.

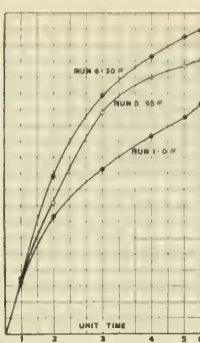


FIG. III—EFFECT OF PRESSURE

Chip,  $\frac{3}{16}$  in.  
Extraction, 15 min.

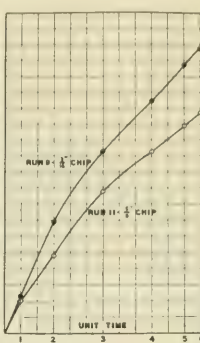


FIG. IV—EFFECT OF SIZE OF CHIP

Pressure, 30 lbs.  
Extraction, 15 min.

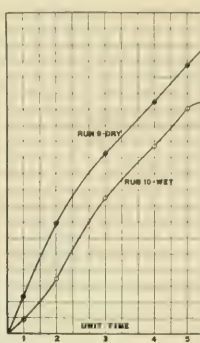


FIG. V—EFFECT OF MOISTURE

Chip,  $\frac{3}{16}$  in.; Pressure, 30 lbs.; Extraction, 15 min.

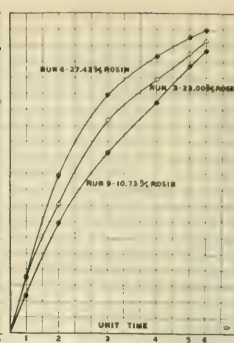


FIG. VI—EFFECT OF ROSIN CONTENT

Chip,  $\frac{3}{16}$  in.; Pressure, 30 lbs.; Extraction, 15 min.

in the chloroform extract, except that the residue was not steam-distilled because no appreciable amount of high boiling oils, such as pine oil, was left in the wood and rosin after the chips were thoroughly steamed.

#### SCOPE OF EXPERIMENTS

The experiments in this first series included a study of the more important fundamental operating variables on the efficiency of the extraction: (1) time, (2) pressure, (3) size of material, (4) moisture, and (5) effect of rosin content on the percentage yield of rosin, based on the amount originally present. The tests also included a preliminary study of the suitability of the extracted material for paper pulp. Two sizes of chips, averaging  $\frac{3}{16}$  in. and  $\frac{5}{8}$  in. with the grain of the wood, were selected for the tests. The  $\frac{3}{16}$ -in. chip is larger than the usual commercial chip used in the extraction process, but is considered the minimum size for making pulp. The material was prepared in a semi-commercial pulp chipper. The wood in each case comprised the whole of the stump including the outer bark. All of the stumps had the roots removed and were practically free from earth and sand.

TABLE II—EFFECT OF VARIOUS FACTORS ON EXTRACTION OF ROSIN

EFFECT ILLUSTRATED	Run No.	Time Min.	Chip In.	Pressure Lbs.	% Rosin in Wood	Rosin Yield Per cent
TIME	1	15	$\frac{3}{16}$	0	29.92	72.6
	2	45	$\frac{3}{16}$	0	25.10	75.0
	3	15	$\frac{3}{16}$	30	23.00	91.60
	4	45	$\frac{3}{16}$	30	25.92	93.70
	11	15	$\frac{5}{8}$	30	12.90	68.5
	12	45	$\frac{5}{8}$	30	12.23	68.9
PRESSURE	1	15	$\frac{3}{16}$	0	29.92	72.6
	6	15	$\frac{3}{16}$	30	27.43	94.3
	5	15	$\frac{3}{16}$	55	29.35	85.3
	2	45	$\frac{3}{16}$	0	25.1	75.0
SIZE OF CHIP	4	45	$\frac{3}{16}$	30	25.92	93.7
	9	15	$\frac{3}{16}$	30	10.73	88.8
	11	15	$\frac{5}{8}$	30	12.9	68.5
	4	45	$\frac{3}{16}$	30	25.92	93.7
MOISTURE, High... Low	12	45	$\frac{5}{8}$	30	12.5	68.9
	9	15	$\frac{3}{16}$	30	10.73	88.2
	10	15	$\frac{3}{16}$	30	10.7	72.1
	10	15	$\frac{3}{16}$	30	10.7	72.1
ROSIN CONTENT	7	15	$\frac{3}{16}$	0	13.32	70.8
	1	15	$\frac{3}{16}$	0	29.92	73.6
	9	15	$\frac{3}{16}$	30	10.73	88.8
	3	15	$\frac{3}{16}$	30	23.00	91.6
	6	15	$\frac{3}{16}$	30	27.43	94.8

#### RESULTS

**EFFECT OF TIME**—Fig. II, based on the results of Runs 1 and 2 (Table II), shows the progress of the ex-

traction. The curve is obtained by plotting the percentages of rosin recovered as ordinates, and the time the solvent was in contact with the wood as abscissas. Referring to Table I, which shows the procedure used in the test, it is seen that in any run Solvent I is in contact with the wood only for the unit time, which is 15 min. for Run 1. Solvent II, however, is in contact with the wood twice as long as Solvent I, Solvents III and IV three times as long as Solvent I, and Solvents V and VI for the same time as Solvents II and I, respectively. The units on the abscissa, therefore, represent the progress of extraction. Since each solvent was analyzed before its first and after its last application, the proportion of the total rosin extracted by each solvent in any run could be determined.

It will be seen that the effect of increasing the time from 15 to 45 min. is slight for the three sets of conditions used, and for practical purposes 15 min. is evidently the maximum time necessary. In Runs 3 and 4, which gave the highest yields, the efficiency was increased only 2.1 per cent when the time was increased threefold. In Fig. II it will be noticed that in the 15-min. extraction a larger proportion was recovered with the first two solvents than when the time was 45 min. This same condition was shown in corresponding curves for Runs 3 and 4 and 11 and 12, but no logical explanation of this was made evident during the experiment.

**EFFECT OF PRESSURE**—The progress of the extraction for Runs 1, 5 and 6, shown in Fig. III, is typical of the effect of pressure. The figure shows that the rosin recovered was increased from 72.6 per cent to 94.3 per cent by increasing the pressure from 0 to 30 lbs. At 55 lbs. pressure there is an apparent break in the curve, and a decided decrease in per cent recovery as compared with 30 lbs. pressure. Since, in a study of the penetrance of creosote in long-leaf pine heartwood at the Forest Products Laboratory,<sup>1</sup> a decided decrease was noted as the pressure was increased from 50 to 75 lbs., the cause of the decreased efficiency of extraction may be a physical

<sup>1</sup> U. S. Dept. of Agric., Bull. 101, "Relative Resistance of Various Conifers to Injection with Creosote."

one. It seems more probable, however, that the explanation is more of a chemical nature and may be due to an increase of the insoluble constituents of the rosin at the higher temperatures, although there was no apparent effect of the higher temperatures on the quality of the rosin recovered. The effect of increasing the pressure in the 45-min. extraction was practically the same as for the shorter time.

**EFFECT OF SIZE OF CHIP**—Fig. IV shows the curve of extraction for Runs 9 and 11. Increasing the size of the chip to  $\frac{5}{8}$  in. decreases the efficiency of extraction from approximately 90 to about 70 per cent, and the result is practically independent of the time of extraction. In the studies of the penetration of creosote in longleaf pine heartwood referred to above, it was also shown that the ratio of longitudinal to radial penetration was 26 : 1, and of longitudinal to tangential was 100 : 1. For practical purposes the action of the solvent is, therefore, almost entirely in the longitudinal direction, which is also the same direction as most of the resin ducts, that is, with the grain in the wood. The decrease in the rosin removed from the longer chips is then undoubtedly a question of decreased penetration of the solvent into longer resin ducts. Since giving the solvent a longer time to penetrate does not increase the yield, as seen in Runs 11 and 12,<sup>1</sup> it seems safe to predict that additional pressure is necessary to penetrate to the center of the longer chips. A continuation of those studies will determine the accuracy of this supposition.

**EFFECT OF MOISTURE**—After steaming the chips for the removal of volatile oil preparatory to extraction, it was the usual procedure to pull a vacuum of about 20 in. on the retort for  $\frac{1}{2}$  hr., the retort being kept hot by means of steam in the closed coils in order to remove as much as possible of the excess moisture caused by steaming. In general, the water removed in this way was equivalent to about 30 per cent of the dry weight of the wood, but the ratio of this amount to the total moisture in the chips after steaming was not determined. As several patents call attention to this feature of the process it was desired to determine its effect. A run was made, therefore, in which the vacuum was omitted and the solvent was run directly on to the chips after steaming. The results of this run compared to a similar run in which the vacuum was used are given in Table II and the progress of the extraction for the two runs is shown in Fig. V.

The effect of removing a comparatively small amount of moisture by the vacuum treatment is more pronounced than might be supposed, since the efficiency is increased over 15 per cent. It will be noted in the curve that the extraction is most retarded at the start; and it is, therefore, quite possible that the excess of moisture is removed by the first wash, after which the extraction proceeds more normally. When the water has once boiled off with the gasoline vapor

and, on condensing in the reflux, flows back into the bottom of the retort, it probably does not interfere to any extent with the extraction. By taking the condensed solvent from the top of the trap in the reflux line it would be possible to get rid of this excess water in a short time, since the moisture could be drawn off at the bottom of the trap and thus be removed from the system. With such an arrangement, increasing the time of extraction should then give almost as high efficiency as when the chips are dried by the vacuum unless, in addition to removing the surface moisture, the vacuum has some mechanical action of opening up the ends of the exposed resin ducts and thus facilitates the penetration of the solvent. It is desired to test this point in future experiments.

**EFFECT OF ROSIN CONTENT**—These tests on the effect of different variables were made on samples of quite different rosin content, one lot being comparatively rich and varying from 23 to 30 per cent rosin, and another lot being comparatively low in rosin and varying from 10 $\frac{1}{2}$  to 13 $\frac{1}{2}$  per cent. An analysis of the data (Table II) from runs made under the same extraction conditions but with chips of different rosin content is of interest.

Runs 3, 6 and 9, made at 30 lbs. pressure and 15 min. extraction, are shown graphically in Fig. VI. It is seen from the table that a higher percentage of rosin is recovered from woods of greater rosin content and the higher recovery is evident throughout the progress of the extraction as shown in the figure. This is probably due to the fact that there is a larger proportion of the rosin which has saturated the cells surrounding the resin ducts proper in the richer wood and this rosin is, therefore, made more accessible to the action of the solvent. The wood containing 13.5 per cent rosin is about as low in rosin as could be extracted commercially.

#### SOLVENT LOSS

The apparatus used in the test was not found to be entirely suitable for the study of the loss of solvent. Because of errors in construction the solvent collected in pockets in the piping and it was, therefore, not recovered until another run. There were also noticeable leaks at several points. In general it was apparent that extraction under pressure tended to increase slightly the amount of solvent retained in the chips but there was no difficulty in recovering this solvent on subsequent steaming. With evident leaks in the apparatus, increasing either time or pressure

TABLE III—SOLVENT LOSSES IN VARIOUS RUNS

Run No.	CHIP In.	PRESSURE Lbs.	TIME Min.	SOLVENT LOSS Per cent	ROSIN YIELD Per cent
2	3.16	0	15	2.38	72.6
7	3.16	0	45	6.87	75.0
3, 6, 9 (Av.)	3.16	30	15	3.46 (a)	91.5
4	3.16	30	45	4.30	93.7
5	3.16	55	15	3.74	85.3
11	5.8	30	15	3.46	68.5
12	5.8	30	45	3.85	68.9

(a) Varied from 3.16 to 3.79.

would, of course, increase the solvent loss. The amount lost in several of the runs is shown in Table III. While the data do not show clearly the effect of the different time and pressure conditions on sol-

<sup>1</sup> The more pronounced effect of increasing the time used in Run 4 to that used in Run 9 may be largely explained by the higher rosin content of the wood used in Run 4, as will be shown in the discussion to follow.



vent loss, it may be noted that a longer time seemed to give a greater increase in solvent loss than a higher pressure.

It was possible to determine approximately the proportion of this loss that occurred in the redistillation of the solvent and this averaged about 10 per cent of the total. The solvent loss will be taken up in detail in a later study.

#### FORMATION OF A PRECIPITATE

An interesting point that came up in the experiments was the discovery of a precipitate in the solvent removed from the chips, especially after extracting wood of high rosin content. Yaryan<sup>1</sup> calls attention to a black pitchy substance which precipitates out of the rosin solution and which he says is due to the action of fire on the stumps or lightwood. The precipitate was at first dark brown, later becoming black; it was quite sticky, and was first thought to be some constituent of the rosin insoluble in petroleum. Further examination indicated that it was largely basic ferric acetate which carried down a small amount of rosin with it. It was no doubt formed by the attack of the iron retorts by the free acetic acid occurring in the old wood, the acetate of iron formed becoming the insoluble basic salt at the high temperature of the boiling solvent. In some of the runs the precipitate amounted to as much as 1 per cent of the dry weight of the wood.

#### SUITABILITY OF THE EXTRACTED CHIPS FOR PULP

Only preliminary experiments have been made with the extracted chips. It was desired first to determine the quality of pulp that could be obtained from the  $\frac{3}{16}$ -in. chip although it seemed that this size would give too short a fiber length for good pulp. By using the sulfate process the unscreened chips from Runs 6 and 9 were cooked in a semi-commercial digester. The time of cooking was 1 hr. in getting up the pressure, and 2 hrs. at 100 lbs. pressure. The cooking liquor contained 15.7 lbs. NaOH and 7.5 lbs. Na<sub>2</sub>S per 100 lbs. of wood. The pulp yield was 43.2 per cent of the dry chips. Two beater treatments were made on the "half stuff," the duration of beating being 5 hrs. in each case. In one run the beater roll was hard down during the last hour, while in the second run the stock was much more dilute and the roll was set so as to give a comparatively light brush. The pulp was run over the machine and the sheets from the two beater treatments gave the following strength tests. The figures from what may be considered a No. 1 Kraft are given in the following table for comparison.

PAPER	STRENGTH FACTOR Points per lb.	SCHOPPER TEST Breaking Length in Meters	FOLDING TEST Times	WEIGHT PER REAM Lbs.
Beater Run No. 1.....	0.72	5425	800	40
Beater Run No. 2.....	0.65	4730	367	38
No. 1 Kraft.....	1.00	6000	1500	40

While Run 1 was stronger, Run 2 gave a softer sheet. Both were a very fair grade of No. 2 Kraft. Further tests will be made by using the larger chips, but since the small chip gives such promise of being

suitable for pulp, they are more desirable, since it is possible to get so much higher yields of rosin from them by extraction.

#### CONCLUSIONS AND THEIR COMMERCIAL APPLICATION

The results of these experiments seem to indicate that a solution of the problem of obtaining another product in the extraction of resinous wood by the solvent process may be found in using a larger chip, whose minimum size is  $\frac{3}{16}$  in., and extracting under a maximum pressure of 30 lbs. by using four washes of 15 min. each. A closed type of battery in which the vaporized solvent can be returned continuously to the retort is advantageous for extracting under pressure. Extraction under pressure for a short time is shown to give much higher yields of rosin than no pressure for a longer time.

As noted in the results given above, the yields by petroleum extraction are based on control analyses made by using chloroform as solvent. It was observed that certain constituents of the rosin are insoluble in petroleum but are soluble in chloroform. Since it is also shown that increasing the time of extraction has no appreciable effect at 30 lbs. pressure, and since 94.8 per cent were recovered under those conditions, it would seem possible that practically all of the petroleum-soluble rosin was extracted at this pressure. It is probable, therefore, that a lower pressure would be as efficient as 30 lbs.

Chips as small as  $\frac{3}{16}$  in. are apparently suitable for paper pulp as they gave a good grade of No. 2 Kraft by the sulfate process. Chips of this size could probably be most advantageously cooked commercially in a rotary type of digester. A plant extracting wood yielding about 250 lbs. or 1.09 bbls. of "F" grade rosin per ton (89 per cent yield of 14.0 per cent rosin), which is about the minimum for practicable commercial operation, would produce extracted chips suitable for making about 750 lbs. of pulp per ton of wood. A 50-ton extraction plant would then supply a 20-ton pulp mill, or since an extraction plant might require about three-quarters of its extracted chips as fuel in case it were not advantageous to buy other fuel, a 200-ton plant would have chips for fuel and still could supply a commercial pulp mill of practicable size.

It is difficult to give cost figures to cover the variety of contingencies met with commercially, but the following estimates of average practice show clearly the effect on the net returns of obtaining extracted chips as an additional valuable by-product.

COST ESTIMATE PER TON ON 200-TON EXTRACTION PLANT			
Cost of Operation		Prices for past 15 yrs.	Returns at Average
WOOD	\$ 2.25	6 gals. turpentine and pine oil at 40 c.	\$ 2.40
SOLVENT 71 gals at 12 c.	0.90	250 lbs. rosin at 1.5 c.	
FUEL 1 ton extracted chips at no cost	0.00	(3.772 2 per net bbl. of 230 lbs.)	3.75
COOPERAGE	0.65		
Superintendence and Labor	0.87		
Selling and shipping, including freight	0.72	Cost of operation	\$6.15
Taxes, insurance and depreciation over 15 years	0.35		5.92
Repairs and miscellaneous	0.18	Net profit	\$0.23
	\$5.92	Selling price 250 lbs. extracted chips at \$1.00 per ton	0.25
		Net profit with chips as by-product	\$ 0.48

<sup>1</sup> U. S. Patent 934,257.

The plant would pay 5.5 per cent on an investment of \$250,000 without the chips and 11.5 per cent assuming the chips to be worth \$1.00 per ton for pulp, which is a low estimate since the material would be in condition for immediate pulping.

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### SOME STUDIES OF SOAP SOLUTIONS

BY VICTOR LENSHER AND MARY V. R. BULL

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The chemical analysis of a soap shows only the constituents of which it is composed. The results indicate the content of water, fatty acid as soap, unsaponifiable matter, alkali (combined or free), glycerin, salt, filler, etc. No satisfactory method has been proposed for the determination of the real value of a soap, namely, its cleansing power. From the time of Chevreul, one of the first to study soap, to the present day, considerable literature has accumulated on the cleansing power of soap. Some of the work is experimental, and some is purely speculative, but with all the thought and energy which has been expended on this subject it must be confessed that we do not possess sufficient data to explain satisfactorily the phenomena ordinarily exhibited by soap solutions, nor can the chemist tell the laundry how much soap is required to remove a definite amount of dirt or wash a given weight of soiled clothing.

Various phases of the question as to how soap acts as a detergent have been studied at different times. These studies are well summarized by Bancroft in his papers on emulsification, now running in the *Journal of Physical Chemistry*.

The various methods which have been suggested from time to time for the evaluation of soaps, have depended largely on the use for which the soap is intended. Hillyer<sup>1</sup> divides soaps into two classes: those used with cold or lukewarm water, such as toilet soaps; and those used with boiling water, as laundry soaps. His method for determining the detergent value of soap is by the Traube stalagmometer method for determining the surface tension of a soap solution against a kerosene which he arbitrarily adopted as a standard. The number of drops formed in a given length of time is regarded as a measure of the amount of soap in solution, the emulsifying power of the soap, and its cleansing power. The number of drops is referred to a curve obtained by running standard solutions of neutral sodium palmitate through standard kerosene and the relative efficiency of the soap is thus approximated. In testing soaps intended for use with hot water, the whole of the apparatus is surrounded by a water bath which is kept at the desired temperature.

Luksch<sup>2</sup> attempted to determine the efficiency of a soap by coloring pieces of chiffon of different sizes and washing them under the same conditions in a washing machine. The results varied 10 per cent, but were sufficiently accurate to show the difference between different soaps. He also studied the weaken-

ing effect of the soaps on the fibers by making tensile strength determinations.

**SURFACE TENSION.** In most of the theories which have been brought forth to explain the detergent value of soap, surface tension has played an important part. In order to study the relation between surface tension and concentration, a number of experiments were made by means of the Traube stalagmometer. While the Traube stalagmometer method for surface tension determinations possesses certain objections, these errors are of minor rather than major character. It was found to suffice in this work, inasmuch as the results are comparative.

A bulb was blown in the stalagmometer so that 5 cc. would be the quantity delivered, and a device used whereby the pressure could be regulated. The whole was surrounded by a water bath and the outlet allowed the drops to form in the air or in a given liquid. In the measurements made by this method, the number of drops were counted and the time taken when a definite volume of liquid was allowed to flow out through the pipette.

Sodium oleate solutions were prepared from pure sodium hydroxide and very pure oleic acid. When soap solutions are made to form drops under the surface of an oil or of a liquid immiscible with water, the number of drops formed is much greater than when an equal volume of water is made to form drops under similar conditions, that is, the surface tension between oil and water is much greater than the surface tension between oil and soap solution, or, the surface tension is inversely proportional to the number of drops formed. The relation between concentration of soap solutions and their surface tensions toward some liquids immiscible with water is shown in the accompanying curves. In all cases the temperature was controlled at 25°.

The first point on each of the curves is not as accurate as the others because at the *N*/10 concentration hydrolysis is fairly rapid. The significance of the points is that they show the general direction of the curves. The error of the observations is considered to be approximately 0.5 per cent. Theoretically, the point of minimum surface tension should be at the point at which the maximum number of drops is formed. In all of the cases investigated, with the single exception of the experiment with air, the surface tension was lower with the concentrated solutions than with the dilute solutions, and the general direction of the curves is the same.

It has been observed that the surface tensions of sodium oleate solutions toward air are increased with the dilution. The actual surface tensions of various concentrations of sodium oleate solution toward air were found by the Traube stalagmometer method to be at 25° as follows, expressed in dynes per centimeter:

<i>N</i> 10	<i>N</i> 20	<i>N</i> 40	<i>N</i> 80	<i>N</i> 160	<i>N</i> 320	<i>N</i> 640	<i>N</i> 1280
28.20	26.21	25.33	24.17	24.77	24.91	25.55	41.28

By the same method water showed 71.78 toward air. It is interesting to note that with *N*/10 to *N*/320 sodium oleate there is such a small variation in the

<sup>1</sup> *J. Am. Chem. Soc.*, **25**, 1256.

<sup>2</sup> *Seifensieder-Ztg.*, **40**, 413, 444.

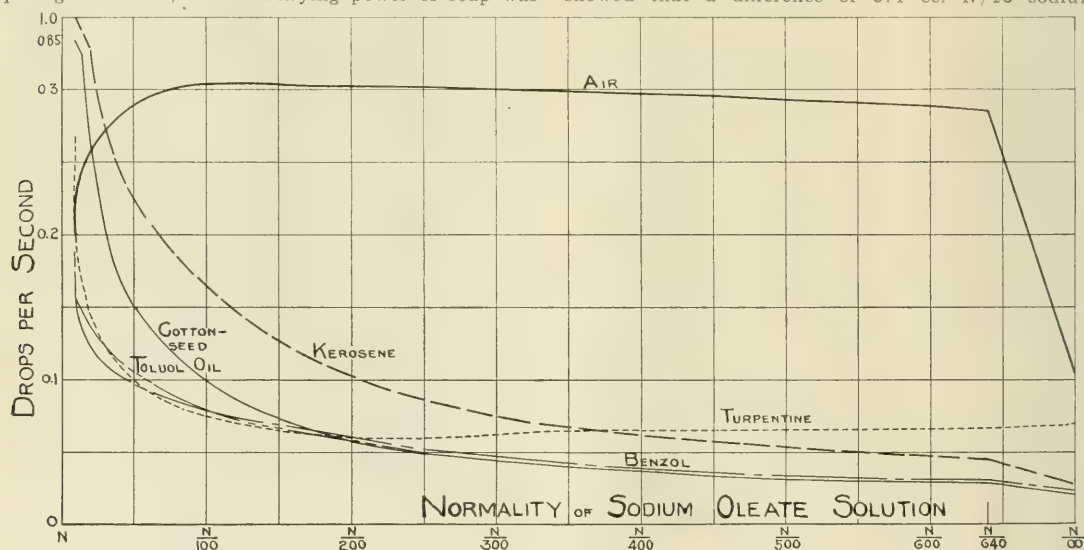


surface tension, especially when the surface tension is so different from that of water. The solutions in this range of concentration are the ones which foam so well. When a dilution of  $N\ 0.40$  is attained the solutions commence to take on a milky appearance. The fact that the foaming is so much more profuse between  $N/80$  and  $N/320$  affords evidence to the view that in these concentrations we have the soap acting as an emulsifier to produce the foam which is an "emulsion of air in soap solution."

While the above observations were taken at  $25^\circ$ , a study was made at temperatures of  $20$ ,  $22$ ,  $24$  and  $25^\circ$ , and it was found that within this range of temperature the surface tension measurements if plotted as a curve form a straight line, showing that the rate of flow is directly proportional to the temperature.

#### EMULSIFYING ACTION OF SOAP

Following the lines of our modern methods of preparing emulsions, the emulsifying power of soap was



studied. Emulsions of kerosene and water were made by shaking kerosene with an excess of soap solution in a wide-mouthed, glass-stoppered bottle. After the mixtures had stood for a few minutes, the excess of soap solution separated out at the bottom of the bottle, leaving all of the kerosene emulsified in the upper layer. These emulsions remained permanent for months. If insufficient soap is present when one attempts to make an emulsification of this character, either no emulsification or only partial emulsification takes place.

In order to study this emulsifying action of the soap with water and immiscible liquids, it is noted that, as with other emulsions, simply a uniform shaking, such as given by a shaking machine, is insufficient. A shaking machine, even when running at high speed, gives unsatisfactory results. In fact, a shaking machine does not give as satisfactory results as does the jerky double motion given by hand. The ap-

paratus found to be best adapted for the purpose was a thin stirring paddle made of German silver in which a large number of holes were cut. The paddle was electric motor-driven and the jar in which it was revolved was immersed in a constant temperature bath.

Whenever possible, equal volumes of water and immiscible liquid were used and the amounts of soap varied. In the first experiments, the object was to ascertain the minimum quantity of soap which would act as an emulsifier under definite conditions. An emulsion was considered satisfactory if there was no visible separation of either constituent at the end of 5 min., the time of stirring being 5 min. This standard is not so arbitrary as it might seem at first sight, because in most cases if the emulsion separates at all, it does so in the first half-minute. This is especially true of the emulsions produced at the lower temperatures. A test of the accuracy of the method showed that a difference of  $0.1$  cc.  $N/20$  sodium

oleate solution, corresponding to  $0.0015$  g., could be readily detected. In the results given, the accuracy has not been worked out to such a high degree, but is approximately  $0.5$  cc.  $N/20$  sodium oleate, or,  $0.0075$  g. The experiments were conducted at  $20^\circ$  and the water used was highly purified.

SUBSTANCE	WATER Cc.	SODIUM OLEATE NECESSARY FOR EMULSIFICATION Grams
50 cc. Turpentine.....	50	0.6331
50 cc. Carbon Tetrachloride.....	50	0.1140
50 cc. Chloroform.....	50	0.7824
50 cc. Benzol.....	50	0.9804
2.5 g. Vaseline.....	50	1.5200

It is obvious that entirely different amounts of soap are necessary to emulsify under the same conditions the same volume of different substances which are immiscible with water. The experiment with vaseline can hardly be compared with the others, nor is its accuracy so great on account of the physical condition of the vaseline, but is introduced simply to show its behavior under these conditions.

## EFFECT OF CONCENTRATION ON EMULSIFICATION

The effect of the relative amount of water present in emulsions with turpentine was observed.

TURPENTINE Cc.	WATER Cc.	N/20 SODIUM OLEATE NECESSARY Cc.	TOTAL VOLUME OF WATER Cc.	SODIUM OLEATE NECESSARY Gram
25	0	30	30	0.4560
25	25	18	43	0.2736
25	50	8	58	0.1216

It follows from these results that weak solutions of sodium oleate are more economical in the emulsification of turpentine with water than the more concentrated solutions. It is, therefore, apparent that the volume of water in which a given amount of soap is dissolved is an important factor in its detergent effect.

## EFFECT OF TEMPERATURE ON EMULSIFICATION

TEMPERATURE	SUBSTANCE	WATER Cc.	SODIUM OLEATE NECESSARY Gram
20° C.	50 cc. Chloroform	50	0.7828
50°	50 cc. Chloroform	50	0.4636
20°	50 cc. Olive Oil	50	0.6384
100°	50 cc. Olive Oil	50	0.3040

It is evident from these observations that a definite amount of sodium oleate will emulsify more of these materials at high temperatures than at low temperatures. The emulsions produced are, however, not so stable at high temperatures as the low temperature emulsions. The emulsions were, however, permanent for 5 min. in all cases. For this kind of a study no objection can be raised to emulsification of this character, inasmuch as in the actual process of washing, as soon as the emulsion is formed, it is washed away. It is in general true that sodium oleate solutions wash more efficiently at high temperatures than at low. Soaps which are relatively high in oleic acid content are often spoken of as cold water soaps. From this it might be inferred that they wash better in cold water than in hot. This is not the case. It is true that they wash better in cold water than the stearate or palmitate soaps, which have only a slight detergent action in cold water. In general, the oleates wash better in hot water than in cold.

## EFFECT OF AGE ON SOAP SOLUTION

Strong solutions of sodium oleate decompose on standing with the formation of a precipitate which in chemical composition is an acid soap. This precipitate is relatively insoluble and cannot be entirely brought back into solution by boiling. Experiments were made to find the relative emulsifying power of fresh N/10 sodium oleate solutions, and of N/10 solutions in which this precipitate had formed. The solutions were thoroughly shaken in order to insure the precipitate being uniformly suspended through the solution.

SUBSTANCE	WATER ADDED TO MAKE UP TO Cc.	AGE	SODIUM OLEATE NECESSARY Gram
50 cc. Chloroform.....	50	Fresh	0.7828
50 cc. Chloroform.....	50	3 mo.	0.7904
50 cc. Chloroform.....	50	4½ mo.	0.7965

From these experiments it is evident that the emulsifying power of sodium oleate solutions is impaired only very slightly by the hydrolysis, and a soap solution which has stood for a long time washes appar-

ently as well as water in which the soap has been freshly dissolved.

## COMPARATIVE EMULSIFYING POWERS OF THE SODIUM SOAPS WHEN USED HOT

A comparison of the emulsifying powers of pure sodium oleate, stearate and palmitate has been made. N/20 solutions of the three soaps were prepared from the pure fatty acids and pure sodium hydroxide. The solutions of the stearate and palmitate were prepared hot. Both the stearate and palmitate solutions solidify to a jelly on cooling. It is obvious that when a sufficient concentration is necessary to emulsify an immiscible liquid with water, it is necessary that these soaps be used at a high temperature. Such liquids as benzol, carbon tetrachloride and chloroform as were used at lower temperatures were not serviceable at 100°. Highly inflammable liquids could not be used in our apparatus; hence olive oil was selected as the most satisfactory liquid for the purpose. The end-points are not as definite at high temperatures as at 25°. The oil was well emulsified by very small quantities of soap, but a considerable excess of soap is necessary to render the emulsions permanent for 5 min.

TEMPERATURE	OLIVE OIL Cc.	WATER TO MAKE UP TO Cc.	REQUIRED FOR EMULSIFICATION
100° C.	25	25	0.1672 g. Sodium Oleate
100°	25	25	0.1390 g. Sodium Palmitate
100°	25	25	0.2250 g. Sodium Stearate

In this comparison it appears that at 100° sodium palmitate emulsifies olive oil more efficiently than the oleate or the stearate. These data are very suggestive as to the relative detergent values of the three soaps at the boiling temperature, but more experiments should be made along these lines with various substances before it is possible to generalize.

## SUSPENSIONS

In studying the action of soap solutions with suspended matter, such as ferric oxide and manganese dioxide, concentrations of sodium oleate from N/20 to N/1280 were used. 250 cc. of the sodium oleate solutions were shaken up with the sifted minerals and allowed to stand from 5 days to 3 weeks. The results with the two minerals were of the same order, and though it was impossible to make accurate quantitative measurements, it was noted that the maximum suspension invariably occurred with about N/320 solution.

Further studies on soap solutions are in progress in this laboratory.

UNIVERSITY OF WISCONSIN, MADISON

## VANILLA EXTRACT

By J. R. DEAN AND J. O. SCHLOTTERBECK

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(Concluded from our previous issue)

## SECOND-GRADE EXTRACTS

The conclusion reached in regard to the use of alkali was entirely in regard to a first-class extract where the aroma of the extract is of the greatest importance. It is often desirable, however, to prepare second-



grade extracts, either from second grade beans or from the dregs left in the manufacture of the highest grade product. Here it would seem that the use of a little alkali might prove of value. These secondary extracts are never of as high a quality as the first-grade extracts and are usually incorporated into substitutes or imitations with coumarin or tonka extract. By the careful use of alkali it would be possible to obtain a nicely colored product and, although its flavor would not be equal to a pure extract, the addition of vanillin, coumarin or tonka extract, would tend to make up this lack of flavor. Such an extract could not be sold as a pure extract of vanilla and it is not a very difficult problem to prove that such an extract is not official.

It is doubtless certain that there are a great number of such extracts on the market, some of which are represented to be straight extracts. Their flavors differ greatly, but some are fairly good and are comparable with some straight extracts. There is a difference, however, and it will usually make itself appar-

The behavior of the ash indicated that an alkali had been used on exhausted beans and that the extract had not been made from prime vanilla beans. The flavor of this extract was fairly good, but it was far from being equal to a pure extract of vanilla.

#### SUGAR, SAND AND GLYCERIN

Sugar and sand, independently and together, packed with the beans in the percolator, tend to make possible a more uniform pack and reduce the chances of the menstruum forming canals through the pack, leaving part of the beans untouched. We made several extracts with both sugar and sand and each separately to see if either would be of any more service than the other in yielding a more complete extraction, but it was found that they are of about the same value.

In Table I we report the results obtained from extracts made with both, together and independently. In some of these, especially those made from undried beans, there were noticeable variations, but the variations were not constant and often conflicting. This

TABLE IV—DIFFERENT MENSTRUUA WITH AND WITHOUT SUGAR, SAND AND GLYCERIN(a)

BEANS	PERCENTAGES		LEAD	EXTRACT		FILTRATE		RATIO OF RED TO YELLOW	REMARKS
	Alcohol	Vanillin		Red	Yellow	Red	Yellow		
Mexican	60	0.19	0.70	33.0	103.0	1.8	7.1	1:3.1	Alcohol and sand
	60	0.19	0.65	35.0	103.0	2.0	8.6	1:2.9	Alcohol and sugar
	60	0.16	0.69	41.0	123.0	2.0	8.8	1:3.0	Alcohol and glycerin(b)
	35	0.17	0.82	31.0	75.0	1.8	6.6	1:2.4	Alcohol and sand
	35	0.17	0.79	28.0	75.0	2.0	7.5	1:2.4	Alcohol and sugar
	35	0.18	0.80	40.0	90.0	2.0	7.5	1:2.3	Alcohol and glycerin
Bourbon	60	0.19	0.61	34.0	108.0	1.9	8.2	1:3.2	Alcohol and sand
	60	0.19	0.57	39.0	119.0	2.4	10.0	1:3.1	Alcohol and sugar
	60	0.20	0.58	43.0	133.0	2.0	9.6	1:3.1	Alcohol and glycerin
	35	0.17	0.71	30.0	73.0	1.8	7.0	1:2.4	Alcohol and sand
	35	0.17	0.66	31.0	78.0	2.2	8.0	1:2.4	Alcohol and sugar
	35	0.19	0.68	50.0	110.0	2.4	8.4	1:2.2	Alcohol and glycerin
Tahiti	60	0.11	0.43	13.0	40.0	0.6	2.6	1:3.1	Alcohol and sand
	60	0.11	0.44	15.0	40.0	0.7	3.1	1:2.7	Alcohol and sugar
	60	0.11	0.43	24.0	53.0	0.7	3.3	1:2.2	Alcohol and glycerin
	35	0.09	0.39	15.0	30.0	1.2	4.0	1:2.3	Alcohol and sand
	35	0.09	0.44	15.0	33.0	1.3	4.4	1:2.2	Alcohol and sugar
	35	0.10	0.40	15.0	33.0	0.9	3.3	1:2.0	Alcohol and glycerin
1st Grade	0.20	0.49	24.0	77.0	1.5	6.1	1:3.2	1:4.6	
2nd Grade	0.20	0.53	31.0	92.0	1.7	7.2	1:3.1	1:4.4	
3rd Grade	0.19	0.55	32.0	104.0	1.8	7.6	1:3.3	1:4.3	
4th Grade	0.17	0.58	35.0	113.0	2.1	8.7	1:3.2	1:4.1	
5th Grade	0.15	0.59	35.0	111.0	1.9	7.5	1:3.1	1:4.0	
20 to 23 cm. long	0.20	0.52	30.0	99.0	1.8	7.6	1:3.3	1:4.3	
15 to 19 cm. long	0.18	0.55	32.0	100.0	1.7	7.2	1:3.2	1:4.3	
10 to 14 cm. long	0.18	0.56	33.0	104.0	2.1	8.4	1:3.2	1:4.1	

(a) U. S. Dept. of Agr., Bur. of Chem., *Bull.* 152, p. 157. (b) The beans in the glycerin extracts were rubbed up twice their weight of sand. The glycerin extracts contained 20 per cent glycerin.

ent on a close comparison with a pure extract. The chief difference lies in the delicacy of the flavor and in the way in which these extracts deteriorate with age.

The analysis of some of these extracts compare very well with the analyses of a pure extract in regard to vanillin and color, and often even in the lead number value. The total acidity of an extract made with alkali is usually lower and the alkalinity of the ash is usually higher than that of a pure extract. These cheap and alkali-made extracts yield an ash more quickly than do the pure extracts and the nature of the ash is often very different.

We had occasion to examine an extract that was called "Extract of Vanilla," "Non-Official," and which was claimed to have been made from prime vanilla beans. The vanillin content was normal, about 0.18 per cent; the lead number was low, about 0.300; the color was normal and the extract was perfectly clear. The total acidity, however, was only half of that of a pure extract and it was found that the solids of the extract burned with great ease, leaving an ash that contained a very large amount of iron oxide.

was especially so in regard to the dried bean extracts where about the same results were obtained from three extracts made in all three ways. Thus in extract No. 16, the lead number was 0.8034 and both sugar and sand were used; in extract No. 17, the lead number was 0.8011 and only sand was used; and in extract No. 24, the lead number was 0.8095, and only sugar was used. The color values of all of these three extracts were about the same. The samples containing the sugar were a little cloudy and this was found to be the case in every extract made by packing the beans and sugar together in the percolator, and would, it seems, prove that sugar should never be packed with the beans but should be added to the percolate.

Glycerin, however, does tend to increase the color of the extract and should be added to the menstruum. In Table IV we have copied, in part, the results obtained by the Bureau of Chemistry of the Department of Agriculture, in their work on vanilla extract relative to the use and value of 35 and 60 per cent alcohol, with and without sugar, sand and glycerin.<sup>1</sup>

<sup>1</sup> U. S. Dept. of Agr., Bur. of Chem., *Bull.* 152, 158.

These results agree with ours in that glycerin is of value in making a darker extract. And, also, that there is no preference between sand and sugar.

Glycerin also serves to give the desired "body" or gravity to the extract and imparts a sweet taste that is often desired. Some manufacturers use both sugar and glycerin in their extracts, the glycerin being added to the menstruum and the sugar to the percolate.<sup>1</sup>

#### GRADE AND LENGTH OF BEANS

In Table IV we have also included the results obtained by the above observers on extracts made from vanilla beans of different grades and lengths. These figures show that, in general, the highest grade beans of all the various varieties contain the most vanillin, decreasing as the grades become lower. The lead numbers and color values, on the other hand, were found to increase as the grades decreased.

The vanillin content of the longest beans was found to be higher than that of the shorter beans. The lead numbers and color values were the same here as with the different grades of beans, being increased as the beans were shorter. These differences, although slight, point to a small degree of inferiority of the shorter beans.<sup>2</sup>

#### THE SOLVENT ACTION OF VANILLA EXTRACT ON CERTAIN METALS

The solvent action of vanilla extract on metals is of twofold interest to the manufacturer. In the first place the deterioration of the containers used to manufacture and store the extract is of great importance from a straight economical viewpoint and the presence of some metals in the extract is of no lesser importance from the viewpoint of their toxic effects. It is well known that vanilla extract has quite a solvent action on some metals,<sup>3</sup> especially copper, and that the food authorities object seriously to the presence of copper, lead, etc., because of their toxic properties. It was for the purpose of determining the relative solubility of certain metals in vanilla extract that the following experiment was carried out:

Pieces of pure tin, copper, aluminum, zinc, lead, nickel and silver 1 cm. sq. were placed in 25 cc. portions of vanilla extract and allowed to remain at room temperature for two months. At the same time a piece of gold foil and a piece of "Monel metal" wire were treated in the same way. The original weights of all the metals were known. After the two months of exposure to the extract, the metals were again weighed in order to see how much of the metal had gone into solution during that period of time from a surface of 2 sq. cm. in 25 cc. of the extract. This equals a unit square surface to 12.5 units of volume or 4.68 sq. in. to one gal. The results are recorded in Table V.

The object in trying out gold and silver was partly to make the experiment more complete, but chiefly

<sup>1</sup> Special attention is called to this article on vanilla extract, for it is by far the most complete to be found in the literature on this subject. Especial attention is given by it to the analytical data obtainable from vanilla extracts made in various ways.

<sup>2</sup> U. S. Dept. of Agr., Bur. of Chem., Bull. 152, 156.

<sup>3</sup> 1914 Minutes of the F. E. M. A. Convention, p. 42.

to see if it would be practical to use either gold- or silver-plated containers in connection with vanilla extract. Either of these two metals would be ideal if the cost of the plating is not prohibitive and if the containers are not subjected to sufficient friction to quickly wear away the rather thin coating of the metal.

The next best metal was found to be tin and is no doubt the most practical of all. Tin dissolves to some extent but, according to our experiments, at a much slower rate than any of the other metals, excepting gold and silver.

TABLE V. MILLIGRAMS OF METAL DISSOLVED BY EXPOSURE OF 2 SQ. CM. OF SURFACE TO 25 CC. OF VANILLA EXTRACT FOR TWO MONTHS

Gold	Silver	Tin	Aluminum	Lead	Monel metal	Nickel	Zinc	Copper
0.0	0.0	1.8	3.2	3.6	4.8	5.8	7.2	8.0

Aluminum has the peculiar property of becoming pitted when it is exposed to vanilla extract. Both of the samples of aluminum which we experimented with were soon eaten through, one on the edge and the other well towards the center of the square. This pitting property of aluminum would make it unfit for use in connection with vanilla extract if the same result is obtained where the surface of the metal is exposed to the extract on only one side, as would be the case in a container.

The color of the samples of extract which contained the pieces of copper were very different from the samples containing the other metals; there was a suggestion of green in the color which made them very unsightly. We accidentally obtained this same thing in a much magnified form in some extracts prepared by suspending the chopped beans in copper wire baskets in the upper portion of the menstruum. At the end of one month these extracts had a greenish cast and were a vivid green at the end of two months. Half of the extracts were prepared from undried beans and half from dried beans; and curiously enough, the dried bean extracts were the first to show the green colors. The rate of solution of copper would make its use undesirable and all copper vessels which are used in connection with vanilla extract should be heavily coated with pure tin and watched closely in order to prevent exposure, due to the wearing away of the tin.

The sample of extract which contained the piece of nickel seemed to be darker than the rest and had a blackish appearance very similar to that produced in vanilla extract by metallic iron.

There was nothing of interest except the solvent action of the extract in the cases of the other metals. It is certain that copper, aluminum, lead and zinc should not be used from their solubility, and copper and nickel are undesirable from the color viewpoint as well as from their solubility. The sample of "Monel metal" did not alter the color of the extract and, in view of the fact that this sample was in the form of a wire which exposed a great amount of its surface, it would seem that this alloy might prove of service. It is noted for its non-rusting ability which would make it very easily kept clean and bright.



## AGING VANILLA EXTRACT

The aging of vanilla extract is a part of the manufacture of the extract that seems to have received all too little attention. Most manufacturers agree that aging is beneficial but there is little agreement as to either the period of aging or the temperature at which it should be done. In fact, the literature contains nothing on this subject beyond the simple fact that the flavor is improved if the extract is aged.

It is well known that whiskey is greatly improved by aging and a long study has been made on this subject. And, from the similarity in the alcoholic content and the fact that both of these substances owe their chief value to their aroma, it seems logical to consider the problems as being closely related, and to apply, as best we can, the facts learned from this investigation on whiskey.<sup>1</sup>

In part, the conclusions of this investigation are as follows:

A chemical change takes place in whiskey when stored in wood, for three or four years in which acids, aldehydes and esters are formed and which reach a state of equilibrium at this age which is maintained thereafter, any improvement of the flavor after this time being largely due to a concentration of the reduction of the volume. This reduction of the volume is also largely due to loss of water and accounts for the increase of the alcoholic content of whiskey after being stored. It is their opinion that the water passes through the wooden barrels, by a process of osmosis, at a much greater rate than does ethyl alcohol, and that the same selective action is shown with the acids, aldehydes, and esters. It is evident that the changes taking place in the spirit is dependent on the storage of the spirit in porous receptacles as none occur when the spirit is placed in glass, tin, or even barrels, the inside of which has been covered with paraffin or glue. It is also evident that the condition of the outside of the barrel, as to moisture, temperature, etc., will have a decided influence on the rate of osmosis.

## REDUCTION OF VOLUME

They also found that whiskies which had been aged at low temperatures suffered a comparatively low loss in volume but at the same time they were not matured to anything like the same degree as those which were stored at higher temperatures and which lost considerable of their volume.

REDUCTION IN VOLUME OF WHISKIES DURING STORAGE

VOLUME	BOURBON (a)		RYE (b)	
	Gal.	Loss—Per cent	Gal.	Loss—Per cent
Original.....	47.4	....	46.7	....
First year.....	43.9	.8	42.8	8.4
Second year.....	Not given	...	40.5	14.0
Third year.....	40.5	1.5	37.7	19.0
Fourth year.....	38.2	2.2	35.2	27.0
Eighth year.....	32.5	31.5	24.2	48.0

(a) Stored at 80° F. in summer and 45° in winter.

(b) Stored at 80 to 85° F. during entire year.

It was found that the greater part of the chemical changes had taken place at the end of the first year and, with the exception of only a few cases, the remaining changes were small as compared with that of the first year. The reduction of the "new spirit" taste and the production of color are two items of

great importance in whiskey aging that would not enter into vanilla extract aging at all and, since the larger amount of the chemical changes take place in the first year, it would seem that a one year's aging would be the most profitable. From the above evidence it would also seem that the extract ought to be aged at room temperature and in wooden barrels, that are not painted, in order to permit the process of osmosis.

## METHODS OF MANUFACTURING VANILLA EXTRACT

The methods of manufacturing vanilla extract are very numerous and varied in character. They range from plain percolation to hot maceration under the influence of strong agitation and extend over periods of time varying from twenty-four hours to one year. Each different method contains some good and some bad features, producing extracts that vary quite a little in their physical and chemical properties, as well as in their flavoring strengths. There is no one method which all manufacturers agree in calling the best, in fact, favorable comment can be obtained for most any of the methods, some preferring one and some another. Because of this great difference of opinion in regard to this question, we think that it will not be amiss to give a short description of some of the methods that are employed.

**MACERATION AND PERCOLATION**—This is possibly the oldest and best known of all of the methods used but its value seems to be very questionable. It is the method employed in the U. S. P. and the one commonly used by the smaller producers since it is by far the most convenient.

The method consists of a maceration of the beans in desired menstruum (65 per cent in the 8th U. S. P.) which is followed by percolation of the finished product. The period of maceration varies from twenty-four hours U. S. P., to one or more years, according to the personal opinion of the operator. The method of packing the beans in the percolator also varies very greatly. Some pack the beans alone, some use sugar either with or without a preliminary maceration, and some use various amounts of sand, with or without sugar. The packing of the chopped beans is the most important part of the whole process, for upon it depends whether or not a good degree of extraction will be obtained. This method usually results in a clear and bright extract, but one that, as a rule, does not contain much color. It is also claimed that it is not possible to extract completely the whole of the beans in the percolator due to the rather coarse subdivision of the beans which makes a firm packing impossible, and which tends to allow the menstruum to form canals instead of passing through the whole of the pack. As in all other methods, an increase in temperature seems to increase the color and other extractive matter.

**CIRCULATORY DISPLACEMENT**—This is a modification of the above method where the chopped beans are held in the upper portion of the menstruum instead of in the lower. The usual method is to place the chopped beans in a perforated basket, suspended from the sides of the containing vessel in such a way

<sup>1</sup> Crampton and Tolman, *J. Am. Chem. Soc.*, **30** (1908), 98.

that the top of the basket is just below the surface of the menstruum, and, it is claimed, that a much better result will be obtained if the basket is removed from the menstruum once or twice during the process and allowed to drain before being replaced.

The principle of this method is the circulatory motion of the menstruum due to the always increasing gravity as the soluble constituents are dissolved. In this way the bean is repeatedly exposed to the menstruum because as the menstruum in contact with the beans becomes charged with soluble matter, its gravity increases and it sinks, forcing fresh menstruum up in its place. This action will continue in this way until a state of equilibrium is reached throughout the entire container when the extract can be drawn off in a perfectly clear and bright condition. This method is slow in action, requiring at least three months, but it is without doubt one of the best known and produces an extract that is very rich in delicate aroma as well as high in physical constants.

The containers should be made of oak and be well painted on the outside to prevent undue evaporation. The basket should be of oak or of heavily tinned metal and the outlet should be about an inch above the bottom of the container to allow the separation of any solid matter that might have passed through the small holes in the basket. By this method the extract is made and partly aged at the same time and need not require any attention from the time it is started until it is finished. The method is usually employed at room temperature but, obviously, higher temperatures could be used by storing the containers in heated rooms.

**AGITATION**—This method is in reality a maceration process in which the chopped beans and the menstruum are kept in motion by means of a mechanical agitator and, as in all other methods, the time of maceration and the temperature are regulated to suit the various conditions. This method has the advantage of exposing the beans to the solvent action of the menstruum over and over, producing a highly colored product, especially where the menstruum is kept warm. The one big disadvantage of the method is the separation of the finished product from the rather fine pieces of the dregs. This is done either by pressing out the extract or by transferring the whole to a percolator and percolating. The latter, however, is to be preferred in order to reduce the evaporation of the alcohol as far as possible. The containers used are usually of metal and should be kept well covered with tin. Where the extract made in this way is made cold and aged, it is comparable with that made with the circulatory displacement method but it seems positive that an extract made with a hot menstruum is inferior because of the lack of the delicate aroma and excessive amount of inert extractive matter which seems to cover up the delicate flavor so noticeable in the extract prepared by cold methods.

**FRACTIONAL SOLUTION**—This method differs from those given above only in that the menstruum is added in fractions, one after the other. The chopped beans are agitated or macerated with one-third or one-

fourth of the total amount of the menstruum for the desired length of time and then drawn off as finished extract. The partly extracted beans are then treated again in the same manner until the total amount of extract is obtained from the weight of beans taken. If the different amounts of menstruum are allowed to remain in contact with the beans long enough to become saturated, this method will no doubt produce the greatest extraction possible but only long macerations will suffice, even if more menstruum is to be added, because the extractive matter in vanilla beans is so difficultly soluble, except vanillin, that it requires a rather long time to effect their solution and it is possible that the menstruum would be withdrawn before it has accomplished its purpose.

**AGITATION AFTER MACERATION**—In this method the chopped beans are allowed to macerate with a portion of the menstruum, say one-half, for the desired period of time and the liquid then drawn off as finished extract. The resulting partly extracted beans are then agitated with the remaining portion of the menstruum heated to about 100° F. until the desired color is obtained and the dregs are exhausted. This liquid is then separated from the dregs and added to the first portion to form the complete extract.

It would seem that there are two objections to this method and two serious ones. In the first place, the maceration is accomplished by allowing the chopped beans to stand in the menstruum without motion and it is certain that the beans settle to the bottom and become surrounded by a layer of saturated menstruum and slow diffusion must be depended upon to bring the unsaturated menstruum in contact with the incompletely extracted beans. And this is so slow that it is doubtful if a very great portion of the menstruum is ever in contact with the beans. The second objection is the hot after-treatment which is believed to be detrimental to a first-class extract of vanilla.

It is unfortunate that we did not have the necessary apparatus to prepare extracts by all of the different methods so that we could report on their relative values from a physical constant standpoint. We did have an opportunity, however, to watch the progress of an experiment made with the circulatory displacement method and analyzed a sample of the extract at the end of three and six months. The results are given in Table I, extracts Nos. 33 and 33A. These results show that the extraction was about complete at the end of the three months but it was found that the extract had a much finer flavor at the end of six months than it did at the end of three months, and will no doubt improve in this respect for sometime. The analytical data obtained from extracts made from these same beans, but with heat and agitation, are not obtainable now, but it is known that they did not exceed those of the circulatory displacement extract to any great extent even in regard to the color.

#### QUESTIONS AND ANSWERS

In order to get the opinions of different manufacturers on some of the most important questions rela-



tive to vanilla extract, we sent out a list of such questions to twenty members of the Association for their answers. These questions were largely ones that could not be answered by laboratory experiments and which seemed to us as being of interest to the entire membership of the Association. We have received twelve sets of answers and wish to take advantage of this opportunity to thank these members for their kind coöperation in the preparation of this report.

A composite of the questions and the number of like answers received for each question is given below. The letters in the parentheses refer to the sections of the different questions; the numbers refer to the number of manufacturers who gave like answers to the same questions.

QUESTION—Do vanilla beans improve with age?

Answers: Yes, 11. No, none. Doubtful, 1.

QUESTION—If so, is the improvement due to (a) a change in the beans, or (b) is it due to concentration caused by loss of moisture?

Answers: (a), 4. (b), 4. (a and b), 2. Doubtful, 1.

QUESTION—What do you consider the best method of grinding vanilla beans?

Answers: Sausage grinder, 1. Chopping machine, 9. Both, 1. Doubtful, 1.

QUESTION—Do you ever dry your bean before extracting it, and if so, to what extent?

Answers: Yes, 3. No, 9. Two or three remove only the excess moisture; the other dries to constant weight at 70° C.

QUESTION—In your estimation should vanilla extract be made by (a) maceration, (b) percolation, (c) agitation, or by some combination of two or more of these?

Answers: (a), 1. (b), 1. (a and b), 6. (a, b and c), 1. (c), 1.

QUESTION—In your opinion, what is the best menstruum for the complete extraction of vanilla?

Answers: 40 per cent, 1. 50 per cent, 5. 52.5 per cent, 1. 57 per cent, 1. 60 per cent, 3.

QUESTION—Do you prefer glycerin to sugar in vanilla extract?

Answers: Yes, none. No, 9. Use both, 3.

QUESTION—Does sugar interfere in the percolation of the extract?

Answers: Yes, 5. No, 3. Doubtful, 3.

QUESTION—Will either one increase the color?

Answers: Yes, 3. No, 8. Doubtful, 1.

QUESTION—Will either one prevent baking-out or freezing-out of the flavor?

Answers: Yes, 3. No, 4. Doubtful, 4.

QUESTION—When sugar is used do you add it before or after percolation?

Answers: Before, 3. After, 7.

QUESTION—Does aging vanilla extract improve its flavor?

Answers: Yes, 12. No, none.

QUESTION—If so, will it improve in glass as well as in wood?

Answers: Yes, 2. No, 8. Doubtful, 2.

QUESTION—Should the extract be aged at, (a) room temperature, or (b) at reduced temperature?

Answers: (a), 7. (b), 2.

QUESTION—How long do you think that the extract should be aged?

Answers: Six months, 4. One year, 4. Longer the better, 3.

QUESTION—In your experience what is the average loss due to evaporation when wooden containers are used?

Answers: 1 to 3 per cent, 2. 3 to 6 per cent, 1. 11 per cent, 1. Doubtful, 5.

QUESTION—Does the hot process impair the flavor of the finished extract?

Answers: Yes, 6. No, 1. Yes, if over 100° F., 1. Yes, if over 110° F., 1. Doubtful, 2.

QUESTION—Does the hot process yield a stronger extract than the cold process?

Answers: Yes, 5. No, 5.

This leaves but little doubt in regard to questions Nos. 1, 3, 4, 7, 9, 12 and 14, and shows an almost equal division of opinion in regard to the other questions. It is regretted that more data are not available in regard to the loss in volume of the extract on aging. We are, however, of the opinion that about the same loss will result here that has been found in the case of whiskey where the extract is stored under like conditions, namely, about 8 per cent in the course of a year. This question seems to have received all too little attention by manufacturers and it would seem to be a question that is worthy of great consideration.

#### CONCLUSIONS

1—Vanilla beans are improved on aging where the aging is conducted under proper conditions.

2—Vanilla beans should be chopped and not ground.

3—Vanilla beans can be dried without material loss of flavor if the drying is carefully carried out at room temperature (60 to 70° F.).

4—Extracts made from dried beans have higher color and lead number values than those made from the same but undried beans.

5—Where the beans are not dried the menstruum should be regulated to suit the moisture present in the beans.

6—The physical constants are not greatly affected by the various amounts of alcohol in the menstruum as long as the amount of alcohol is sufficient to produce a clear extract. The color values are slightly increased and the lead number values are slightly decreased by an increase of alcohol up to a maximum of about 65 per cent.

7—The flavor of an extract prepared with 60 per cent alcohol is superior to that made with 50 per cent alcohol.

8—The resins of vanilla beans are of no value as flavoring agents but are of value as fixatives for the flavoring compounds present and as coloring matter for the extract.

9—Alkaline menstrua produce extracts that are higher in color and lead number values but the alkali impairs the natural flavor of the beans.

10—Short maceration and percolation will not produce the maximum extract. The hot process produces an inferior extract, one that is lacking in delicate aroma. The most desirable extract is produced only by long maceration at room temperature as in the circulatory displacement method.

11—Sugar does not increase the color of the extract and should be added to the percolate. Glycerin tends to increase the color and should be added to the menstruum before percolation or maceration.

12—Vanilla extract should not be left in contact with any metal that is not completely covered with tin.

13 Vanilla extract is decidedly improved by aging. The period of the aging should be at least one year and should be carried out at room temperature (60 to 70° F.) and in unpainted, porous, wooden barrels.

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## RELATIVE OIL YIELD OF FLORIDA ORANGES

By S. C. HOOD

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In connection with experiments carried on to determine the commercial possibilities in the manufacture of orange oil from Florida cull oranges, it seemed advisable to determine how early in the shipping season the oil was present in commercial quantities, and also to secure some data on the relative oil yield of different varieties and from various localities. In the fall of 1915 a series of tests was made beginning at the opening of the shipping season of the early varieties and extending until well into the season for all except the very late varieties. The writer is indebted to Mr. M. G. Mastin of the Bureau of Chemistry for the material used in this study.

## VARIETIES SELECTED

The Parson Brown was selected as being the principal commercial early variety, and although mature enough to ship at the time the experiments were begun, yet the color was bright green. At the close of the work this variety was well colored. Another variety of very early maturity is the Ilsworth Early; and on November 12th it was fully mature and beginning to show a slight yellow color. The Homasassa was taken as the type of the early mid-season orange, and on the date of the first tests was still green in color, although fairly well matured. The Pineapple being one of the leading mid-season varieties, was taken as the type of this group, and samples from three widely separate localities were secured. These were still immature and green in color when the experiment began. Since the common seedlings are still extensively grown in Florida, and there are wide differences in the fruit, samples were taken from eight



TABLE I—PERCENTAGES OF OIL IN FLORIDA ORANGES

VARIETY	LOCALITY	PERCENTAGES CALCULATED ON WEIGHT OF FRUIT						PERCENTAGES CALCULATED ON WEIGHT OF PEEL							
		Nov. 1-6	Nov. 7-13	Nov. 14-20	Nov. 21-27	Nov. 28-Dec. 4	Nov. 5-11	Nov. 12-18	Nov. 1-6	Nov. 7-13	Nov. 14-20	Nov. 21-27	Nov. 28-Dec. 4	Nov. 5-11	Nov. 12-18
Parson Brown	Lake Weir	0.41		0.35		0.50			2.74						
Isworth Early	Wandermere		0.43		0.24		0.40	0.36		2.51		1.52	3.18	2.35	1.91
Homasassa	Florence Villa		0.51	0.49	0.35	0.58	0.51	0.50		2.63	2.56	2.00	3.26	2.94	2.67
	Palatka		0.40			0.25				2.44			1.62		
Jaffa	Palatka									2.13			1.74		
Carlton Seedless	Wandermere		0.42		0.30		0.41	0.41		2.47		1.78	2.42	2.42	2.24
Pineapple	New Smyrna	0.13		0.14		0.14		0.15	1.00		1.14		1.20		0.99
	Palatka		0.17			0.30		0.30		1.42			1.83		
	Florence Villa		0.30	0.32	0.35	0.32	0.35	0.41		2.00	1.88	2.30	1.95	2.21	1.84
Seedlings	Plant City	0.39					0.37		2.02					2.27	
	New Smyrna	0.25		0.28		0.27		0.36	1.70		2.17		1.95		2.18
	Lakeland	0.21		0.17		0.14				1.55		1.34	0.83		
	Tampa		0.16		0.14			0.27		1.00		0.88			1.43
	Ozona		0.11		0.25			0.34		0.92		1.45			1.91
	Orlando		0.32		0.25		0.41			1.91			2.51		
	Wauchula		0.40		0.35			0.36		2.53		2.74			2.15
	Geneva		0.44			0.41		0.47			2.40		2.50		2.68
Valencia	Florence Villa	0.38	0.44	0.50	0.31	0.46	0.35	0.53	2.46	2.58	2.50	1.95	2.60	2.00	3.04
	Oakland	0.32	0.36			0.43				2.20			2.76		
	Wandermere		0.46		0.35			0.24		2.47		2.00			1.41
	Manatee			0.37		0.38		0.41			2.10		2.38		2.27

localities. On November 1st, all of these were livid green in color, but at the close of the tests they were mature and well colored. Since the Valencias do not mature until the latter part of the winter, the tests were not continued on this variety to maturity. Most of the samples of this variety were only partially grown at the beginning of the tests, and at the close were of full size, but still very immature and green in color. Each series of samples was gathered from the same tree at intervals of one to two weeks from November 1st to December 18th.

## METHODS

Each sample consisted of 12 oranges picked from the tree set apart for these tests. Usually 1 to 3 days elapsed between the date of picking and the date of the tests. The oranges were peeled with a knife and care was taken to remove all of the peel without cutting the pulp cells. Care was also taken to prevent breaking of the strip of peel and consequent loss of oil. The fresh peel was then finely ground in a food chopper and the ground material distilled with water in a Remington still. The colorless oil secured was taken as the total oil content. Since this oil consisted almost entirely of limonene, it does not represent the actual oil content of the peel, but the loss of the oxygenated constituents would be fairly constant in each sample, and this method may be used as a relative means of the total oil determination. The percentages, Table I, were calculated on both the weight of the peel and the weight of the fresh fruit.

It will be noted from Table I that in the case of most samples there was a considerable increase in oil content as maturity advanced, but that there is a high percentage of oil in the peel of the fruit sometime prior to the change in color. This is especially marked in the case of the Valencias. It will also be noted that there is a very wide difference in the oil content of the same variety from different localities. From this preliminary investigation it is not possible to determine whether this variation is due to soil and climatic conditions, or to the degree of care which the trees have received. From the appearance of the fruit as received, however, it is believed the latter is the case. Especially in the case of seedlings this difference was marked, and fruit showing by its form and texture that the trees were highly fertilized and

well cared for, showed a higher oil content. There was a marked drop in oil content in most samples during the two weeks from November 14th to 27th. During this period there was an excessive rainfall throughout the entire state. Table II gives the rainfall records of the Weather Bureau in the localities where samples were secured during the period of these experiments.

TABLE II—RAINFALL IN INCHES IN LOCALITIES WHERE ORANGE SAMPLES WERE GATHERED

Names in Parentheses are Weather Bureau Stations Nearest to Place where Orange Samples were Taken

	Nov. 7-13	Nov. 14-20	Nov. 21-27	Nov. 28-Dec. 4	Nov. 5-11	Nov. 12-18
Lake Weir (Lynn)		1.93	0.26			0.16
Wandermere (Clermont)	0.03	3.46	0.11			0.10
Florence Villa (Lucerne Park)		1.82				0.58
Palatka (Satsuma Heights)	0.04	0.67	0.10			0.05
New Smyrna		2.34				0.01
Plant City		3.15		0.20		0.30
Lakeland		2.18				0.12
Tampa		2.89	0.09			0.30
Ozona (Tarpon Springs)		3.77	0.63			0.65
Orlando		2.22		0.02	0.05	0.20
Wauchula (Fort Meade)		3.59				0.15
Geneva (Sanford)	0.08	1.85				0.14
Oakland (Clermont)	0.03	3.46	0.11		1.10	0.26
Manatee		2.62	0.10	0.26	0.66	

In some cases no observations are available from the places where the samples were taken, and the records of the nearest observer are given. It will be noted that this decrease in oil content immediately follows the period of rainfall, and that where the rains extended over a longer period, the oil content was retarded in its increase.

## EFFECT OF RUST MITE

It has long been believed that the typical brown coloring of the orange skin known as "russet" following the presence of large numbers of the rust mite, *Eriophyes oleivorus* Ashm., is due to the puncturing of the oil cells. In order to determine if this insect injury decreased the oil yield of the fruit, tests were made on the fruit of the same tree at two stages of maturity. The first test was made on November 26th while the fruit was immature and the second on January 25th after the oranges had reached full maturity. Each sample consisted of 12 bright and 12 russet fruit. The results are given in Table III.

TABLE III—OIL YIELD OF RUSSET AND BRIGHT FRUIT OF SAME TREE

PER CENT OIL IN:	NOVEMBER 26		JANUARY 25	
	Fruit	Peel	Fruit	Peel
Bright Fruit	0.20	1.25	0.40	2.26
Russet Fruit	0.10	0.60	0.40	2.68

These results indicate that early in the season there is a lower oil content on the fruit infected by rust mite,

but as the orange matures a normal amount of oil is formed. The results secured in the commercial tests on large lots of bright and russet fruit also indicate that an equal amount of oil may be secured from each kind of fruit.

#### CONCLUSIONS

These preliminary results show that there is a wide variation in the oil yield of Florida oranges under different climatic and cultural conditions, and that the question of variety is likely to have some bearing on the commercial production of orange oil. The oil content has not reached its maximum until the oranges are fully mature, but the oil is present in commercial quantities before the fruit are ready for harvest.

The occurrence of heavy rainfall during the season of harvest will cause a considerable decrease in the oil content. The presence of rust mite does not decrease the percentage yield of oil of the mature fruit, but may show some effect early in the season.

BUREAU OF PLANT INDUSTRY, WASHINGTON

### A NUMERICAL EXPRESSION FOR COLOR AS GIVEN BY THE IVES TINT PHOTOMETER

By OTTO KRESS<sup>1</sup> AND G. C. McNAUGHTON<sup>2</sup>

Received May 27, 1916

The matter of a numerical expression of a definite shade of color is one on which various investigators have expended considerable energy with varying degrees of success. In almost countless phases of commercial and experimental work it is extremely desirable that there be a means by which an exact shade of color may be communicated to others or so recorded that this shade may be matched or referred to when the original is not available. One readily comprehends the importance and practicability of an instrument which would give an accurate reading of color.

So far as the authors know, there are but two instruments on the market, which would appear to be practicable from a scientific and a possible mill standpoint, for measuring the depth of color of either liquids or solids. These instruments are known as the Ives Tint Photometer and Colorimeter. The tint photometer, being the more simple instrument, was used in these experiments.

The original purpose of the experiments following was, (1) to determine if color indications as shown by the Ives tint photometer could be employed as a means of measuring the progress of beating, and (2) to observe the relation between the numerical expressions for depth of color as read from the instrument and the relation of the shades as noted by the eye.

The tint photometer (Fig. 1) consists essentially of a form of telescope into which light from two sources is reflected, by means of a mirror (*A*), into two apertures, and focused by a special lens into two semicircular fields. Each semicircle is uniformly illuminated by passing the light from the apertures, or slits, through a rotating wheel (*B*) mounted with lens,

the object of which is to blend the light. The amount of light reflected through the left-hand aperture is controlled by a shutter actuated by a long lever (*C*) that moves over a scale (*D*) so divided into 100 divisions or parts that at zero reading the sliding shutter is entirely closed and at 100 divisions is wide open.

By means of a thumb screw (*E*) the second aperture may be adjusted but through much narrower limits. The base of the eye-piece tube is equipped with a sliding carrier (*F*) in which are mounted red, green, and blue color screens, as well as one of colorless glass. The light under which the tests are made is received through a south window covered with tracing cloth.

In using the instrument two magnesia blocks are first placed directly beneath the reflecting mirror and in front of a vertical mirror (*G*). The lever operating the shutter is set at 100, to give full opening of the left aperture, and the right-hand aperture adjusted by the thumb screw until the two halves of the field are of uniform intensity. This adjustment made, the mag-

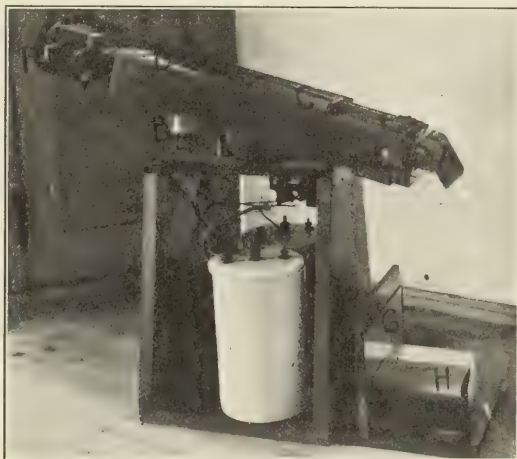


Fig. 1

nesia block on the right is removed and the paper (*H*) to be tested is substituted. Using each of the color screens successively (*i. e.*, red, green, and blue) the amount of light entering the left aperture is decreased until it is of the same intensity as that entering the right aperture from the paper sample, or until the two halves of the field appear of one luminosity. The position of the lever when this matched condition of fields is obtained with each screen indicates numerically the proportion in which red, green, and blue light are reflected by the paper under test.

For example, the white standards show 100 parts each of red, green, and blue, while a certain sample of an undyed sulfite paper gives readings of 77 parts red, 71 parts green, and 67 parts blue. The sum of the three colors in the case of the white standard is 300, while in the case of the paper it is but 215. For purposes of convenience it has been assumed that in the latter case there exists a darkening effect of 85 parts of black (in 300). This factor of "parts black" which

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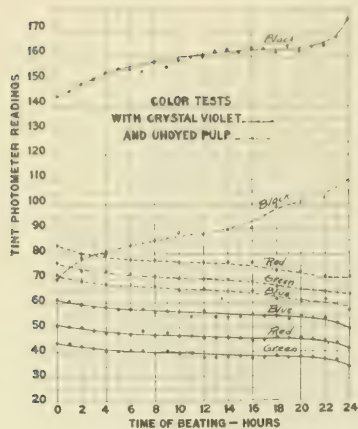


FIG. 2

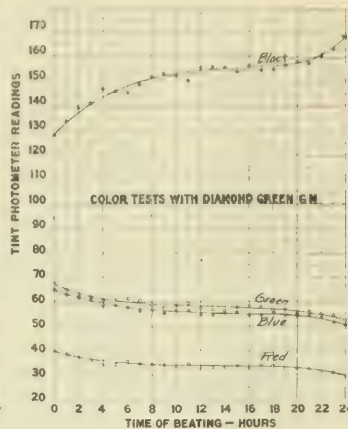


FIG. 3

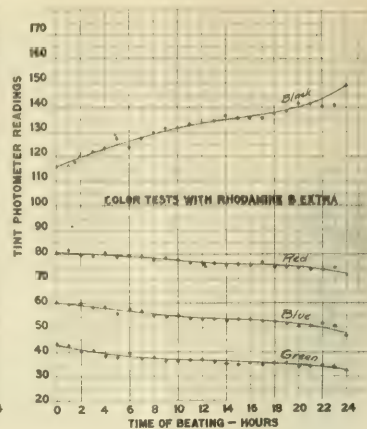


FIG. 4

is secured, not by direct reading of the instrument, but by the subtraction of the sum of the three colors from 300, immediately expresses the relative brilliancy of the color examined although it conveys no idea of the tint if the other three readings are not given. The authors have found no difficulty in checking within one division (or part) the values secured in previous tests. The inventor of the tint photometer claims that the personal equation becomes practically negligible in operating this instrument, and that even a marked color-blindness does not affect the readings of the instrument.

The tests were divided into two groups, (1) where depth of color was secured by prolonged beating effect, using the same amount of dye, and (2) where depth of color was obtained by different amounts of dye employed.

In the first group unbleached spruce sulfite pulp was beaten in an experimental Marx beater of 50 lbs. capacity. The beater tub is of concrete construction, with a specially formed trough for rapid circulation. The roll is 24 in. in diameter by 18 in. face, with a cluster filling of iron bars, and was operated throughout the experiments at a peripheral speed of 2,000 ft. per min. A very light treatment was given in order that the comparatively short stock used would not be badly cut before the end of the operation. The treatment extended over a period of 24 hrs. Representing by zero the position of the roll above the bed plate when a very faint hum could be heard as the roll turned in the empty beater, the following table shows the manner in which the roll was gradually lowered. Even at the end of 24 hours the stock was

Time at which roll was lowered	Position of beater roll
At start.....	+0.10"
At end of 2 hrs....	+0.05"
8 .....	+0.01"
17 .....	+0.002"
20 .....	+0.000"
21 .....	-0.002"
22 .....	-0.004"
23 .....	-0.006"
24 .....	roll raised

but slightly shortened and as it still was rather far from pergamin stock it is probable that greater differences in color tests would have been secured had

the stock been submitted to a more severe brush after the first few hours of beating.

In this group of tests a sample of the stock in the beater was removed every hour. For the various dyeings, pulp samples of 3 g. (dry) weight were employed which were secured as follows: A large sample of about 3.3 per cent density was pressed by the palm of the hand on a 70-mesh screen until no water dripped from it (about 12 per cent dry) and then thoroughly mixed. After determinations of moisture content of the pressed stocks were made, amounts equivalent to 3 g. (dry) were weighed out and bottled with 100 cc. distilled water. This method presents the difficulty of obtaining a homogeneous mixture of the pressed stock, but was by far the best method available.

When ready for the dyeing, the pulps were washed out of the bottles with 250 cc. of water into enamelware cups  $3\frac{1}{2}$  in. in diameter and  $3\frac{5}{8}$  in. deep. In these the stock was agitated by a mechanical stirrer for a total of 20 min.—color, sizing and alum being added in the order named.

In the cases of the red and green dyes, respectively, 0.5 g. of Rhodamine B Extra and 0.5 g. of Diamond Green G. N. were dissolved with the addition of a little acetic acid in a liter of water and a volume equivalent to 0.1 per cent of the dry weight of the stock used for each sample. This gave dyeings of 1 lb. per 1000 lbs. of stock. The strength of the Crystal Violet was but half of the others. Dilute solutions of size and alum were standardized and volumes equivalent to 1 per cent of size (calculated as rosin) and  $1\frac{1}{2}$  per cent of alum employed.

The finished stocks were made into hand sheets on a special circular mold  $6\frac{3}{4}$  in. in diameter, pressed between the press rolls of an experimental paper machine and dried between sheets of blotting paper on one of the driers. During the drying the hand sheets were turned frequently to avoid the burning of the color to the surface, and so cause an unevenness in depth of color on the two sides of the sheet.

The wire side of the sheet was in every case used for the color tests with the tint photometer. In making these tests all sheets of one color were ob-

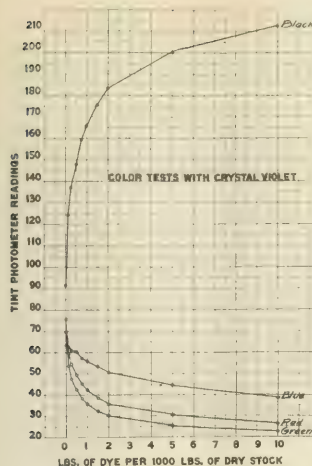


FIG. 5

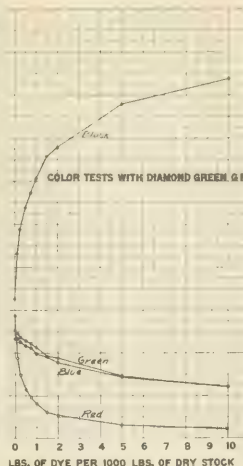


FIG. 6

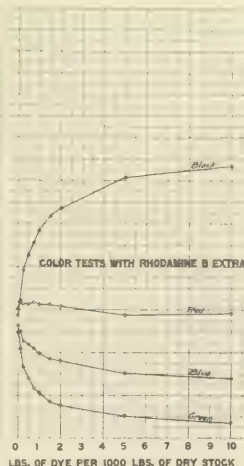


FIG. 7

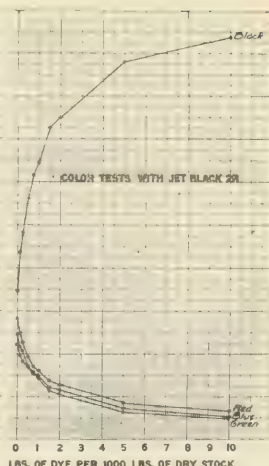


FIG. 8

served in consecutive order and continuously in order to avoid any great variation in lighting conditions.

The results of the tint photometer observations are shown graphically in Figs. 2, 3, and 4, in which the readings of parts red, green, and blue, as given by the instrument, are plotted against the duration of the beating treatment. The calculated "parts black" also have been plotted in these figures. When comparing the depth of tint as determined by the tint photometer with the ratings exhibited to the eye, it was noted that an almost identical arrangement could be made. However, as the instrument does not distinguish as readily as does the eye between very slight differences of shade, it is necessary to be very exact in the adjustments. Reference to the curves in Figs. 2, 3, and 4 will give the reader an idea of the rather small differences in color between consecutive papers. While it will be noted that many of the values obtained do not fall upon the smooth curve, this fact is not exceedingly serious, since the paper samples when viewed by the eye do not show an absolutely regular progressive darkening that should be expected. Such irregularities would occur if error had been made in the rather involved method of sampling the stock, and where such a number of samples were taken it is not improbable that errors were occasionally introduced. Slight variations from 3 g. (dry) weight would cause the stock to assume a deeper or lighter tint, depending on whether the samples were too light or too heavy. Unfortunately, in trimming the colored samples to fit the special paper holder that comes with the instrument, the clippings were discarded—consequently the authors had no means of establishing the experimental error.

The accelerated hydration and the corresponding darkening of the stock, when the brushing became more severe near the end of the beating treatment, are clearly shown in all of the figures. Fig. 2 is especially interesting in that curves for the undyed beaten stock have been plotted on the same scale as that used for the blue stock.

As is well known, the longer the stock is beaten, causing increased hydration, the less dyestuff will be required to produce the same depth of color. This is well shown in all of the curves, as the same amount of dyestuff per 1000 lbs. of stock was used, and the increased depth of color is due solely to hydration.

That a color may be expressed in numbers—even though the numbers allow a slight variation in shade—is far more satisfactory than to attempt a description of the color. For example, a red may be on the yellowish cast tending to approach the orange, or may be on the bluish cast tending towards the violet. The addition of any other primary color such as green would, in the case of red, not form a greenish red but would be a step towards darkness. It is absolutely impossible to record scientifically either a shade of red or the intensity of a red shade, by merely describing it as either a *light or dark bluish red* or a *light or dark orange* shade. The addition of color in all practical dye work must be considered as a step towards darkness, and it is common practice in the mill to avoid mixtures of colors if brilliant shades are desired, especially in view of the fact that the practical dyes used are never of a pure shade.

A second series of color tests was made in order to observe the behavior of the Ives tint photometer with various colors and intensities of colors. It will be remembered that in the first series difficulty was met with, due to an almost exact similarity of many of the test papers. In this second group of experiments all of the papers were made from one mass of pulp that was removed from the beater after a light brush and tinted with various amounts of dye. The colors employed were "Diamond Green G. N.," "Rhodamine B Extra," "Crystal Violet," and "Jet Black 2 R," which were made up to strengths of 0.5 g. dye in 1 liter of water, sufficient acetic acid being used to prevent hydrolysis, and volumes of each used equivalent to 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100 lbs. of dry stock. As before, the 3 g. (dry) samples of the stock were secured from the wet stock,



after it had been squeezed by hand and its moisture determined as described in the previous tests. The manner in which the color, size and alum were added and mixed was similar to that formerly employed, with the exception that the total time of stirring was increased to 30 min., and that an excess of size and alum (2 and 2½ per cent, respectively) were used in order to set the heavy shades. Up to about 2 lbs. of dye the back-waters were practically colorless. The method of preparing the hand sheets from the dyed stock was identical with that used in the previous series.

The gradations in shade of these papers were very distinct, and offered no difficulty in making a visual selection of the sheets in the order of the strength of dye employed. The tint photometer also gave uniform readings of color which are shown graphically in Figs. 5, 6, 7, and 8 where "parts red, green and blue" and also "parts black" are plotted against the strength of dye used.

While we are not prepared to say just how the readings of the three colors should be interpreted or how matching a shade could be facilitated from them, it is very evident to us that with this instrument a shade or tint may be given a definite numerical value.

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## NOTES ON THE DETERMINATION OF ALUMINUM

By C. F. SIDENER AND EARL PETTJOHN

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The determination of aluminum in the form of aluminum oxide, after precipitation with ammonium hydroxide, is frequently made. As ordinarily carried out, there are several points in the determination that might give rise to variations in results. The purpose of this piece of work is to determine the best procedure with regard to some of these points.

In looking up the literature on the subject of this precipitation, considerable difference of opinion was found. The ordinary directions are to boil until the liquid just smells of ammonia, though it was very early discovered<sup>1</sup> that at this point ammonium chloride may have hydrolyzed to such an extent with volatilization of ammonia that the solution is actually acid. In this case, of course, aluminum hydroxide would be redissolved and quantitative results could not be obtained.

L. Blum<sup>2</sup> worked on this precipitation and found that ammonium chloride was decomposed in solution at 100° C. with loss of ammonia; he advises filtration when the liquid is still quite strongly ammoniacal. He also states, and many others verify his statement, that ammonium hydroxide dissolves a certain amount of freshly precipitated aluminum hydroxide, which amount is considerably lessened by the presence of ammonium salts. C. F. Cross,<sup>3</sup> using ammonium hydroxide solutions of varying strength, found that aluminum hydroxide was dissolved at the moment of precipitation, that the amount dissolved bore no

relation to the concentration of the ammonium hydroxide, and that ammonium salts lessened the solubility of the hydroxide. Penfeld and Harper,<sup>4</sup> in testing for dissolved aluminum hydroxide, found that it was not present in the filtrate but was present in the wash water. They tried using, instead of boiling water, an ammonium nitrate solution, made by neutralizing 2 cc. of pure nitric acid with ammonia, and making up to 100 cc. With this washing solution they claim that the precipitation can be made from solutions containing larger or smaller amounts of ammonium salts, and that no very great care is needed in adding ammonia.

On a number of points, exactly opposite opinions as to procedure are held. Hillebrand, in his "Analysis of Silicate and Carbonate Rocks," states that, contrary to the usual belief, aluminum hydroxide is not volatile in presence of ammonium chloride, and that, for the determination, washing free from chlorides is unnecessary. Washington, in his "Rock Analysis," and Mahin, "Quantitative Analysis," take the opposite view, and say that aluminum hydroxide must be washed free from every trace of chloride or low results will be obtained. With regard to boiling the solution for precipitation, the same difference of opinion exists. Washington advocates boiling (for not more than 1 min.) with a slight excess of ammonia, while Handy<sup>5</sup> boils for 20 min. under the same circumstances. For washing the precipitate, ammonium nitrate is frequently recommended, Treadwell, Penfeld and Harper, Washington and others making use of it. Renz,<sup>6</sup> however, found that when aluminum hydroxide was precipitated with ammonium hydroxide in presence of ammonium nitrate, a small quantity remained in solution. Fresenius, Handy and several others advise the use of hot water.

There is a similar difference of opinion as to the ignition of the precipitate. Allen and Gottschalk<sup>4</sup> found that the highest heat of the blast lamp was required to effect complete dehydration: precipitates heated to 1100° C. and cooled for half an hour were still hygroscopic. Handy<sup>5</sup> also considers the oxide very hygroscopic and advises intense ignition. Carnelley and Walker,<sup>6</sup> on the other hand, obtained complete dehydration by gradual heating to 850° C.

The points which this paper covers are as follows:

1—To determine whether the precipitate need be washed free from chlorides before ignition.

2—To determine whether an excess of ammonia has any solvent effect on the freshly precipitated hydroxide.

3—To determine whether water or ammonium nitrate solution is more suitable for washing the precipitate free from chlorides.

4—To determine a satisfactory time for ignition to constant weight.

An aluminum chloride solution was made up from

<sup>1</sup> *Am. J. Sci.*, **20**, 9, 181.

<sup>2</sup> *J. Am. Chem. Soc.*, **18**, 766-82.

<sup>3</sup> *J. Chem. Soc. (London)*, **2** (1903), 729.

<sup>4</sup> *Am. Chem. Jour.*, **24** (1900), 292-304.

<sup>5</sup> *J. Am. Chem. Soc.*, **18**, 766-82.

<sup>6</sup> *J. Chem. Soc. (London)*, Trans., **53**, 87.

*Z. Anal. Chem.*, **2**, 394, 1, 66

*ibid.*, **27**, 19

<sup>2</sup> *Chem. News*, **39**, 161.

sheet aluminum and hydrochloric acid. The ammonium chloride used volatilized without residue, as did the aluminum hydroxide. The ammonium hydroxide solution was filtered into a ceresin bottle: the specific gravity of the solution was 0.955.

In all of the precipitations made with these solutions, the following general conditions were maintained: The volume of the solution from which the precipitation was made was 250 cc. and in every case 25 cc. of the total volume was a 10 per cent solution of ammonium chloride. All precipitations were made in porcelain casseroles, the solution being boiled for 1 min. and filtered hot. The precipitates were ignited moist, in platinum crucibles: the ignited precipitates, after cooling somewhat in the air, were left in the desiccator for 20 min. before being weighed: the crucibles were covered while in the desiccator and on the balance. Twenty-five cc. of aluminum chloride solution were used in every case. The filtrate and wash water from each determination were evaporated separately and tested for the presence of aluminum.

#### STRENGTH OF SOLUTION

The strength of the aluminum chloride solution was first determined in terms of the oxide. Two methods were used: (1) direct evaporation of the solution and ignition of the residue; and (2) evaporation and ignition after adding enough ammonium hydroxide to precipitate the aluminum hydroxide.

TABLE I—STRENGTH OF ALUMINUM CHLORIDE SOLUTION  
(1) Direct Evaporation of the Chloride (2) Evaporation after Addition of Ammonium Hydroxide

0.2303	0.2303	0.2300	0.2302	0.2303
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The results in Table I tend to show that the same value is obtained if the chloride solution made ammoniacal is evaporated as if the pure chloride is evaporated. This result would hardly be expected if aluminum chloride is volatile under the given condition, since the amount of aluminum present as chloride is much less in the first case than in the second. A slight loss might, however, occur in both cases so that a second series of test determinations was made. The amount of aluminum in terms of aluminum oxide was determined in a sample of Kahlbaum's crystallized aluminum sulfate. A second series was run parallel to this one, using some of the

TABLE II PER CENT $Al_2O_3$ IN $Al_2(SO_4)_3$ EFFECT OF $NH_4Cl$ ON $Al(OH)_3$					
Per cent		Per cent			
No.	Sample Grams	$Al_2O_3$ Found	Sample Grams	$NH_4Cl$ Gram	$Al_2O_3$ Found
1	0.5841	17.24	0.5336	0.3	17.17
2	0.6435	17.17	0.7723	0.3	17.17
3	0.7018	17.17	0.9590	0.3	17.18
4	0.9150	17.18	1.1417	0.3	17.18
5	0.9301	17.22	0.9561	0.5	17.24
6	1.0571	17.17	1.2990	0.5	17.21
7	1.2964	17.24	1.6290	0.5	17.20

same sample, but, after solution in a little water, adding some ammonium chloride and enough ammonium hydroxide to precipitate the aluminum as hydroxide.

The results, in Table II, show that there is no loss by volatilization of aluminum chloride when the precipitated hydroxide is ignited in presence of ammonium chloride.

#### EFFECT OF VARYING AMMONIUM HYDROXIDE

The next point taken up was the effect on the precipitation of varying the amount of ammonium hydroxide present. Water was used to transfer the precipitate from the casserole to the filter paper, as small an amount as possible being used. In no case did the wash water show a test for aluminum, while the filtrate from those determinations giving low results did give a test for aluminum. The results appear in Table III.

TABLE III EFFECT OF EXCESS OF AMMONIUM HYDROXIDE IN PRECIPITATION OF ALUMINUM HYDROXIDE

Very Slight Excess	10 cc Excess	15 cc Excess	20 cc Excess
0.2303	0.2281	0.2294	0.2288
0.2302	0.2271	0.2289	0.2305
0.2308	0.2287	0.2294	0.2302
0.2297	0.2304	0.2297	0.2287
0.2299	0.2304	0.2274	0.2291
0.2305	0.2283	0.2282	0.2265

The uniformity of results in the first column is very evident, as compared with that of the other three, although the uniformity there is not as great as desired. An excess of ammonia has a decided solvent effect, not proportional to the excess of ammonia added. The variation in results obtained in each of the other three columns must be due to very slight variations in procedure, such as time of filtering. The results in Column 1 check those obtained in evaporating the solution in a platinum crucible, as was to be expected.

#### EFFECT OF WASHING PRECIPITATE FREE OF CHLORIDES

On the effect of washing the precipitate free from chlorides, the results in Table IV were obtained.

TABLE IV EFFECT OF WASHING ALUMINUM HYDROXIDE FREE FROM CHLORIDES BY VARIOUS WASHES

Hot Water	1 Per cent $NH_4NO_3$ Solution	2 Per cent $NH_4NO_3$ Solution	3 Per cent $NH_4NO_3$ Solution
0.2285	0.2277	0.2262	0.2263
0.2281	0.2286	0.2263	0.2276
0.2280	0.2286	0.2262	0.2282

For the precipitations, 5 cc. of ammonium hydroxide were added, about 2 cc. of this being in excess. In no case was aluminum hydroxide found in the filtrate. In the first series, in all three cases, the wash water gave a test for aluminum hydroxide. In the second experiment the precipitate obtained was filtered off, ignited, and found to weigh 0.0022 g., which brings the total weight of the precipitate up to the value 0.2303 g. formerly obtained.

In every experiment the wash water was tested for aluminum and it was found to be present, so that the final conclusion was that ammonium nitrate solution, as used, was unsatisfactory for washing purposes.

#### EFFECT OF BLASTING IN VARIOUS WAYS

For heating the precipitates to constant weight an ordinary blast lamp was used. The amount of air used and type of lamp might change the results obtained. The first precipitates were blasted for 10-min. periods until constant weight was obtained.

Typical results appear in Table V. The weights given indicate the weight in grams of crucible and precipitate.

It is seen that three 10-min. periods or two 20-min.



periods served to effect a constant weight. Slight differences are undoubtedly produced by the size, weight and thickness of the crucible.

TABLE V.—TIME REQUIRED IN HEATING ALUMINA TO CONSTANT WEIGHT

Time Min.	No. 1	No. 2	No. 3	No. 4	Heated in 20 Min.	Heated in 40 Min.	Heated in 60 Min.
10	36.9670	29.6670	21.0588	29.6647	29.6838	29.6830	29.6637
20	36.9648	29.6683	21.0870	29.6638	33.7635	33.7637	33.7628
30	36.9605	29.6643	21.0869	29.6638	33.7760	33.7760	
40	36.9605	29.6643			36.9671	36.9603	36.9603
					29.6730	29.6730	29.6730

One precipitate was given a special series of blastings to determine whether or not the alumina was hygroscopic after the blasting. The results (Table VI) indicate that this change in weight was very largely

TABLE VI.—SHOWING HYGROSCOPIC PROPERTY OF ALUMINA

	Weights
Constant weight obtained (true + ppt.)	21.0598
Left 6 days in the desiccator	21.0636
Blasted 10 min.	21.0611
After 24 hrs. blasted 20 min.	21.0605
After 24 hrs. blasted 20 min.	21.0604
After 24 hrs. blasted 20 min.	21.0603
Blasted a second 20 min.	21.0598
Left covered in the balance case 24 hrs.	21.0624

due to the precipitate, since a platinum crucible treated in much the same way did not change appreciably in weight.

#### CONCLUSIONS

I—Boiling for 1 min. completely precipitates all aluminum present, and longer boiling may lead to a re-solution of part of it.

II—Aluminum hydroxide need not be washed free from ammonium chloride before ignition.

III—The excess of ammonia present when precipitation is made should be as small as possible and never more than 1 or 2 cc. in 250 cc. of solution.

IV—Aluminum hydroxide freshly precipitated is soluble to a slight extent in water and to about the same extent in dilute ammonium nitrate solution.

V—The precipitated hydroxide, when large, must be blasted 40 min. to insure its being reduced to a constant weight.

VI—The ignited alumina is strongly hygroscopic.

NOTE—Since this paper was written a paper has been published by W. H. Daudt, *THIS JOURNAL*, 7 (1915), 847, confirming what we have found to be true regarding the presence of ammonium chloride at the time of ignition.

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#### THE ANALYSIS OF SOAP POWDERS

By LOUIS ROSENBERG AND VICTOR LENHER

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During recent years great progress has been made in those industries which supply cleansing materials. The advent of the modern washing powder has brought into the household a convenient, economical cleanser. The powders which to-day are in common use divide themselves into three general classes:

I—So-called Washing Powders, composed of trisodium phosphate, borax, or a mixture of various proportions of sodium carbonate and bicarbonate: it is obvious from the composition of these powders that their main efficiency lies in their ability to soften the water used.

II—Soap Powders proper, a mixture consisting of various proportions of sodium carbonate and soap, the soaps used are commonly prepared from cottonseed soap stock and have as a filler sodium carbonate, which itself is a water softener of great value.

III—Scouring Powders, which contain an abrasive and soap either with or without the addition of sodium carbonate.

In this article are described various experiments which have been conducted on the soap powders proper. The basic scheme used is that given by Leffmann in Allen's "Commercial Organic Analysis." During our studies, Dr. Leeds published a scheme for the analysis of soap, which is quite similar to the one used by us for the analysis of soap powders. Additions and modifications to the older schemes were made as the work progressed, and it is to aid the soap analyst that important details are described.

Our purpose in presenting this paper is to offer our experience to those interested in the analysis of soap powders, and we do so because the particular problems we have found are not discussed in the form that is desirable for those who have similar problems to solve.

#### MOISTURE

The ordinary methods for determining water in soap are not satisfactory when applied to washing powders. Experiments have repeatedly demonstrated that heating a 10-g. sample at 105° C. until the weight becomes constant is worthless, for the odor of decomposing soap is usually observed before this temperature is reached. When heated for 1 hr. to 105°, most of the soap powders give off a strong odor of decomposed soap, hence the determination is of little value. Further, the soap powder upon heating to 105° frequently forms lumps which prevent complete drying: even if a weighed glass rod is used to break up the lumps, it is difficult to keep the sample from caking. In powders which contain as high as 30-40 per cent water, spattering frequently occurs. Leffmann's suggestion for soap—that the drying be done on a sand bath—is useless with many powders, inasmuch as even with the greatest care, decomposition takes place. The methods in use for the determination of moisture in a high-grade stearic acid soap are unsatisfactory, as they frequently fail entirely when applied to soap powders containing cottonseed soap stock or low-grade tallow soap.

The method of Fahrion, in which the sample is heated with three times its weight of oleic acid until a clear solution is obtained, indicating the removal of the water, was found to be inapplicable, as difficulty was experienced in determining when the solution became clear. The recommendation of Fahrion, to heat the sample (to which has been added oleic acid) in a platinum dish over a free flame, was also tried with the soap powders, but even with the greatest care decomposition of the soap took place. On a sand bath the powder soon decomposed. Sample 1, containing actually 37.8 per cent of water, was used in experimenting with oleic acid in order to test this method for moisture. Six samples of 2 g. each were

mixed with 6 g. of anhydrous oleic acid. On heating, the odor of decomposing soap was noticed from all. The two samples showing the clearest solution and the least odor indicated 56.5 per cent and 60.3 per cent water, respectively, or an error of 50 to 60 per cent more water than they actually contained.

The method recommended is one in which the heating can be done at low temperature. A vacuum drying oven is admirably suited for this purpose. The various powders examined in our studies were heated between 60 and 65° at a pressure of 60 mm. until the weight became constant. In the 2-g. samples used, constant weight was attained only after 10 hrs. heating, and in some cases 20 hrs. of heating were required. No odor was observed and the samples did not cake. The results (percentages) were as follows:

No. 1, 37.85 and 37.82; No. 2, 23.75 and 23.99.

The recommendations commonly given to heat for 12 hrs. are insufficient. No. 3, for example, required 20 hrs. heating in the vacuum oven before constant weight was attained.

#### PETROLEUM ETHER EXTRACTION

The usual procedure of extraction with petroleum ether, with a Soxhlet extractor, was used in order to determine the unsaponified fat, unsaponifiable matter from the fat and free fatty acids. A 10-g. sample of the soap powders frequently required as much as 15 hrs. of extraction with petroleum ether. The solvent was subsequently evaporated and the residue weighed. All of the powders examined were found to contain less than 1 per cent of unsaponified matter.

#### FATTY ACID DETERMINATION

The determination of the fatty acids in the soap powders is, of course, of the greatest importance, inasmuch as it means the soap content of the powder. Of the various methods which have been suggested for the determination of the fatty acid content in soaps, the most important are: (1) Direct weighing; (2) petroleum ether extraction; (3) potassium soap; (4) volumetric. Fendler and Frank<sup>1</sup> have shown the inaccuracies of all of these methods.

In the direct weighing method, a piece of weighed paraffin or stearic acid is added to the liberated fatty acids, and the cooled solidified mass is subsequently weighed. The results are frequently very high. Extraction of the fatty acids with petroleum ether and evaporation of the solvent commonly gives low results. The variation in the results depends largely on length of drying of the fatty acids obtained. In one instance the percentage of fatty acids was reduced nearly 60 per cent by long drying. Fendler and Frank preferred for accuracy the potassium soap method, but inasmuch as the potassium soap must be dried for 20 to 28 hrs. on a water bath, the method is rather too time-consuming for ordinary commercial analysis. Volumetric methods can be said to give only fair results.

The cake method is a simple, rapid method; but unless due precautions are taken, discordant results

are obtained. The inaccuracies of the cake method, according to Noerdlinger, are attributed to the stearic acid used to collect the fatty acid. If the stearic acid is previously heated to 160° the inaccuracies are avoided. In our experiments the cake method was adopted as the most satisfactory procedure, and was carried out as follows:

A 2-g. sample of the powder is placed in a tall, narrow, 200-cc. beaker 4 in. high, and the sample dissolved in hot water. An excess of  $N/2$  nitric acid is then added to separate the fatty acids. The solution, stirred continuously, is heated for  $1/2$  hr. in boiling water, and a weighed portion of 4 g. of stearic acid, previously heated to 160°, added. The solution is stirred repeatedly and warmed for another  $1/2$  hr., after which the beaker and contents are allowed to cool. The stirring rod, which should be about 1 in. longer than the beaker, is allowed to remain in the beaker. The fatty acid and the stearic acid on cooling solidify, and can be easily lifted out of the beaker by means of the stirring rod. The liquid in the beaker can be filtered in order to collect any solidified fat which has not adhered to the cake, but usually this amount is small. The circle left by the cake around the beaker can be readily scraped off and added to the cake. The cake is then wiped with filter paper and placed upon a weighed cover glass, allowed to dry for several hours, after which it is weighed. The weighed cake less the weight of the stearic acid added gives the amount of fatty acid in the sample.

If the melted fat is allowed to cool rather slowly, a more uniform cake is formed, and the cake can be more easily removed from the beaker; whereas if the cake be cooled quickly, the rapid solidification causes moisture to be enclosed in the cake. If cavities are formed, these are likely to enclose the solution. A 200 cc. beaker of the tall, narrow type is a convenient size, inasmuch as a cake suitably fitted to the balance pan is formed. Furthermore, the addition of mineral acid to a washing powder commonly causes much effervescence, due to large percentages of sodium carbonate: the use of a tall beaker lessens the danger of overflow during this sudden effervescence.

#### TOTAL ALKALI DETERMINATION

Should the percentage of total alkali be required, the excess of standard acid required to liberate the fatty acid can be titrated back with  $N/2$  alkali. In washing powders, the total alkali reported does not have the significance that it does in soap. The presence of sodium carbonate marks the amount of alkali combined as soap. A total alkali determination cannot be used as a means for determining the relative merits of different powders, since the powder with the highest per cent of sodium oxide may be the one which contains the lowest per cent of soap. A total alkali determination is unnecessary, unless it is desirable to check the individual alkali determinations.

#### SODIUM CHLORIDE DETERMINATION

In our hands the gravimetric method is preferable over the volumetric method for the determination of chlorides in soap powders.

<sup>1</sup> *Z. angew. Chem.*, **22** (1909), 252-61.



## ALCOHOL EXTRACTION

In order to separate the soap content of the powders from such fillers as sodium carbonate, sodium silicate, borax, etc., it is necessary to make an extraction with alcohol. Due to the fact that soap powders contain a high percentage of water, it is preferable to use absolute alcohol. If, however, the analysis is to be made on a sample which has been dried in the vacuum oven, 95 per cent alcohol is satisfactory.

A 2-g. sample of the powder can be extracted in a 250-cc. beaker with 100 cc. of alcohol for  $\frac{1}{2}$  hr. The alcohol becomes yellow colored and a white residue of the inorganic salts, such as sodium carbonate, sodium silicate, and borax, separates out and can be filtered off and washed with alcohol. In this extract, phenolphthalein will show the presence of caustic alkali. No free alkali was found in any of the powders examined. On the other hand, all of the soap powders showed a trace of free fatty acid. The alkali combined as soap is found by adding a large excess of water to the alcoholic solution and boiling off the alcohol, decomposing the soap with an excess of  $N/2$  nitric acid and titrating back with  $N/2$  alkali. The alkali found is reported as  $Na_2O$ . No distinction need or-

## DETERMINATION OF SODIUM CARBONATE AND SILICATE

The residue from the extraction with alcohol is dissolved in water and diluted to exactly 250 cc. in a volumetric flask. The residue from all of the samples analyzed was completely soluble in hot water. In one or two powders a slight residue remained upon the filter paper, but the amount was too small to warrant further examination. Aliquot portions of 50 cc. are taken for the silica determination. The solution is acidulated with hydrochloric acid and evaporated to dryness, as in the ordinary method for the determination of silica. The acidification and evaporation are repeated. The soluble matter is extracted with hot water and the residue when dried and ignited is weighed as  $SiO_2$ . The percentage of silica was calculated to sodium silicate ( $Na_2Si_2O_5$ ). In the soap powders analyzed the amount of silica found was so small that it was probably present as an impurity rather than as a real constituent of the powder. Borax was not found to be present in any of the powders analyzed. In the absence of borates and with less than 1 per cent of sodium silicate, a fair determination of the sodium carbonate can be made by direct titration with  $N/2$  hydrochloric acid, using methyl orange as the indicator.

TABLE I—SCHEME OF ANALYSIS

Weigh out a 2-gram sample. Dry in vacuum oven at 65° C.		Loss in weight = Moisture. Extract with petroleum ether.
EXTRACT	RESIDUE consists of Soap and Mineral Constituents.	Extract with 95 per cent alcohol.
Contains Uncombined Fat.	EXTRACT consists of Soap and free Alkali.	RESIDUE consists of $Na_2CO_3$ , $NaCl$ , $NaSi_2O_5$ , $Na_2SO_4$ , $Na_2B_4O_7$ , Starch and Insoluble Matter. Dissolve in hot water, dilute to 250 cc. and filter: divide the filtrate into five equal parts.
Evaporate the ether, dry at 110° C. and weigh.	(1) Add 2 or 3 drops of phenolphthalein, and titrate with $N/10$ acid; the amount used corresponds to free caustic alkali: calculate as $Na_2O$ .	1— $Na_2CO_3$ : Titrate with $N/2$ HCl.
	(2) Next add a large excess of water, boil off the alcohol, decompose with excess of $N$ $HNO_3$ and boil: add 4 g. stearic acid, boil again, and cool.	2— $NaCl$ : Precipitate with $AgNO_3$ and weigh as $AgCl$ .
	SOLUTION contains Soda CAKE contains Fatty combined as Soap. Titrate excess of acid back with $N/2$ $NaOH$ . $N$ acid used corresponds to $Na_2O$ combined as Soap.	3— $NaSi_2O_5$ : Add HCl and evaporate to dryness; repeat. Add water, filter, dry, ignite and weigh as $SiO_2$ . Calculate to $Na_2Si_2O_5$ .
		4— $Na_2SO_4$ : Precipitate with $BaCl_2$ and weigh as $BaSO_4$ . Calculate to $Na_2SO_4$ .
		5—Borates: If present, determine by glycerol or mannitol method.
		RESIDUE Consists of Starch and Insoluble Matter.

dinarily be made between the sodium and the potassium in soap powders. The alcoholic extract should be diluted to at least 250 cc. before titrating in order to get a satisfactory end-point.

A rapid method for analysis of soap powders is based on the alcoholic extraction procedure: A 2-g. sample is extracted with absolute alcohol, the solution filtered and the filtrate tested with phenolphthalein for free alkali. If the solution contains free alkali it is titrated with  $N/2$  nitric acid; the alcohol is then evaporated off, leaving a residue of dry soap, which, if it has not been necessary to add nitric acid, can be weighed and reported as percentage of total soap. To determine the alkali combined as soap, the dry residue of soap is dissolved in water and the solution titrated with  $N/2$  nitric acid, using methyl orange as the indicator. The residue from the alcoholic extraction, which consists of sodium carbonate, sodium silicate, borax, etc., can be tested by the methods given below. The percentage of total soap plus sodium carbonate, etc., deducted from 100 per cent will give the approximate amount of water, or, an accurate water determination can be made in the vacuum drying oven.

Should sodium bicarbonate be present in the powder, the treatment of the residue insoluble in petroleum ether and in alcohol, would necessarily need to be materially modified.

## SCHEME OF ANALYSIS

The condensed scheme of analysis outlined in Table I is suggested for soap powders. It is based on the solubility of soap in alcohol and the insolubility of the inorganic constituents. It possesses the advantage that but one sample need be taken for analysis, and the soap itself is separated at once from the other constituents of the powder. In the simple scheme, as given, such substances as fluorides, rosins, glycerin, sugar, and sodium bicarbonate are not provided for. Our experience with the powders examined showed them to be of simple composition.

## DISCUSSION OF RESULTS

The analyses of a number of representative soap powders are given in Table II. Their composition in a number of cases differs materially from that given for the same powder by Bragg<sup>1</sup>. This difference is doubtless due to the introduction of the continuous

<sup>1</sup> *Chemical Engineer*, 18 (1913), 73.

drying apparatus which has changed the formula used by a number of the larger manufacturers. The continuous drying apparatus allowed the manufacturer to

led us to undertake a more careful study of the conditions necessary to make the method work with certainty.

TABLE II—TABULATION OF RESULTS (PERCENTAGES)

Sample No.	Moisture	Partly Anhydrous Soap	Na <sub>2</sub> O	Total Soap	Na <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> SiO <sub>3</sub>	NaCl	Unsat. Saponified Matter	Total Per cent
1	37.82	18.39	2.63	21.02	39.37	0.45	0.55	0.69	99.90
2	22.06	19.44	3.58	23.02	53.53	0.99	0.75	0.24	100.59
3	23.75	21.63	2.71	24.34	50.35	0.72	0.35	0.85	100.36
4	20.86	18.93	2.65	21.58	55.38	0.90	0.86	0.45	100.03
5	18.52	20.34	2.68	23.02	56.45	0.36	1.32	0.74	100.41
6	43.38	16.74	2.23	18.97	36.30	0.72	0.34	0.87	100.58
7	30.40	21.46	2.86	24.32	40.00	0.99	0.72	0.79	97.22

increase the water content of the product and to lessen the amount of soap. Previously this addition of water resulted in an inferior caked powder.

The determinations made show that the soap powders consist essentially of sodium carbonate and soap. This should be the case from the method of manufacture employed, *i. e.*, the soap stock, caustic alkali and soda are incorporated and the product prepared similar to that of soap. After hardening it is ground into the powder form in which it appears on the market.

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## THE DETERMINATION OF CHROMIUM AND VANADIUM IN STEEL BY ELECTROMETRIC TITRATION

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The method to be described includes the solution of the steel in acid, the oxidation of the elements in question under suitable conditions, and the titration of the solution with ferrous sulfate using the electrometric method of determining the end-point. This method of titrating chromates has been described recently by Hildebrand<sup>1</sup> and by Forbes and Bartlett,<sup>2</sup> and has been applied by the authors to the determination of vanadium.<sup>3</sup> The apparatus is in all respects identical with that described elsewhere for the determination of vanadium and therefore will not be dealt with here.

### DETERMINATION OF CHROMIUM IN STEEL

It was hoped that by the application of the electrometric method to the determination of chromium, an accurate and rapid method could be devised for the determination of this element. To this end the oxidation of chromium salts to chromates was undertaken after the methods suggested by Walters,<sup>4</sup> Rich<sup>5</sup> and Tusker.<sup>6</sup> These methods were selected because of their simplicity and because they involve no filtering. In these methods ammonium persulfate is used to oxidize chromium and manganese to chromate and permanganate, sometimes with the addition of silver nitrate. Hydrochloric acid, added in small amounts to the hot solution, serves to reduce the permanganic acid, but is without action on the chromates. On trying the different modifications of this method which have been published, extremely variable and unsatisfactory results were obtained. This experience

It seemed possible to us that the following errors might interfere with the successful working of the method: (a) Incomplete decomposition of ammonium persulfate, (b) incomplete oxidation of chromium, (c) reduction of part of the chromate by hydrochloric acid during the breaking up of permanganic acid, and (d) incomplete reduction by the hydrochloric acid of manganese in the higher states of oxidation. (a) and (d) would tend to make the results too high, while (b) and (c) would have the opposite effect; thus it might be possible for some of the errors to exist undetected because of counterbalancing. We therefore planned to test each point separately.

### DECOMPOSITION OF AMMONIUM PERSULFATE

Eight solutions of 300 cc. volume, each containing 0.0102 g. of chromium as chromate and 65 cc. of sulfuric acid (sp. gr. 1.20), were heated to boiling and 5 g. of ammonium persulfate added. The solutions were then boiled in groups of two for 5, 10, 15 and 30 min., after which they were cooled and titrated with ferrous sulfate, using the electrometric end-point. The potassium dichromate solution had been standardized against ferrous sulfate electrometrically and this in turn had been compared with standardized potassium permanganate solution.

From the experiments shown in Table I, it is evident that 5 min. boiling of such a solution does not

TABLE I—THE DECOMPOSITION OF AMMONIUM PERSULFATE  
0.0102 G. Chromium Present in Each Case

Time of Boiling (min.)	5	10	15	30
Chromium Found (g.)	{ 0.0159 0.0196	{ 0.0101 0.0117	{ 0.0095 0.0094	{ 0.0096 0.0082

completely remove the ammonium persulfate and the oxidizing agents into which it decomposes. Even 10 min. is insufficient in some instances. Boiling for a much longer time has the apparent effect of reducing some of the chromate, for the values are uniformly lower than the expected values. It is not improbable that this reduction goes on from the first, but its effect upon the titration is masked by the fact that other oxidizing agents have not been removed. This may be explained as due to the breaking down of the ammonium persulfate in acid solution to give Caro's acid and hydrogen peroxide, both of which reduce chromium. We believe that any method depending upon ammonium persulfate alone for its oxidizing action can give correct results only by a balancing of errors. This opinion is supported by other experiments in which the sulfuric acid mentioned above was changed to higher and lower concentrations, and in which it was partly and completely replaced by nitric acid.

### DECOMPOSITION OF AMMONIUM PERSULFATE IN THE PRESENCE OF SILVER NITRATE

Marshall<sup>1</sup> suggested the use of ammonium persulfate and silver nitrate in dilute nitric acid as an oxidizing agent for manganese. Experiments parallel

<sup>1</sup> *J. Am. Chem. Soc.*, **35** (1913), 869

<sup>2</sup> *Ibid.*, **35** (1913), 1527

<sup>3</sup> *Ibid.*, **38** (1916), 341.

<sup>4</sup> *Met. Chem. Eng.*, **12** (1914), 310

<sup>5</sup> *Ibid.*, **13** (1915), 239.

<sup>6</sup> *Chem. Ztg.*, **39** (1915), 122.

<sup>1</sup> *Chem. News*, **83**, 16



to those shown in Table I were tried, using the same volume of solution and the same amounts of ammonium persulfate and potassium dichromate, but adding in every case 10 cc. of a solution of silver nitrate which contained 1.5 g. of  $\text{AgNO}_3$  in a liter. The sulfuric acid (sp. gr. 1.20) was replaced by nitric acid (sp. gr. 1.13) as indicated in Table II.

TABLE II—DECOMPOSITION OF AMMONIUM PERSULFATE IN PRESENCE OF SILVER NITRATE

Initial Volume, 300 cc.	0.0102 G. Chromium Present in Each Case		
Acid Used	60 cc. $\text{HNO}_3$	60 cc. $\text{H}_2\text{SO}_4$	60 cc. $\text{HNO}_3$
Time of Boiling	5 min.	30 min.	30 min.
Chromium Found (G.)	0.0103	0.0101	0.0101

The variations found in the experiments recorded in Table II are within the experimental error of the method and show that in the presence of silver nitrate the course of the decomposition of ammonium persulfate is very different from that which it follows when this salt is absent. This follows from the fact that no oxidizing materials, except the chromium, were present after 5 min.' boiling, and 30 min.' boiling did not result in the reduction of any chromate. The presence of nitric acid does not appear to be necessary, but since in the analysis of steel the iron in the sulfuric acid solution of the sample is most conveniently oxidized with nitric acid, the effect of nitric acid was determined.

#### THE REDUCTION OF OXIDIZED MANGANESE WITH HYDROCHLORIC ACID

Solutions containing 0.005 g. of manganese as manganoous sulfate, an amount corresponding to 0.5 per cent of manganese in a 1-g. sample of steel, were treated with nitric or sulfuric acid, as specified in Table III, and made up to a volume of 300 cc. The

TABLE III—EFFECT OF SMALL AMOUNT OF COLD HYDROCHLORIC ACID ON TITRATION OF MANGANESE

$\text{HNO}_3$ (Sp. Gr. 1.13)	$\text{H}_2\text{SO}_4$ (Sp. Gr. 1.20)	CHROMIUM		Oxidizing Materials Found in Terms of Chromium
		Taken	Found	
3 drops	300 cc.	0.0010	0.0010	0.0000
	60 cc.	0.0069	0.0070	0.0001
60 cc.		0.0081	0.0081	0.0000
60 cc.		0.0081	0.0081	0.0000

solutions were heated to boiling and 10 cc. of the silver nitrate solution added, followed by 5 g. of ammonium persulfate. After boiling 7 min., 1 cc. of dilute hydrochloric acid (1 acid : 2 water) was added, and boiling continued for 5 min. In all cases the solutions had a red color after the addition of ammonium persulfate; and they became colorless after the addition of hydrochloric acid. To detect oxidizing substances left in the solution, after cooling, a measured amount of potassium dichromate was added and the solution titrated with ferrous sulfate as usual.

Under the conditions of the experiments shown in Table III, the oxidation and reduction of manganese were entirely satisfactory for the purposes of the method, inasmuch as no unreduced manganese compounds were left in the solution after the treatment with hydrochloric acid.

Subsequent work on the method as finally established for the analysis of steel showed that the oxidation of manganese by ammonium persulfate was by no means as simple as might be supposed. On the addition of the oxidizing agent to the hot solution, the

colors resulting after a few minutes' boiling would vary from a light pink, a deep red, a murky brown and finally an actual precipitate of manganese dioxide, depending on the amount of manganese present. On the addition of hydrochloric acid to such solutions, those having a pink or red color would grow yellow (in the presence of chromium) or colorless, in the course of 2 min. The dark brown solutions would lose their color and turbidity only after boiling 5 to 7 min., while solutions containing precipitated manganese dioxide failed to clear up, except on prolonged boiling with a larger amount of hydrochloric acid. In spite of the fact that large amounts of manganese cause the solution to become murky and even to precipitate manganese dioxide, it has been found possible to determine Cr in a 1-g. sample of steel when the amount of manganese corresponded to 3 per cent. This is possible for two reasons: (a) When such a solution is obtained in the presence of the other products of solution of steel there is less tendency for the manganese to precipitate as oxide; and (b) if the acid concentration is kept reasonably high (60 cc. of sulfuric acid of sp. gr. 1.20 to 300 cc. of solution) a very high percentage of manganese is necessary to cause precipitation. However, the latter condition may be carried too far, for if the concentration of acid amounts to as much as 100 cc. of sulfuric acid of this strength, both the chromium and manganese oxidize with greater difficulty and may not oxidize at all.

#### THE OXIDATION OF CHROMIUM AND THE EFFECT OF BOILING WITH HYDROCHLORIC ACID

In order to test the usefulness of the method for the oxidation of chromium, solutions containing varying quantities of potassium dichromate and 2 cc. of  $N/10$  potassium permanganate solution were reduced with an excess of ferrous sulfate in the presence of 30 cc. sulfuric acid (sp. gr. 1.40). The excess of ferrous iron was oxidized by heating with 15 drops of concentrated nitric acid. The solution, now containing a known weight of chromium with some ferric salt and manganese, was diluted to 300 cc. and treated with 10 cc. of dilute silver nitrate solution and 5 g. of ammonium persulfate as usual. After boiling 10 min., 5 cc. of hydrochloric acid (1 to 3) were added and the solution boiled 5 min. longer. The solution was then cooled and titrated electrometrically.

TABLE IV—DETERMINATION OF CHROMIUM IN THE PRESENCE OF MANGANESE

0.0022 G. Manganese Added in Each Case			
Chromium Taken (G.)	0.0102	0.0203	0.0404
Chromium Found (G.)	0.0101	0.0203	0.0403

The few figures given in Table IV are sufficient to illustrate that the oxidation of chromium by ammonium persulfate and silver nitrate is a quantitative process and that hydrochloric acid effectively reduces the manganese oxidized at the same time without reducing the chromium.

#### OBSERVATIONS CONCERNING THE ELECTROMETRIC TITRATION OF CHROMIUM

The apparatus and method used was identical with that used by Forbes and Bartlett,<sup>1</sup> except as

noted in our paper on the determination of vanadium. In titrating pure chromate solution with ferrous sulfate, we noted the anomalous rise first observed by Forbes and Bartlett. Thus on setting the needle of the galvanometer on the middle of the scale and adding ferrous sulfate, a retrograde motion of the needle began at once, continuing until it had covered about seven divisions on the scale. The movement became less and less as more ferrous sulfate was added until just before the end-point was reached, when it remained stationary until a slight excess of ferrous sulfate caused it to move rapidly in the direction opposite to that in which it had been moving. As soon as enough dichromate solution had been added to cause the needle to return to its stationary position the titration was considered completed.

It was noted early in the course of these experiments that the anomalous rise in potential either was absent or was much less marked in solutions which had been treated with an oxidizing agent, such as ammonium persulfate. During the titration of the solution of a sample of steel which had been so oxidized, the needle remained within a few divisions of the original point during the addition of the first portions of ferrous sulfate, and would remain absolutely stationary during the addition of the last portions, when an excess would produce a decided movement. Ferric iron likewise seemed to inhibit this phenomenon. In one instance, a solution of chromium sulfate, after oxidation with potassium permanganate, was boiled with ammonia to decompose the permanganate. The solution so obtained, when filtered to free it from manganese dioxide, showed no anomalous rise on titrating. Our limited investigation of this point leads us to believe that amounts of oxidizing agents other than chromate, which are too small in amount for detection otherwise, are effective in suppressing this anomalous behavior of the cell.

#### THE EFFECT OF FERRIC IRON ON THE ACCURACY OF THE TITRATION

Having noted that ferric salts interfered with the anomalous rise, we became interested to know how these salts would affect the titration if they were present in large amounts. Accordingly, solutions containing 1, 2 and 3 g. of ferric iron were prepared and known quantities of chromium added. Each solution had a volume of 250 cc. and contained 25 cc. of sulfuric acid (sp. gr. 1.40) and 0.0253 g. of chromium as chromate. The ferrous sulfate solution was of such strength that one drop was equivalent to 0.00005 g. of chromium. In Table V the

fore and after the end point. After the final throw of the needle, enough potassium dichromate solution was added to cause the needle to return to the end point and two drops additional.

The experiments recorded in Table V indicate that the end-point is as sharp for large amounts of chromium as for small amounts (cf. electrometric titration of vanadium<sup>1</sup>), but is much affected by the presence of ferric salts, especially as regards the anomalous rise. That the amount of change for a given increment of ferrous salt would be less in the presence of a large amount of ferric iron would be expected from a consideration of the ferric-ferrous potential, although we should not expect the differences to be so large as those found. The expression,<sup>2</sup>

$$\pi = 0.988 + \frac{RT}{F} \ln \frac{Fe^{++}}{Fe^{+++}}$$

gives the value of the potential which is established when the first drop of ferrous iron in excess is added. A given amount of ferrous iron will obviously produce a greater change in the value of  $\pi$  when the concentration of  $Fe^{+++}$  is small than when it is large. The effect upon the anomalous rise cannot be so readily explained. The differences observed in the above experiments show that there might be a tendency to add more ferrous sulfate when titration is made in the presence of large amounts of ferric salt, but if the titration is carefully made the end-point is the same.

#### THE SENSITIVENESS OF THE END-POINT

It seemed possible that while our method of noting the potential change was simpler than that used by Forbes and Bartlett, perhaps it was less sensitive. To test this point we diluted our solutions to ten times the volume and made titrations with these. The original solutions of potassium dichromate contained 0.001 g. of chromium per cc. The diluted solution therefore contained 0.0001 g. per cc. In working with this and an equivalent solution of ferrous sulfate we had no difficulty in making duplicate titrations on 30 cc. of solution within 0.30 cc. This corresponds to an error of 0.000033 g. It would thus appear that our apparatus was sufficiently sensitive for practical purposes.

#### ACID CONCENTRATION AND THE EFFECT OF CHLORIDES

Numerous experiments on the titration of chromium in steel failed to show any effect of temperature on the accuracy or position of the end-point. The acid concentration should be quite high, particularly in the presence of chlorides, as it prevents irregular movements of the needle. Our experiments on the titration in the presence of chlorides showed that small amounts were without effect, intermediate quantities gave irregular results, but cold solutions containing large amounts of hydrochloric acid gave excellent titrations.

#### THE TITRATION OF CHROMIUM AND VANADIUM

Since chromium and vanadium often occur together in steel, the fact that any device for oxidizing chromium

GRAMS IRON ADDED AS	GRAMS CHROMIUM		GALVANOMETER CHANGES AFTER SUCCESSIVE DROPS $FeSO_4$					ANOMALOUS RISE BEFORE END POINT
	Taken	Found	1	2	3	4	5	
Alum.	None	0.0253	0	1	3	4	4	12 divisions
1	0.0253	0.0252	0	0.5	2	3	3	2 divisions
2	0.0253	0.0252	0	0.5	2	2	3	None
3	None	None	0	2	2.5	3	3	1 division
None	0.0051	None	0	2	2.5	3	3	10 divisions

change of reading of the galvanometer is shown for each drop of ferrous sulfate added immediately be-

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Peters, *Z. phys. Chem.*, **26**, 1878, 305.



oxidizes the vanadium at the same time, made it necessary to adapt the method to the determination of both elements. When the procedure employed for the analysis of plain chromium steel is applied to the analysis of a solution containing chromium as chromate and vanadium as vanadate, both are reduced by titration with ferrous sulfate. The end-point obtained under these circumstances is less sharp than the one obtained when chromium alone is titrated. The end-point observed is really the vanadium end-point, the characteristics of which have been described elsewhere.

To test the accuracy of this titration, known quantities of chromium as chromate solution were mixed with known quantities of vanadium. These mixed solutions were reduced with excess of ferrous sulfate and oxidized with nitric acid, silver nitrate and ammonium persulfate under the conditions described above. The solutions were then boiled with a small amount of hydrochloric acid. After cooling to 20° C. they were titrated electrometrically with ferrous sulfate in a volume of 250 cc. The chromium was assumed as the amount taken, the difference being taken as vanadium.

TABLE VI—TITRATION OF SOLUTIONS CONTAINING BOTH CHROMIUM AND VANADIUM

Chromium Assumed (G.).....	0.0203	0.0101	0.0203
Vanadium Taken (G.).....	0.0255	0.1000	0.0255
Vanadium Found (G.).....	0.0254	0.1001	0.0252

This titration gives the oxidizing value of both chromium and vanadium. As the percentage of vanadium in steels is often quite low, it is convenient to take a 3-g. sample for the vanadium determination, of which an aliquot portion may be used for the total chromium and vanadium determination.

#### THE APPLICATION OF THE METHOD TO THE DETERMINATION OF CHROMIUM AND VANADIUM IN STEEL

**PROCEDURE IN THE ABSENCE OF VANADIUM**—A 1-g. sample of steel is dissolved in 60 cc. of sulfuric acid (sp. gr. 1.20), evaporated until salts separate, diluted to a volume of 60 cc. and while still hot oxidized with dilute nitric acid. Evaporation until salts separate is recommended here as a device for breaking up carbides: the completeness with which this has been accomplished may usually be judged by an examination of the diluted solution, for, if carbides remain undestroyed, a more or less well marked turbidity, possibly accompanied by clearly visible, dark particles, will be noted: when this method fails to break up carbides, a more vigorous attack may be had by dissolving in 60 cc. of dilute hydrochloric acid (sp. gr. 1.15) after which the solution should be oxidized with nitric acid; this solution, however, must be evaporated with 60 cc. dilute sulfuric acid to the appearance of fumes to give complete separation of hydrochloric acid. However prepared, the solution (containing the equivalent of 60 cc. sulfuric acid of sp. gr. 1.20) should be diluted to a volume of 300 cc. and heated to boiling. To the boiling solution are then added 10 cc. of a solution of silver nitrate containing 2.6 g. per liter and 5 g. ammonium persulfate, conveniently used in the form of a solution containing 50 g. of the salt in a volume of 250 cc.

The solution is boiled vigorously for 10 min., after which 5 cc. dilute hydrochloric acid (1:3) are added and the boiling continued for 5 min. After cooling to a convenient temperature and the addition of a little more sulfuric acid, the solution is ready to titrate electrometrically.

It is generally possible to tell if the process has failed at any point by certain readily noted signs. Thus the failure to break up carbides may be noted by examining the solution. If the solution contains chlorides which would interfere with the catalysis of the ammonium persulfate oxidation by the silver nitrate, a precipitate of silver chloride will appear. If the oxidation of the chromium is unsatisfactory, the deep red color of the permanganic acid will fail to appear. If the decomposition of the permanganic acid with hydrochloric acid is incomplete, the solution will not have a clear yellow color. The chief pitfalls into which the analyst may fall are, (1) incomplete breaking up of carbides of chromium, (2) incomplete oxidation of chromium due to high concentration of acid, precipitation of silver or the presence of too little ammonium persulfate, (3) failure to remove all of the products of the decomposition of the oxidizing agent (which may be accomplished by boiling 10 min.), and (4) failure to remove the chlorine liberated by the action of hydrochloric acid on the permanganic acid for which 5 min. boiling is necessary.

**PROCEDURE IN THE PRESENCE OF VANADIUM**—A 2 or 3 g. sample of steel is dissolved as in the above procedure, using up to 100 cc. of dilute sulfuric acid where this is necessary. The solution is diluted to 200 cc., heated to 80° C., and after the addition of 5 g. of sodium phosphate, is titrated with *N*/10 potassium permanganate until the first "gray" color appears. The solution is then cooled to 10 to 20° C. by adding ice, and more sulfuric acid is added, when it is ready for the electrometric titration with ferrous sulfate. After the titration, the stirrer and the electrodes are rinsed into the solution, which is then made up to definite volume and a portion representing 1 g. of the steel is taken for the chromium determination. This portion is diluted to 300 cc., heated to boiling and otherwise treated as described under the procedure for chromium, except that before the titration with ferrous sulfate, the solution should be cooled thoroughly. The amount of chromium present is calculated from the amount of ferrous sulfate used, as corrected for the amount of vanadium present and the amount of chromium used in finding the end-point in this and the previous titration.

When tungsten is present the precipitate of  $WO_3$  makes it difficult to deal with the carbide present. The addition of 5 g. of sodium phosphate, as suggested by Wdowiszewski,<sup>1</sup> by keeping the tungstic oxide in solution, makes this much easier.

The fact that potassium permanganate will oxidize chromic salts in hot acid solution causes the end-point obtained by oxidizing with this reagent to be somewhat fleeting. Usually the end-point is visible for 2 min. In general, there is very little difficulty in find-

<sup>1</sup> Chem.-Ztg., 34, 1365.

ing the end-point if the solution is hot (70 to 80° C.), fairly dilute (200 cc.) and the chromium content is not too high. The addition of some sodium phosphate prevents interference from the yellow color of the ferric iron, but green chromic salt is the main cause of difficulty. The first change of color which appears (from green to "gray") should be taken as the end-point. If too much permanganate is added, a few drops of ferrous sulfate may be added and the end-point sought again.

TABLE VII—ANALYSIS OF SAMPLES OF STEEL FOR CHROMIUM AND VANADIUM

Expt. No.	SAMPLE	Sample Weight G.	Per Cent Mn Added	PER CENT CHROMIUM			PER CENT VANADIUM		
				Present	Added	Found	Present	Added	Found
1	Private Standard	1	0.50	1.46		1.46			
2		1	0.80	1.46		1.49			
3		1	1.50	1.46		1.47			
4		1	3.10	1.46		1.44			
5		1	1.46			1.44			
6		1	1.46			1.45			
7		1	1.46			1.40			
8		1	1.46			1.45			
9		1	1.46			1.44			
10		1	1.46			1.44			
11		1	1.46			1.43			
12		1	1.46			1.46			
13		2	1.46			1.46			
14		2	1.46			1.47			
15		2	1.46			1.47			
16		3	1.46			1.47			
17		3	1.46			1.47	0.13	0.13	
18		3	1.46			1.47	0.26	0.26	
19		3	1.46			1.46	0.53	0.52	
20		2	1.46			1.47	1.04	1.03	
21		2	1.46			1.46	1.57	1.55	
22		2	1.46			1.46	2.55	2.58	
23		2	1.46			1.46	2.55	2.58	
24	Bureau of Stds. No. 32	1	0.89		2.08	3.54			
25	32	1	0.89		3.60	5.08			
26	32	1	0.89			0.92			
27	32	1	0.89			0.93			
28	31	1	3.51			3.51			
29	31	1	3.51			3.56			
30	31	1	3.51			3.54			
31	31	1	3.51			3.56			
32	34	1	0.01			0.01			
33	34	1	0.01			0.003			
34	34	1	0.01		2.53	2.55			
35	34	1	0.01		2.53	2.55			
36	10(b)	1	0.005			0.007			
37	10(b)	1	0.005		2.53	2.54			
38	10(b)	1	0.005		2.53	2.54			
39	16(a)	1	0.008			0.007			
40	30	3	1.35			1.37	0.21		0.20
41	30	3	1.35			1.36	0.21		0.20
42	30	3	1.35			1.36	0.21		0.20

The results given in Table VII were obtained by using the procedure given above. Besides the standards issued by the Bureau of Standards, a standard prepared in this laboratory, having a chromium content of 1.46 per cent, was analyzed with and without varying amounts of added chromium, manganese and vanadium.

RESEARCH DEPARTMENT, THE MIDVALE STEEL COMPANY  
PHILADELPHIA

## POMACE WINES: THEIR COMPOSITION AND DETECTION<sup>1</sup>

By JOHN R. EOFF, JR.

Received April 21, 1916

Desiring some information on the composition of various types of American wines, the laboratory of the Internal Revenue Bureau undertook in 1913-14 the collection and analysis of a large number of these wines, and it particularly desired to ascertain the composition of the so-called pomace wines, at that time being rather extensively manufactured in certain sec-

tions of the East. The result of the investigation of the pomace wines has been very gratifying and it has enabled us to recognize this product with assurance. Having received from various sources urgent and repeated requests for the information obtained from this work the author feels this demand a sufficient reason for its publication. For the benefit of those who are not acquainted with the manufacture of pomace wines a brief outline of the processes used is included in this paper with the hope that it will aid in interpreting the results.

### I GRAPE POMACE

For the purposes of this article, grape pomace may be defined as the residue of the grape after the juice has been partially or thoroughly removed, before or after fermentation. Pomace may be divided into two main divisions—white and red.

(a) **WHITE POMACE**—This pomace is almost invariably that from the Catawba grape. The grapes are ground and the juice pressed from the skins, seeds and pulp, the juice so obtained being fermented separately. The residue (pomace) can never be pressed entirely free of juice and often contains as much as 8 per cent sugar. Sometimes the pomace is immediately used for pomace wine, but oftener it is packed tight into barrels and allowed there to ferment. The length of time the pomace is kept in barrels before use varies from a few weeks to a year or more.

(b) **RED POMACE**—The principal grape from which this pomace is derived is the Concord. To a lesser extent Concord and Ives mixed furnish this type of pomace, and though in this investigation there is no record of them, the writer has seen used the heavier colored varieties such as Norton and Clinton. The red pomace is obtained in three ways: (1) In making red wines the grapes are ground and the whole mass—juice, skins, pulp and seeds—is allowed to ferment, and at the proper stage the new wine is pressed off and the pomace packed in barrels; (2) instead of pressing off the wine the pomace is sometimes allowed to drain and, without pressing, immediately used for pomace wine: this procedure is infrequent; (3) in the manufacture of red grape juice the fruit is crushed, the mass heated to about 150° F., and then pressed.

### II—POMACE WINES

For the purposes of this article, pomace wine may be defined as the product obtained by the alcoholic fermentation of sugar solution upon grape pomace, accompanied by the usual cellar treatment. The Commissioner of Internal Revenue<sup>1</sup> has held that the manufacture of pomace wine is prohibited by Section 3282, U. S. Revised Statutes, "except in a building or on premises of a distillery duly authorized according to law."

**GENERAL METHOD OF MANUFACTURE** A quantity of pomace ranging from 650 to 1500 lbs., according to quality of pomace and product desired, is placed in open fermentation vats of sufficient capacity, and upon this are run 700 to 800 gals. of "sugar water," the mash being yeasted or not, as conditions require. The "sugar water" is prepared from cane or corn sugar

<sup>1</sup> Published by permission of the Commissioner of Internal Revenue

<sup>1</sup> Treasury Decision 1949, 2-16-11



and contains in the neighborhood of 20 per cent sugar. Ammonium chloride is often added to the mash to facilitate fermentation, especially when old, dry pomace is used. The time allowed for the fermentation to proceed on the pomace varies from 4 to 16 days, after which the wine is drawn off and, if the fermentation is not complete, allowed to finish in closed casks. The wine is then almost immediately clarified and placed on the market, often blended with other wines, or it is aged in cellars for varying periods. The red pomace wines are often artificially colored, placing malvae flowers in the fermentation vats being a common method of coloring.

### III COLLECTION OF SAMPLES

In order that the investigation might deal with a product made in a manner identical with that found upon the market, an officer of the Internal Revenue Bureau was detailed to collect samples of pomace wines from three wine cellars engaged in the commercial manufacture of this article. He was instructed

### V DEDUCTIONS

In the following discussion it is presumed that an analyst desiring to establish pomace origin in a wine is sufficiently familiar with wines and wine analysis to enable him to recognize to what general type his sample belongs, and the characteristics of this type, for without such knowledge it were a hopeless undertaking to attempt to arrive at an intelligent conclusion. To illustrate this, unfortified pure dry Eastern wines will rarely contain less than 0.2 g. total tartaric acid in 100 cc., and in any wine which contains a less amount of total tartaric acid and which belongs to this general group one may be suspicious of pomace origin. There is another class of dry, or practically dry, wines whose tartaric acid content is normally about 0.1 g. in 100 cc., or less—the dry sherries. A novice might confuse the two; one with experience, never.

NITROGEN—Should the analysis show a figure for this element below 10 mg. per 100 cc., there is strong indication of pomace origin, and should the figure

TABLE I

TABLE I													
WHITE POMACE WINES			Wine		SUGAR SOLUTION		Amount		Days				
Lab. No	Col-lection	SAMPLES Taken	Cellar Analyzed	Kind of Sugar	Gallons	Degrees Balling	Temp. ° F.	Pomace Lbs.	Condition of Pomace	on Pomace	NH <sub>4</sub> Cl Oz.	Kind of Pomace	
61869	3	10/28/13	1/5/14	1	Cerelose	800	19.4	92	1021	Fresh	6	None	Catawba
61870	4	10/28/13	1/5/14	1	Cerelose	1600	19.3	91	2010	Fresh	6	None	Catawba
61871	5	11/1/13	1/5/14	1	Cerelose	1600	19.0	92	2134	Fresh	4	None	Catawba
61872	6	11/6/13	1/5/14	1	Cerelose	800	19.2	86	920	Fresh	5	None	Catawba
61877	11	11/12/13	1/5/14	1	Cerelose	1600	19.4	70	1896	Fresh	5	None	Catawba
61880	14	11/22/13	1/5/14	1	Cane	800	18.7	90	951	Fresh	7	None	Catawba
61884	18	12/3/13	1/14/14	1	Cane	800	18.9	86	953	Fresh	7	None	Catawba
61873	7	11/3/13	1/5/14	2	Cane	700	19.3	65	693	Old, dry, pale	12	About 30	Catawba
61875	9	11/12/13	1/5/14	2	Cane	700	19.3	65	693	Old, dry, pale	12	About 30	Catawba
61876	10	11/13/13	1/5/14	2	Cane	800	19.4	70	1056	Old, dry, pale	14	About 30	Catawba
61879	13	11/22/13	1/5/14	2	Cane	700	19.5	70	781	Old, dry, pale	14	About 30	Catawba
61883	17	12/1/13	1/14/14	2	Cane	700	19.2	70	700	Old, dry, pale	14	About 30	Catawba
61885	19	12/3/13	1/14/14	2	Cane	700	19.2	70	700	Old, dry, pale	14	About 30	Catawba
61887	21	12/8/13	1/14/14	2	Cane	700	19.3	75	728	Fresh; poor color	16	28	Catawba
63032	32	12/17/13	2/20/14	2	Cane	800	19.2	70	874	Fair	13	32	Catawba
63035	35	12/27/13	2/20/14	2	Cane	800	19.2	70	1052	Old, dry, pale	15	32	Catawba
63039	39	1/8/14	2/20/14	2	Cane	700	19.2	73	843	Old, dry, poor	13	28	Catawba
61882	16	11/29/13	1/14/14	3	Cerelose	800	19.0	72	641	Moist, fair	8	24	Catawba
61890	24	12/8/13	1/14/14	3	Cerelose	800	24.2	72	938	Moist, fair	14	24	Catawba
61894	28	12/12/13	1/14/14	3	Cerelose	800	19.2	70	665	Moist, fair	8	24	Catawba
63031	31	12/13/13	2/20/14	3	Cerelose	700	19.2	70	1270	Moist, fair	5	24	Catawba
63034	34	12/22/13	2/20/14	3	Cerelose	800	19.0	70	705	Moist, fair	10	24	Catawba
63038	38	1/6/14	2/20/14	3	Cerelose	800	24.6	70	691	Moist, fair	13	24	Catawba
RED POMACE WINES													
61886	20	12/8/13	1/14/14	1	Cane	800	18.8	90	1490	Good	6	None	Concord Grape Juice
61896	30	12/13/13	1/14/14	1	Cane	800	18.7	80	1508	Good	5	None	Concord Grape Juice
63033	33	12/22/13	2/20/14	1	Cane	800	18.7	82	1528	Good	5	None	Concord Grape Juice
61874	8	11/8/13	1/5/14	2	Cane	675	20.0	70	1078	Dry; poor color	12	About 30	Concord and Ives
61878	12	11/19/13	1/5/14	2	Cane	800	19.4	70	1440	Dry; poor color	14	About 30	Concord
61891	25	12/9/13	1/14/14	2	Cane	700	19.2	70	886	Fresh; poor color	14	28	Concord
61895	29	12/13/13	1/14/14	2	Cane	700	19.5	70	904	New, dry, poor color	14	28	Concord and Ives
63037	37	12/30/13	2/20/14	2	Cane	800	19.3	70	1201	Dry; poor color	13	32	Concord and Ives
63036	36	12/29/13	2/20/14	3	Cerelose	800	19.2	70	1023	Fair; part wet; part dry	11	24	Concord and Ives

to observe personally the various steps in the manufacture and to make full records of them. This he has done most painstakingly and thoroughly, and through the courtesy of the wine makers, has collected many details. For the purposes of this Bureau it was of especial importance that the wine should be collected at the time it was drawn from the pomace, so most of the samples were secured as that stage. In case of fermentations not having been completed, the samples were to be sterilized directly after bottling. For wines of this character the conclusions drawn from the following analyses will hold for older wines of the same type.

### IV—HISTORY AND ANALYSES OF POMACE WINES

In Table I is included a brief history of the pomace wines collected, and the analyses of them appear in Table II. For comparative purposes the latter table also contains the analyses of two pure Catawba wines made in the fall of 1913.

fall to 5 or below it is almost a foregone conclusion that one is dealing with a pomace wine. Nitrogen in the form of ammonia or nitrate has never been observed in any wine analyzed by the author.

CHLORINE—This constituent is of peculiar interest. Its determination not only aids in detecting spurious wines, but often furnishes evidence of their manner of manufacture. Natural wines are invariably low in chlorine content, the great majority containing less than 5 mg. in 100 cc. Some California wines have been known to exceed double this amount, but as a general rule any chlorine content above 10 mg. may be viewed with suspicion. The excess chlorine may be due to either of two causes, or to both: (1) the use of ammonium chloride as a fermentation accelerator; (2) the use of corn sugar solution in the manufacture of the wine. Since it is rarely the custom to add ammonium chloride to a normal wine fermentation, its presence not being necessary, one is justified in con-

PURE POMACE WINES

TABLE II.—ANALYSES OF POMACE WINES WITH ANALYSES OF TWO PURE WINES FOR COMPARISON

Laboratory No.	Alcohol Vol. %	Extract	Nonsugar Extract	Reducing Sugar as Invert	Acidity		Total	Free	Cream Tartar	Combined (a)	Tannin and Coloring Matter	Pentosans	Volatile Esters	Ash		Sol.	Insol.	N	Cl	K <sup>+</sup>	Na <sup>+</sup>	CaO	MgO	SO <sub>3</sub>	Total	H <sub>2</sub> O Soluble	H <sub>2</sub> O Insoluble	Polarization V. 100° C.	N in HCl per 100 cc	P <sub>2</sub> O <sub>5</sub> in Ash	Specific Gravity 15.6° C.
					as Tartaric	as Tartaric								P <sub>2</sub> O <sub>5</sub>	Total																
61889	9.37	6.56	2.3	1.83	0.517	0.435	0.092	0.394	0.237	0.00	0.12	0.14	0.28	0.286	0.0114	Trace	0.0114	0.0045	0.0888	0.0729	0.0584	0.0210	0.0094	0.0268	16.8	6.4	10.4	14.7	10.1	0.975	
61890	8.91	6.67	2.65	4.02	0.491	0.443	0.052	0.290	0.00	0.13	0.13	0.028	0.276	0.0096	Trace	0.0096	0.0034	0.0236	0.0094	17.2	7.0	10.2	14.8	8.1	0.976	12.2	7.0	10.2	14.8	8.1	0.976
61881	8.01	8.40	2.88	5.82	0.365	0.409	0.031	0.370	0.230	0.00	0.14	0.12	0.033	0.250	0.0080	Trace	0.0080	0.0045	0.0902	0.0655	0.0585	0.0184	0.0093	0.0154	16.0	7.6	8.4	19.8	3.2	1.0214	
61882	8.30	6.80	3.6	4.14	0.528	0.401	0.031	0.362	0.219	0.00	0.16	0.09	0.033	0.256	0.0078	Trace	0.0078	0.0039	0.0817	0.0616	0.0584	0.0160	0.0087	0.0171	18.4	8.6	7.8	17.9	3.1	1.0138	
61883	8.66	7.88	2.85	5.03	0.401	0.377	0.029	0.341	0.206	0.00	0.18	0.06	0.026	0.258	0.0076	Trace	0.0076	0.0028	0.0852	0.0608	0.0584	0.0160	0.0087	0.0171	18.4	8.6	7.8	17.9	3.1	1.0138	
61880	8.98	7.13	1.61	5.52	0.369	0.386	0.041	0.335	0.216	0.07	0.17	0.07	0.038	0.110	0.0076	0.0018	0.0058	0.0050	0.0199	0.0537	0.0040	0.0080	0.0054	0.0032	13.2	8.8	4.4	17.8	6.9	1.0181	
61884	9.98	8.67	1.62	4.35	0.338	0.380	0.056	0.315	0.185	0.02	0.11	0.07	0.033	0.105	0.0060	0.0008	0.0052	0.0039	0.0028	0.0507	0.0030	0.0116	0.0072	0.0128	10.8	6.0	3.8	17.1	5.8	1.0098	
61885	1.38	1.80	1.52	0.07	0.600	0.315	0.076	0.220	0.107	0.00	0.13	0.00	0.028	0.147	0.0114	0.0022	0.0002	0.0039	0.0170	0.0791	0.0067	0.0056	0.0098	0.0065	13.0	9.6	5.8	4.4	7.7	0.9893	
61886	12.45	1.57	1.51	0.06	0.602	0.424	0.070	0.307	0.278	0.01	0.22	0.09	0.026	0.160	0.0116	0.0042	0.0004	0.0050	0.0185	0.0887	0.0046	0.0060	0.0104	0.0070	12.8	11.8	6.0	4.3	7.2	0.9900	
61887	12.30	1.57	1.50	0.07	0.604	0.442	0.083	0.238	0.108	0.00	0.14	0.00	0.031	0.180	0.0176	0.0078	0.0008	0.0056	0.0178	0.1013	0.0038	0.0092	0.0100	0.0034	10.0	12.8	6.2	4.1	9.8	0.9901	
61879	11.8	3.07	1.45	1.62	0.560	0.383	0.071	0.294	0.191	0.00	0.17	0.06	0.060	0.111	0.0026	Trace	0.0026	0.0011	0.0199	0.0538	0.0058	0.0076	0.0058	0.0031	13.6	9.0	4.6	7.8	2.3	0.9964	
61888	10.80	1.17	1.65	0.75	0.522	0.469	0.059	0.305	0.285	0.02	0.24	0.08	0.024	0.150	0.0122	0.0042	0.0080	0.0056	0.0199	0.0826	0.0042	0.0108	0.0101	0.0025	18.0	12.6	5.4	4.1	8.1	0.9908	
61885	10.80	1.17	1.65	0.75	0.471	0.450	0.115	0.306	0.287	0.00	0.17	0.00	0.024	0.224	0.0146	0.0070	0.0076	0.0043	0.0192	0.0869	0.0388	0.0084	0.0106	0.0031	28.0	22.0	6.0	29.3	6.5	1.0299	
61887	11.37	3.36	1.68	1.88	0.587	0.521	0.132	0.356	0.253	0.05	0.20	0.07	0.022	0.156	0.0122	0.0022	0.0100	0.0028	0.0234	0.0721	0.0031	0.0098	0.0102	0.0027	15.2	10.1	4.8	7.4	8.0	0.9972	
61882	12.16	1.99	1.46	0.83	0.522	0.431	0.074	0.338	0.222	0.00	0.20	0.07	0.023	0.130	0.0050	0.0004	0.0046	0.0028	0.0265	0.0690	0.0051	0.0108	0.0109	0.0015	16.0	10.4	5.6	7.5	3.8	0.9919	
61883	11.85	2.40	1.82	0.58	0.564	0.604	0.160	0.404	0.278	0.00	0.26	0.07	0.033	0.173	0.0176	0.0022	0.0154	0.0025	0.0192	0.0955	0.0051	0.0110	0.0125	0.0094	18.8	13.8	8.0	3.8	10.7	0.9944	
61880	11.86	1.76	1.55	0.21	0.604	0.506	0.110	0.368	0.266	0.02	0.20	0.07	0.009	0.153	0.0138	0.0052	0.0086	0.0025	0.0185	0.0815	0.0041	0.0094	0.0105	0.0022	15.4	10.6	4.8	0.8	8.9	0.9943	
61882	10.48	3.33	2.45	0.78	0.508	0.460	0.060	0.285	0.129	0.00	0.07	0.08	0.051	0.242	0.0106	0.0008	0.0008	0.0045	0.0096	0.0355	0.0750	0.0164	0.0108	0.0190	10.4	3.6	6.8	3.85	4.4	0.9981	
61880	13.08	4.37	3.29	1.17	0.582	0.469	0.072	0.379	0.198	0.02	0.08	0.12	0.062	0.309	0.0144	Trace	0.0144	0.0056	0.1136	0.0836	0.0663	0.0170	0.0109	0.0232	12.2	4.2	8.0	11.3	4.6	1.0001	
61884	9.75	2.97	2.20	0.77	0.608	0.575	0.057	0.338	0.161	0.00	0.08	0.10	0.055	0.238	0.0098	0.0004	0.0004	0.0036	0.0023	0.0494	0.0620	0.0150	0.0101	0.0130	11.0	4.2	6.8	9.6	4.3	0.9984	
61881	10.97	3.10	2.50	0.60	0.637	0.508	0.079	0.299	0.155	0.00	0.08	0.09	0.045	0.245	0.0101	0.0003	0.0008	0.0034	0.0044	0.0506	0.0668	0.0150	0.0105	0.0154	11.6	4.2	7.4	4.2	4.1	0.9975	
61883	11.40	3.26	2.50	0.76	0.613	0.424	0.056	0.354	0.195	0.01	0.09	0.11	0.029	0.265	0.0030	0.0004	0.0004	0.0028	0.0088	0.0563	0.0590	0.0162	0.0080	0.0167	12.2	5.0	7.2	8.4	4.0	0.9975	
61888	14.11	4.44	3.00	1.44	0.775	0.440	0.055	0.381	0.225	0.03	0.11	0.11	0.033	0.281	0.0168	0.0010	0.0158	0.0034	0.0093	0.0662	0.0750	0.0152	0.0166	0.0166	13.0	5.6	7.4	11.5	6.0	0.9993	

RED POMACE WINES	
61886	9.28 7.63 2.01 5.62 0.452 0.420 0.053 0.354 0.186 0.04 0.10 0.07 0.114 0.118 0.0105 0.0007 0.0098 0.0095 0.0036 0.0501 0.0043 0.0138 0.0080 0.0255 9.8 5.2 4.6 18.0 9.0 0.9169
61896	10.88 3.64 1.81 1.83 0.460 0.450 0.038 0.402 0.188 0.04 0.09 0.07 0.119 0.114 0.0090 0.0024 0.0066 0.0084 0.0036 0.0462 0.0037 0.0124 0.0073 0.0270 9.6 5.0 4.6 6.7 8.0 0.9997
61803	10.66 4.00 1.69 2.31 0.455 0.433 0.040 0.385 0.159 0.05 0.07 0.06 0.107 0.023 0.105 0.0058 0.0004 0.0054 0.0025 0.0028 0.0470 0.0031 0.0110 0.0109 0.0232 7.6 3.6 4.0 8.8 5 1.0014
61874	12.41 2.12 1.74 0.97 0.650 0.518 0.088 0.408 0.263 0.01 0.23 0.07 0.040 0.134 0.0050 0.0010 0.0040 0.0039 0.0178 0.0893 0.0027 0.0072 0.0002 0.0061 0.0021 17.2 12.4 4.8 4.4 3.7 0.9944
61878	12.11 2.21 1.26 0.36 0.607 0.563 0.118 0.388 0.279 0.00 0.26 0.07 0.033 0.050 0.166 0.0120 0.0040 0.0080 0.0039 0.0170 0.0992 0.0040 0.0040 0.0072 0.0030 19.0 14.0 5.0 1.0 7.2 0.9924
61891	11.92 1.86 1.71 0.15 0.528 0.388 0.115 0.344 0.272 0.00 0.26 0.06 0.048 0.158 0.0082 0.0024 0.0058 0.0042 0.0192 0.0791 0.0047 0.0112 0.0107 0.0026 19.2 13.8 5.4 1.0 5.2 0.9916
61895	11.63 3.10 1.71 1.39 0.530 0.529 0.110 0.391 0.281 0.02 0.23 0.08 0.036 0.055 0.158 0.0080 0.0016 0.0064 0.0028 0.0241 0.0832 0.0076 0.0110 0.0080 0.0017 17.6 12.4 5.2 6.3 5.1 0.9968
61807	12.50 1.99 1.74 0.25 0.572 0.380 0.080 0.391 0.333 0.00 0.30 0.08 0.040 0.055 0.238 0.0116 0.0028 0.0088 0.0050 0.0270 0.1050 0.0066 0.0116 0.0080 0.0079 22.8 16.0 6.8 0.8 5.8 0.9976
61806	11.13 3.12 2.45 0.67 0.594 0.398 0.070 0.298 0.143 0.01 0.04 0.11 0.041 0.079 0.032 0.207 0.0176 0.0003 0.0023 0.0176 0.0045 0.0846 0.0502 0.0601 0.0192 0.0116 0.0054 9.7 2.0 7.2 6.9 7.6 0.9974

ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE	ALBUQUERQUE</
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REPO POMACE WINES

61886 9.28 7.63 2.01 5.62 0.453 0.420 0.053 0.354 0.186 0.04 0.10 0.07 0.114 0.118 0.0105 0.0007 0.0098 0.0095 0.0036 0.0501 0.0043 0.0138 0.0080 0.0255 9.8 5.2 4.6 18.0 9.0 1.0169

61886 10.88 3.64 1.81 1.83 0.460 0.450 0.038 0.402 0.188 0.04 0.09 0.07 0.119 0.114 0.0090 0.0024 0.0066 0.0084 0.0036 0.0462 0.0037 0.0124 0.0074 0.0270 9.6 5.0 4.6 18.0 9.0 1.0169

61883 10.66 4.00 1.69 2.61 0.455 0.435 0.040 0.385 0.150 0.05 0.07 0.06 0.107 0.105 0.0058 0.0004 0.0004 0.0025 0.0028 0.0470 0.0232 7.6 3.6 4.0 18.0 9.0 1.0169

61884 12.41 2.71 1.74 0.97 0.650 0.518 0.088 0.408 0.263 0.01 0.23 0.07 0.140 0.134 0.0050 0.0010 0.0050 0.0039 0.0178 0.0893 0.0027 0.0072 0.0061 0.0021 12.2 12.4 4.8 14.4 3.7 0.9944

61887 12.11 2.12 1.76 0.36 0.657 0.536 0.118 0.388 0.279 0.00 0.26 0.07 0.133 0.166 0.0120 0.0040 0.0080 0.0039 0.0170 0.0992 0.0040 0.0114 0.0072 0.0030 19.0 14.0 5.0 1.0 7.2 0.9924

61891 11.92 1.86 1.71 0.15 0.528 0.428 0.115 0.344 0.272 0.00 0.26 0.06 0.048 0.158 0.0082 0.0024 0.0006 0.0042 0.0192 0.0791 0.0047 0.0112 0.0107 0.0026 14.2 13.8 5.4 4.0 5.2 0.9916

61895 11.68 3.10 1.71 0.35 0.520 0.429 0.110 0.301 0.281 0.02 0.23 0.08 0.056 0.085 0.158 0.0080 0.0016 0.0065 0.0028 0.0241 0.0852 0.0076 0.0100 0.0080 0.0017 17.6 12.4 5.2 6.3 5.1 0.9968

61897 12.50 1.99 1.74 0.29 0.527 0.480 0.071 0.391 0.253 0.00 0.20 0.08 0.053 0.028 0.201 0.0116 0.0028 0.0068 0.0050 0.0270 0.1050 0.0066 0.0116 0.0069 0.0079 22.8 16.0 6.6 0.8 5.8 0.9915

61896 11.15 3.12 2.45 0.67 0.594 0.398 0.080 0.298 0.143 0.01 0.04 0.11 0.041 0.079 0.032 0.237 0.0179 0.0003 0.0176 0.0045 0.0846 0.0502 0.0601 0.0192 0.0116 0.0154 9.2 2.0 7.2 6.9 7.6 0.9974

PURE CAVARIA WINES

65011 11.60 3.23 1.98 1.25 0.516 0.724 0.065 0.643 0.444 0.21 0.15 0.11 0.064 0.033 0.125 0.0154 0.0040 0.0114 0.0246 0.0028 0.0540 0.0051 0.0116 0.0131 0.0067 15.6 8.2 7.4 6.5 12.3 0.9973

65042 11.31 3.31 2.05 1.26 0.505 0.755 0.050 0.672 0.446 0.23 0.13 0.11 0.022 0.068 0.021 0.121 0.0192 0.0060 0.0132 0.0213 0.0028 0.0531 0.0055 0.0122 0.0151 0.0055 14.4 7.0 7.4 6.5 15.8 0.9979

(a) Combined with alkaline carbin. (b) A clarified, finished pomace wine, ready for marketing. (c) Sucrose = 9.09.



cluding that it is added in case of poor fermentation, such as is the case with sugar solution over old, dry pomace. In this event the chlorine will be close to 20-30 mg. per 100 cc. When the chlorine figure approaches 100 mg. per 100 cc., with a corresponding increase in the content of soda, one has practical proof that corn sugar has been used in the preparation of the wine and, with the aid of other determinations, that it is pomace wine. Polarization at 87° C. after inversion is useful in substantiating the presence of corn sugar or corn-sugar residue. The practice of using corn sugar for sweetening or gallizing wines, once considerably in vogue, has greatly decreased and it may often be disregarded.

**SODA**—The ranges and interpretation of this figure are similar to those for chlorine.

**TOTAL TARTARIC ACID**—Pomace wines are low in total tartaric acid as compared with wines with which they are likely to become confused. A figure of 20 cg. per 100 cc. or under is suspicious, and any unfortified wine falling below 10 cg. of this constituent may usually be deemed spurious. The author has been informed of some supposedly pure unfortified European wines whose tartaric acid content is below 10 cg. per 100 cc., but the history of the wines proved to be incomplete.

**FIXED ACID AS TARTARIC**—Any figure below 50 cg. per 100 cc. is ground for suspecting pomace origin.

**ASH**—For white dry wines an ash of 20 cgs. per 100 cc. or over indicates pomace. For red wines this figure is of but general value.

**ALKALINITY OF ASH**—The alkalinity of the water-soluble ash of pomace wines often falls as low as 8 cc. *N/10* HCl per 100 cc. wine or under, which is unusual for American wines. When the alkalinity of the water-insoluble ash exceeds the alkalinity of the water-soluble ash the fact is very characteristic of pomace wines.

**NONSUGAR EXTRACT**—Any figure below 1.5 g. per 100 cc. for white wines and 2.0 g. per 100 cc. for red wines is suspicious.

**PENTOSANS**—For white wines, any figure below 50 mg. per 100 cc., and for red wines, below 100 mg. per 100 cc., is suspicious.

**PER CENT  $P_2O_5$  IN ASH**—Having this figure below 10 is almost a constant property of pomace wines.

**NEUTRALIZATION TEST**—This test, which is communicated by Dr. B. G. Hartmann, of the Bureau of Chemistry, has been found very valuable as an aid in the detection of white pomace wines: "Straight wines or gallized wines, when neutralized with sodium hydroxide, darken slightly and acquire a brownish pink tint; pomace wines acquire a brownish color and very often contain a sediment after standing."

**ADJUSTMENT OF ASH AND NONSUGAR EXTRACT**—In cases where corn sugar is indicated in the manufacture of the suspected wine it is advisable to adjust the figures for ash and nonsugar extract to those of true grape material, *i. e.*, make allowance for the effect of the corn-sugar residue on these constituents. The corrections to be made can be determined by referring

to the analyses of pomace wines given above. Necessarily these corrections will be more or less arbitrary, but the results obtained will be of value in differentiating between pomace wines and wines gallized with corn sugar.

The following determinations are of secondary importance in judging pomace origin, but they are of value in sustaining interpretations of the cardinal determinations given above:

**FREE TARTARIC ACID**—Pomace wines contain little or no free tartaric acid.

**CREAM OF TARTAR**—Below 15 cg. per 100 cc. is suspicious.

**SULFURIC ACID ( $SO_3$ )**—Below 5 mg. per 100 cc. is suspicious.

**MAGNESIA**—For white wines, any striking variation from 10 mg. per 100 cc. is suspicious.

In searching for pomace origin in wines the determination of any single constituent never closes the problem, and it is equally true that few, if any, pomace wines will show all the peculiarities of this product. The organoleptic examination is of great aid in making the final decision and the color of the wine is often helpful.

In conclusion, the author wishes to express his sincere appreciation to Mr. D. W. Campbell, of Sandusky, Ohio, for the untiring interest shown in the collection of the wines represented in the above analyses. Thankful acknowledgment is also extended to several colleagues in the Internal Revenue Laboratory for timely aid in the analysis of the wines: to Mr. W. V. Linder for determining nitrogen, volatile acids and pentosans in Samples 61882-96; Mr. J. M. Doran, total acid and tannin, Samples 61882-96, and lime and magnesia, Samples 61869-80; Mr. P. Valaer, specific gravity and tannin, Samples 63031-42.

U. S. INTERNAL REVENUE LABORATORY, WASHINGTON

## CHEMICAL COMPOSITION OF ALFALFA AS AFFECTED BY STAGE OF MATURITY, MECHANICAL LOSSES, AND CONDITION OF DRYING

By C. O. SWANSON AND W. L. LATSHAW

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This paper is a partial report on the chemical work done on alfalfa cut at the time of budding, one-tenth bloom, full bloom, and at seed formation, in an experiment carried on jointly by the departments of chemistry, agronomy, and animal husbandry at the Kansas Experiment Station.<sup>1</sup> This paper discusses one phase of the work, *viz.*, the chemical composition as affected by variations in maturing and curing.

The alfalfa was cut from duplicate and triplicate 0.1 acre plots. As soon as cut, a sample was taken from the green material and spread in an attic room to dry. When the cut hay in the field was dry enough to stack, it also was sampled: this sample was weighed and taken to the same attic room to dry thoroughly. After the green sample was partially wilted a small sub-sample was taken and the relative amount of

<sup>1</sup> We desire here to express our appreciation of the hearty cooperation received from Professors L. E. Call, Ralph Kenney, and W. A. Cochel. The expense of this experiment was met by the Adams Fund, Kansas Agricultural Experiment Station.

leaves and stem was determined on an air-dry basis. Samples of alfalfa cut at the same stages of maturity were also obtained at the time of feeding. These five different kinds of samples will be designated as: *sampled when cut, sampled when stacked, leaves from the material sampled green, stems from the material sampled green, and sampled when fed.*

This experiment has been carried on for two years. The summer of 1914 was moderately dry, while 1915 was unusually wet. By analyzing the samples from each cutting, data were obtained in regard to the change in composition during each of these seasons. It was found, however, that the stage of maturity so strongly influenced the composition that it more than offset any effect due to the time of season. Therefore, only the averages calculated on a 10 per cent moisture basis, for each stage of maturity, are given in the following tables. There were from 4 to 6 cuttings on the first three stages, and 3 cuttings on the last stage.

TABLE I COMPOSITION OF ALFALFA CUT AT DIFFERENT STAGES OF MATURITY—SAMPLED WHEN CUT

YEAR	PORTION ANALYZED	STAGE OF MATURITY	Crude				Ether Extract
			Ash	Protein	Fiber	N-free Extract	
1914	Whole Plant	Bud	10.53	19.65	22.50	35.06	2.36
		1/10 Bloom	9.59	18.38	23.58	35.41	2.93
		Full Bloom	8.79	16.30	25.01	36.07	3.77
		Seed	7.54	14.97	26.53	37.37	3.54
	Leaves	Bud	10.78	26.17	13.64	36.01	3.27
		1/10 Bloom	10.52	26.16	14.06	37.40	4.06
		Full Bloom	9.11	22.10	13.66	39.32	3.72
		Seed	8.70	21.25	14.55	39.66	5.48
	Stems	Bud	8.78	12.57	33.54	33.92	1.23
		1/10 Bloom	7.97	10.63	35.12	32.97	1.33
		Full Bloom	7.62	9.72	36.33	35.83	1.22
		Seed	7.12	10.22	36.41	34.86	1.39
1915	Whole Plant	Bud	10.24	19.94	26.86	31.29	1.67
		1/10 Bloom	9.18	16.12	30.80	32.08	1.82
		Full Bloom	8.76	15.70	30.90	32.62	2.03
		Seed	8.08	14.48	31.56	33.95	1.93
	Leaves	Bud	10.63	27.30	15.58	32.91	3.56
		1/10 Bloom	10.64	24.60	18.04	33.44	3.29
		Full Bloom	10.01	22.70	15.91	37.78	3.60
		Seed	9.49	22.21	17.28	37.91	3.11
	Stems	Bud	8.77	13.04	36.62	30.58	0.99
		1/10 Bloom	6.74	10.80	40.60	38.85	0.96
		Full Bloom	6.38	9.83	43.37	29.15	0.97
		Seed	7.07	8.91	43.21	29.79	1.02

The percentage of feeding constituents in the whole plant, leaves, and stems for the two separate years is given in Table I. The ash and protein decrease regularly as the plant matures; crude fiber and nitrogen-free extract increase. Because of the large amount of chlorophyll in the ether extract, the figures do not give any significant data. The ash content of the leaves is uniformly greater than of the stems. The greatest difference between the leaves and stems, however, is in the content of protein and crude fiber. The leaves contain from 2 to 2½ times as much protein as the stems, while the stems contain over 2½ times as much crude fiber as the leaves. The samples of 1915, in comparison with those of 1914, have a slightly lower ash content, but a considerably higher content of crude fiber. These differences are most pronounced in the stems, and are probably due to the larger growth in 1915.

In 1914 alfalfa was cut from a larger field at the same stages of maturity. This was cured, baled, and stored in a barn, being sampled at the time of feeding. A small amount was taken from each bale on opening, and placed in large bags. In this way three to five composites were obtained from each stage of cutting. These composites were analyzed separately, and the

average figures are given in Table II. In 1915, no samples were taken at the time of feeding, but instead the average figures for the samples obtained at the time of stacking are given in Table II. A comparison of the figures in Table II with those in Table I shows that there is less ash and crude protein, and more crude

TABLE II COMPOSITION OF ALFALFA CUT AT DIFFERENT STAGES OF MATURITY SAMPLED AS HAY

YEAR	STAGE OF MATURITY	Crude				Ether Extract
		Ash	Protein	Fiber	N-free Extract	
1914, when fed	Bud	9.47	18.27	24.30	35.98	2.67
	1/10 Bloom	8.56	15.96	24.34	38.19	2.86
	Full Bloom	7.53	14.62	27.48	37.70	2.64
	Seed	7.28	13.38	28.14	38.84	2.36
1915, when stacked	Bud	10.21	18.01	26.17	34.00	1.61
	1/10 Bloom	8.76	15.46	31.53	32.72	1.53
	Full Bloom	8.25	14.76	31.64	33.56	1.79
	Seed	7.56	13.24	34.87	32.79	1.54

fiber and nitrogen-free extract in the alfalfa sampled as hay. This difference is largely due to mechanical loss of leaves.

The relative amount of leaves and stems in the material sampled when cut was determined by taking a handful selected from different parts of the large sample as soon as the alfalfa was wilted, and by separating this sample into leaves and stems. These were allowed to dry under the same conditions as the rest of the sample, and the relative percentage by weight was determined. The averages of all the cuttings are given in Table III. In 1914 there was a larger percentage of leaves in the first three stages, but in 1915 the percentage of stems was larger in all of the stages. In both years the proportion of leaves decreased and the proportion of stems increased as the plant matured.

TABLE III—RELATIVE PER CENT OF LEAVES AND STEMS IN ALFALFA SAMPLED WHEN CUT

YEAR	—BUD—		1/10 BLOOM		FULL BLOOM		—SEED—	
	Leaves	Stems	Leaves	Stems	Leaves	Stems	Leaves	Stems
1914.....	57.57	42.43	56.40	43.61	51.54	48.22	43.50	56.51
1915.....	47.89	52.11	41.54	58.46	37.65	62.35	36.58	63.42

The exact amount of leaves lost in the process of haymaking is impracticable to determine directly. However the approximate amount can be calculated if the chemical composition of alfalfa leaves and of alfalfa hay containing all of the leaves is known, as well as the composition of the hay when there is a loss of leaves due to handling. The errors involved depend on the correctness of the assumptions made. Since the greatest difference in composition between the leaves and the whole plant is in protein, the figures for protein are used in the calculations. It is assumed that there is no loss of total protein in the process of curing, and that change in composition is solely due to mechanical loss of leaves which contain a large amount of protein. One source of error is in the determination of the relative amount of leaves and stems. The amount of material used in this determination is small in comparison with the total amount of hay under consideration. As this determination was made on a number of samples, however, the errors were largely eliminated in the average. The method of calculation was as follows:

Let  $x$  = number of pounds of leaves lost.

$a$  = per cent of protein in alfalfa sampled when cut.

$b$  = per cent of protein in alfalfa sampled as hay.

$c$  = per cent of protein in the leaves.

Make the calculation on the basis of 100 lbs. air-dry



hay. Then  $100 - x$  = weight of hay after loss of leaves. The formula for calculation would then be:  $b(100 - x) + c(x) = a$ . Substituting the known values for  $a$ ,  $b$  and  $c$ , as obtained in the chemical analysis of any of the samples under consideration, as for bud stage samples of 1915, where  $a = 10.94$ ,  $b = 18.01$ ,  $c = 27.30$ , the equation becomes  $0.1801(100 - x) + 0.2730 x = 10.94$  (per cent loss of leaves by weight).  $x = 20.77$ . Using this method of calculation, and the figures for the percentage amount of leaves given in Table III, Table IV is produced presenting the percentage loss of leaves and crop.

TABLE IV—PERCENTAGE LOSSES OF LEAVES AND CROP

MATURITY YEAR	Bud Leaves	1/10 Bloom Crop	1/10 Bloom Leaves	Full Bloom Crop	Full Bloom Leaves	Seed Crop	Seed Leaves
1914	25.04	14.35	19.67	11.00	23.85	12.72	25.77
1915	20.77	9.95	7.22	3.00	11.84	4.46	13.82

The figures in Table IV show that the loss of leaves is an important matter. The relative amount of leaves was larger in 1914,<sup>1</sup> the drier year, and the loss of leaves was also greater than in 1915.

The total amount of nutrients produced per acre was one factor to be determined in the present experiment. The pounds of nutrients per acre in the total alfalfa crop as grown, as well as in the leaves and stems, may be obtained by using the data of yield per plot at time of stacking, as obtained by the agronomy department (see Table V), the figures for dry matter in the samples taken at this time, the figures in Table IV for loss in handling, and the figures for composition in Table I. In 1914 the largest amount of all nutrients was obtained in the bud stage. In 1915 the largest amounts were obtained at full bloom.

TABLE V—POUNDS OF NUTRIENTS PRODUCED PER ACRE IN THE TOTAL CROP, LEAVES AND STEMS, 10 PER CENT MOISTURE BASIS

YEAR	STAGE OF MATURITY	Ash	Crude Protein	Crude Fiber	N-free Ether Extract
1914 Whole Crop	Bud	817.01	1483.66	1815.57	2674.92
	1/10 Bloom	664.35	1235.92	1734.61	2390.51
	Full Bloom	534.61	967.17	1589.52	2167.56
	Seed	331.40	674.55	1310.24	1786.94
	Leaves Bud	487.06	1145.44	582.41	1501.87
	1/10 Bloom	405.43	946.55	556.12	1422.32
	Full Bloom	281.07	693.07	429.39	1258.41
	Seed	182.21	423.12	286.00	804.76
	Stems (by difference)	329.95	338.22	1233.16	1173.05
	1/10 Bloom	258.92	289.37	1178.49	977.19
1915 Whole Crop	Bud	878.31	1710.30	2303.80	2683.76
	1/10 Bloom	1066.34	1767.20	3376.50	3516.62
	Full Bloom	1165.08	2088.10	4109.71	4338.46
	Seed	792.31	1419.88	3094.71	3329.07
	Leaves Bud	436.63	1121.35	639.95	1391.65
	1/10 Bloom	484.55	1120.28	821.54	1522.86
	Full Bloom	501.25	1136.69	796.69	1891.82
	Seed	340.40	796.66	619.83	1359.82
	Stems (by difference)	441.68	588.95	1663.85	1292.11
	1/10 Bloom	521.79	646.92	2554.96	1993.76

The change in composition due to mechanical loss has been shown in the preceding paragraphs, but no attempt was made to determine the total loss of any chemical constituent. That there are losses of chemical constituents during the process of haymaking has been shown by Fleishmann,<sup>2</sup> these losses depending on the conditions of drying. He found that the greatest losses occur under unfavorable weather conditions and that the losses of chemical constituents fall most

heavily on the carbohydrates, and to a much less extent on the ether extract. Fleishmann found also that there were very important changes in the form of phosphorus and nitrogen compounds. These changes, to an important extent, also occurred under favorable conditions of drying. Headden<sup>1</sup> found that great losses of nutrients, due to chemical and bacterial action, occurred under unfavorable drying conditions. Honcamp<sup>2</sup> also found that losses of chemical constituents occur to some extent even under favorable conditions of drying in the sun. He also found that the digestibility of hay depends to an important extent on the method of curing. This has been shown by other investigators.<sup>3</sup>

That the amount of pure protein as determined by Stutzer's method is decreased by slow drying was found in the present investigation. The nitrogen by Stutzer's method<sup>4</sup> was determined on all the samples taken at the time of cutting and at the time of stacking. The results are summarized in Table VI. The green alfalfa samples taken at the time of cutting were usually brought to the chemical laboratory in the evening. The temperature in the attic room where they were spread to dry was always high in the summer. Nevertheless the drying here was much slower than in the open field where there was a free movement of air, and usually sunshine.

TABLE VI—AVERAGE FIGURES SHOWING RELATIONS BETWEEN TOTAL AND PURE (STUTZER'S) PROTEIN IN ALFALFA SAMPLES WHEN CUT, SAMPLED AS HAY, AND IN THE LEAVES AND STEMS

MOISTURE-FREE FOR 1914		Percentages		Protein Pure Protein	
YEAR	ALFALFA SAMPLED	STAGE OF MATURITY	Total	Pure	Diff. in % of Total
1914	When Cut	Bud	22.27	15.96	6.31
		1/10 Bloom	20.62	15.33	5.08
		Full Bloom	18.34	14.77	3.58
		Seed	17.16	14.40	2.77
	As Hay	Bud	20.01	17.24	2.77
		1/10 Bloom	18.82	15.76	2.86
		Full Bloom	16.22	13.97	2.25
		Seed	14.71	12.50	2.21
	Leaves	Bud	28.55	21.63	6.93
		1/10 Bloom	26.94	21.04	5.90
		Full Bloom	25.21	20.42	4.79
		Seed	23.94	19.86	4.08
TEN PER CENT MOISTURE BASIS	1915	When Cut	Bud	19.90	12.83
			1/10 Bloom	16.73	11.28
			Full Bloom	15.38	10.89
			Seed	14.80	11.21
	As Hay	1/10 Bloom	Bud	17.16	13.09
			Full Bloom	15.25	11.33
			Full Bloom	14.85	11.26
			Seed	13.79	10.42
	Leaves	1/10 Bloom	Bud	26.59	19.23
			Full Bloom	24.50	18.18
			Full Bloom	22.58	17.09
			Seed	22.45	17.34
Stems	1/10 Bloom	Full Bloom	Bud	12.81	7.29
			Full Bloom	10.91	6.33
			Full Bloom	9.68	6.11
			Seed	9.05	6.80

A study of the figures in Table VI brings out these facts:

1—The per cent of pure protein in the total protein is less in the samples cured in the shade than in those cured in the sun, or open field. The greatest difference occurs in the samples from the bud stage, and there is a gradual decrease to the seed stage, where

<sup>1</sup> Colorado Experiment Station, Bull. 110.<sup>2</sup> Die Landw. Vers. Stat., 86, 215-275.<sup>3</sup> Ibid., 75 (1911).<sup>4</sup> Bureau of Chemistry, Bull. 107.<sup>1</sup> The figures for protein used in the calculations, 1914, are found in Table VI.<sup>2</sup> Die Landw. Vers. Stat., 76, 237-447.

there is no significant difference; that is, the protein in the younger plants was more profoundly affected by this condition than that from the seed stage, which was very little changed.

2—The differences between total and pure protein are greater in the alfalfa cured in the shade than in that cured in the sun or open field; that is, the proportion of pure protein decreases during the process of drying. This is most noticeable in the earlier stages. The hay cured in the sun contains a larger per cent of pure protein than that cured in the shade.

In comparing the figures obtained on the samples for 1914 with those of 1915, important differences are noticed. The per cent of pure protein in the total protein is less in every instance in the samples of 1915, and differences between the alfalfa cured in the shade and that cured in the sun are less. The more unfavorable drying conditions of 1915, with the necessity of curing under cock covers, allowed a prolongation of the vital activity of the protoplasm, resulting in protein cleavage. The per cent of pure protein in the total protein is from 6 to 9 per cent less in the alfalfa dried in the shade in 1915 than in the same lot in 1914, while the 1915 samples dried in the open field show about 9 per cent less than the 1914 samples. The larger, heavier plants of 1915 took longer to dry. The stems, which dry the slowest, show the greatest differences in comparing the samples of the two years, and the leaves, which dry the fastest, show the least difference.

These facts point to a very profitable line of investigation in regard to the chemical changes which take place under different conditions of haymaking. These changes no doubt include not only the proteins, but also the carbohydrates, fats, and phosphorus compounds. The feeding value of hay is affected not only by mechanical losses due to handling, and the changes due to bacterial action, but also by chemical changes which are little known or noticed.

#### SUMMARY

I—The alfalfa cut in the bud stage had the largest ash and crude protein and the smallest crude fiber and nitrogen-free extract.

II—In each successive stage the crude fiber and nitrogen-free extract increases, and the crude protein and ash decrease. In pounds per ton the alfalfa cut in the earlier stages has more of crude protein and less of crude fiber.

III—The total amount of any or all nutrients produced per acre depends to a large extent on the yield, as shown by the fact that in 1914 the greatest amount of nutrients was obtained in the bud stage, while in 1915 the full bloom gave the greatest amount of total nutrients.

IV—The leaves and stems differ in content of ash, ether extract, and nitrogen-free extract, but the greatest difference is in the per cent of crude protein and crude fiber. The leaves contain over  $2\frac{1}{2}$  times as much protein as the stems, while the stems contain over  $2\frac{1}{2}$  times as much crude fiber as the leaves.

V—In harvesting and handling there is a large loss of leaves, which loss affects the composition of the hay in an increase of crude fiber and a decrease of crude protein.

VI—The alfalfa cured in the sun has a larger pure protein content as determined by Stutzer's method, than that cured in the shade. This difference is so great as to more than offset the influence of the loss of leaves. The differences in respect to pure protein content were most pronounced in the alfalfa cut in the earlier stages.

CHEMICAL DEPARTMENT  
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#### THE VOLATILE OIL OF CALYCANTHUS OCCIDENTALIS

By CHARLES C. SCALIONE

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*Calycanthus occidentalis*, or *Butneria occidentalis*, also popularly known as spice-bush, belongs to the family *Calycanthaceae*, 4 or 5 species of which are found in the United States. The species named is limited to northern California and southern Oregon and is rarely found in large patches, but usually scattered along stream banks or river bottoms or on the lower slopes of hillsides. It is an unarmed shrub, which sometimes reaches a height of 10 ft. It bears an abundance of ovate to oblong lanceolate leaves, somewhat scabrous and of a bright green color, and dark red flowers from 1 to  $1\frac{1}{2}$  in. long. The leaves, bark and wood are all strongly aromatic; the flowers less so.

Considerable interest has been attached to some of the other species of this genus on account of their physiological action.

An alkaloid was discovered in the seeds of *C. glaucus* *C. fertilis*, by R. C. Eccles,<sup>1</sup> in 1888, and named by him Calycanthine. This was confirmed by H. W. Wiley<sup>2</sup> in 1889. H. M. Gordin,<sup>3</sup> in a number of papers, has shown the presence of two alkaloids, calycanthine and isocalycanthine.

The volatile oil of *Floridus* has been studied by Miller<sup>4</sup> and his co-workers and found to consist of pinene, cineol, borneol, bornyl acetate, salicylic acid, possibly linalool and some other esters besides the bornyl acetate. The cineol predominated.

#### EXPERIMENTAL

Four hundred pounds of leaves and twigs from Oriental, California, that had been kindly supplied by officials of the United States Forest Service, at San Francisco, were submitted to steam distillation under a pressure of 4 lbs. The yield of oil obtained from the united distillates amounted to about 0.27 per cent of the weight of the original material.

In transit considerable decomposition of the leaves had taken place and the water distilling over with

<sup>1</sup> Eccles, *Proc. Am. Pharm. Assoc.*, **36**, 84 and 88.

<sup>2</sup> Wiley, *Am. Chem. J.*, **11**, 557.

<sup>3</sup> Gordin, *Proc. Am. Pharm. Assoc.*, **52**, 348, 53, 54.

<sup>4</sup> Miller, *J. Am. Chem. Soc.*, **26**, 2182.



the oil was strongly alkaline. After removing the oil the alkaline distillates were treated with an excess of hydrochloric acid and evaporated to dryness on the water bath. The residual salts were found to have an odor very suggestive of aliphatic amines; they were crystallized from absolute alcohol and the chlorine determined in both the alcohol soluble salt and the alcohol insoluble salt. The former determination gave 37.48 per cent chlorine, which corresponds with the theoretical percentage of chlorine in trimethylamine hydrochloride (*i. e.*, 37.17 per cent). The alcohol-insoluble salt gave 66.18 per cent chlorine which corresponds with the percentage of chlorine in ammonium chloride (*i. e.*, 66.37 per cent). A distillation on some fresh leaves failed to show either of these constituents and whether the trimethylamine and ammonium hydroxide were due to the decomposition of the protein matter alone or whether they were derived from the protein material plus some easily decomposable alkaloid has not been definitely settled. Qualitative determinations with phosphomolybdic acid demonstrated the presence of basic bodies in the leaves. These bodies failed to respond to tests for tannins: they were probably alkaloidal in character. The total nitrogen content was found to be 3.75 per cent by weight of the dry leaf. This nitrogen content is abnormally high if due to protein material alone.

A second sample of the plant, which was grown in a garden at Berkeley and weighed some 30 lbs., was separated into twigs and leaves and the two portions distilled separately while still fresh. The yield of oil from the leaves was about 0.15 per cent and from the twigs 0.37 per cent.

#### PHYSICAL CONSTANTS OF THE OIL

The oil had a greenish yellow appearance, a bitter taste, and a camphoraceous odor. The constants were as follows:

Density at 25° C.....	0.9295	Free acid.....	0.05
Rotation.....	+7° 28'	Saponification value....	54.3
Index of refraction $n_D^{20}$ .....	1.4713	Acetyl value.....	33.5

The oil is soluble in all proportions in 90 per cent alcohol, and in 15 to 16 volumes of 70 per cent alcohol by volume.

#### CHEMICAL EXAMINATION OF THE OIL

**ALDEHYDES AND KETONES**—The oil did not respond to decolorized magenta or sodium bisulfite solution. When tested with phenylhydrazine a distinct cloudiness was produced. This would indicate the presence of a ketone that does not respond to the magenta or bisulfite test, such as camphor.

**FREE ACID**—The free acid value of the oil was so low that it was impossible to identify the acid.

**COMBINED ACIDS**—One hundred grams of oil were saponified with alcoholic potassium hydroxide by heating on the water bath with a reflux condenser for half an hour. Water was added to the mixture and the oil layer separated out. After distilling off

the excess of alcohol on the water bath the alkaline solution was extracted with ether to remove any adhering oil. The remaining solution was evaporated to a small volume, acidified with sulfuric acid and distilled with steam. The distillate was extracted with ether. The ether was evaporated spontaneously, leaving a reddish brown crystalline residue. When tested with ferric chloride a purple color was formed, indicating salicylic acid.

The aqueous portion remaining after the ether extraction was neutralized with sodium carbonate. An aliquot of one-tenth of the original solution was concentrated to a small bulk and precipitated in three fractions with silver nitrate. Fraction 1 yielded 1.0560 g. of Ag salt; Fraction 2, 0.5431 g. of Ag salt; Fraction 3, 0.2114 g. of Ag salt. A perceptible reduction of the silver nitrate showed the presence of formic acid. On ignition the following percentages of silver were obtained from the silver salt: Fraction 1, 65.85 per cent Ag, Fraction 2, 53.1 per cent Ag, Fraction 3, 39.9 per cent Ag. Acetic acid yields 64.6 per cent Ag, butyric acid 55.3 per cent Ag, valeric acid 51.6 per cent Ag, and capric 38.67 per cent Ag.

The combined acids consisted mainly of acetic and salicylic with traces of formic, capric and possibly butyric, or valeric, or a mixture of the two.

#### FRACTIONATION OF THE OIL

The oil was fractionated with a 3-bulb Le Bel fractionating column, the results being given in the table.

TABLE I—FRACTIONATION OF THE OIL OF *CALYCANTHUS OCCIDENTALIS* SHOWING PHYSICAL PROPERTIES OF EACH FRACTION

Fraction No.	Fractionation Temperatures °C.	Percent Distilled over	Specific Gravity 15° C.	Specific Rotation at 15° C.	Index of Refraction 15° C.
1	154–170	8.51	0.8810	+16.42°	1.4590
2	170–180	54.83	0.9119	+ 5.85	1.4585
3	180–190	9.47	0.9215	+ 6.56	1.4650
4	190–200	2.48	0.9290	+ 9.52	1.4665
5	200–220	8.75	0.9635	+36.42	1.4817
6	220–over	10.22	0.9365	+18.85	1.4793
7		5.01	0.9171	...	1.4884

Fractions 5, 6 and 7 were made under reduced pressure at 150–180°. The boiling points of these fractions were redetermined at atmospheric pressure.

From the fractions in Table I it will be seen that this oil contains 5 groups of constituents, the first distilling between 154–170°, the second between 170–190°, the third between 190–220°, the fourth between 220–230°, and the fifth over 230° C.

#### CHEMICAL EXAMINATION OF THE FRACTIONS

**PINENE**—Fraction 1 consisted mainly of pinene. The nitroso chloride was prepared according to the method of Wallach<sup>1</sup> and was found to melt at 102.3°; the pure nitroso chloride melts at 102–103°. The medium value of the specific rotatory power indicates that although the pinene is mainly of the dextro-rotatory form some of the laevo-rotatory form is also present. A quantitative estimation of pinene in the original oil was made by distilling off a fraction between 155 and 170° C. and placing a portion of this fraction in a cassia flask and adding a 50 per cent

<sup>1</sup> Wallach, Liebig's Ann., 245, 251; 263, 251.

resorcinol solution, which absorbed the cineol. From the residual volume it was estimated that about 8.3 per cent of the original oil consisted of pinene.

**CINEOL**—Fractions 2, 3 and 4 combined and refractionated between 175 and 180°. After twice refractionating, the portion boiling at 176° was collected. The physical constants of this fraction and of the melting point of the iodol show that this fraction is mainly cineol.

	Fraction	Pure Cineol
Boiling point.....	176-177°	176°
Density at 20° C.....	0.930	0.929
Index of refraction at 20° C.....	1.4561	1.4559
Melting point of iodol.....	111.2°	112°

A quantitative determination by the resorcinol method gave 60.32 per cent cineol by weight of the original oil.

**BORNEOL AND CAMPHOR**—Fractions 4 and 5 were combined and redistilled under vacuum. They had a strong camphoraceous odor and on freezing crystals separated out which were very difficult to remove from the adhering oil. An attempt to prepare the semicarbazone by the method of Tiemann<sup>1</sup> gave no results.

Phenylhydrazine produced a distinct cloudiness, showing the presence of a ketone. When the fraction was heated to vaporization, and the vapor permitted to cool on a microscopic slide, a white sublimate was obtained which was found to consist of two distinct substances, one crystallizing in plates, the other in smaller irregular aggregates. This would point toward a mixture of borneol and camphor. A portion of this fraction was oxidized with Beckmann's chromic acid mixture, the acid neutralized and the mixture distilled with steam. The semicarbazone was prepared from the product and was found to have the melting point 235.8°; camphor semicarbazone melts at 236-238°. This fact, as well as the evidence of a ketone in the original oil, points to a mixture of borneol and camphor. If the acetyl value be considered due to borneol then there would be 9.21 per cent borneol present. This value is a little high, as some of the sesquiterpene alcohols present combined to form the ester with acetic anhydride, thus raising this constant.

**METHYL SALICYLATE**—Fraction 6 had a strong pleasant odor of esters. Since salicylic acid was found in the original oil, methyl salicylate was suspected. This fraction was treated with cold *N*/5 potassium hydroxide solution in order to form the soluble potassium methyl salicylate salt. After extracting the remaining oil the alkali solution was neutralized with dilute acid and again extracted with ether. On spontaneous evaporation of the ether a small quantity of oil remained, having the characteristic odor of methyl salicylate. Such a small quantity was obtainable that the index of refraction alone was determined and found to be 1.5298. The index of refraction of pure methyl salicylate is 1.536 to 1.538 at 20° C. A further amount of the oil was saponified with concentrated hot alkali solution. The solution was acidified and extracted with ether. The ether extract yielded

a few crystals which gave the characteristic color reactions for salicylic acid. From these data and from the boiling point of the fraction in which this substance appears it can be safely concluded that a small quantity of methyl salicylate was present in the oil.

**LINALYL ACETATE**—The remainder of Fraction 6 had a very pleasant bergamot odor. When saponified with alcoholic potash the saponification number was found to be 277.9. The alcoholic solution was diluted and the excess alcohol distilled off on the water bath. The solution was acidified and extracted with ether. Silver nitrate was added to the solution; the per cent of silver in the silver salt obtained was found to be 64.12 per cent Ag; acetic acid combines with 64.46 per cent Ag. The empirical formula for the ester would then be  $C_{10}H_{17}OOC.CH_3$ . The ether extract from this solution was evaporated spontaneously and the residual oil refractionated. The greater proportion distilled between 197 to 198°. The specific gravity was found to be 0.8703; the index of refraction at 20° C. was 1.4691. If from this data the molecular index of refraction is calculated it is found to be 48.77. The theoretical molecular index of refraction for a compound of formula  $C_{10}H_{17}OH$  with two double bonds is 48.86. This would indicate linalool. The only other alcohol having this structure is geraniol which has a higher boiling point and a greater specific gravity than linalool. The presence of linalool was confirmed by preparing the phenyl urethane derivative which had a melting point at 65.4°; linalool phenyl urethane melts at 65 to 66°.

**SESQUITERPENE ALCOHOLS**—These remained in the fractions boiling above 230° C. Owing to the small quantity of material and due to the fact that considerable polymerization had taken place, it was impossible to determine what they were. They constituted less than 5 per cent of the original oil.

#### SUMMARY

The volatile oil of *Calycanthus occidentalis* is made up of the following constituents in the proportion given:

	Per cent
Pinene ( <i>d</i> and <i>l</i> ).....	8.30
Cineol.....	60.32
Borneol.....	9.21
Camphor.....	...
Methyl salicylate.....	...
Linalyl acetate.....	18.99
Sesquiterpene alcohols.....	...

In the above estimation of the percentages of constituents present, the pinene and cineol were determined directly. The borneol was calculated from the acetyl value: this is perhaps slightly in error, due to the presence of sesquiterpene alcohols. The linalyl acetate was estimated from the saponification value, and is slightly in error, due to a small amount of methyl salicylate.

In conclusion, the writer wishes to thank Professor W. C. Blasdale, of the Chemistry Department of the University of California, for valuable suggestions in carrying out this investigation.

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<sup>1</sup> Tiemann's *Ber.*, 27, 1, 815.



# LABORATORY AND PLANT

## COMMENTS ON THE KREBITZ PROCESS OF SOAP-MAKING AND GLYCEROL RECOVERY<sup>1</sup>

By G. A. WRISLEY

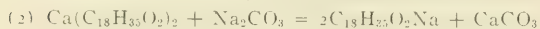
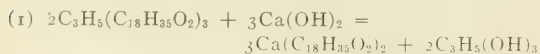
Received May 6, 1916

The process of soapmaking by boiling fats and oils (glycerides) with caustic soda is, in general, considered the most practical process since it yields soaps of uniformly good quality, color and hardness, and at the same time a good amount of glycerol may be recovered by comparatively simple means. The yield of glycerol from the soap lye runs from 60 to 80 per cent of the total amount formed by the saponification of the fats and oils. The loss depends upon the few or many washes that the soap receives. However, it seems that no matter how careful one is to make the washes and changes on the soap, there is always some glycerol,  $\frac{1}{2}$  to 1 per cent, left in the soap. It has also been demonstrated that in evaporating down waste lyes and handling so much salt which cannot be perfectly dried and freed from glycerol, that there is recovered but about 90 per cent of the glycerol that is in the soap lye. Hence even after the glycerol is in the soap lye, there is a loss in its recovery.

With the continually advancing price of fats, oils, and other raw materials, it is becoming more necessary for the soap manufacturer to obtain a large glycerol yield; in fact it is essential that he should recover all the glycerol liberated by the saponification. Then, too, the grade of fats and oils obtainable for soapmaking is lower, because of increased utilization of the better grades for edible purposes, so that the soap manufacturer must strive to produce a good quality soap from a poorer grade of material.

The Krebitz process, here discussed, offers the possibility of recovering the theoretical yield of glycerol, while at the same time the caustic lime exercises some purifying action, especially in the case of a low-grade material. The Allen B. Wisley Company, of Chicago, is the first in this country to work this process on a large scale with good results.

The Krebitz process is based on two simple chemical reactions:



In practice a batch of 10,000 lbs. of fat and oil may be conveniently handled. In a rather shallow tank 1200 to 1400 lbs. of lime are slaked with 3700 to 4500 lbs. of water, and the mass is heated, if necessary, to about 70° C. Then the fat and oil are run in while the entire mass is stirred vigorously. With live steam the mass is heated up slowly to 90–92° C., and taking about one-half hour to gain that temperature, with constant stirring, a thorough emulsion is obtained. The vessel is then covered to prevent loss of heat. Two or three hours after covering the mass is likely to boil and swell considerably. After it has stood 8

to 12 hrs., it has the appearance of a solid porous mass which is still sufficiently warm and soft to allow digging out the lime soap. This lime soap is dropped through a trap door in the bottom of the tank into a hopper and then to the mill where it is ground to the size of fine corn meal.

With the lime and water there will result between 15,000 and 16,000 lbs. of lime soap from 10,000 lbs. of fat and oil. The finely ground soap is carried on a conveyor and allowed to fall loosely into a circular, hopper-shaped tower, a capacity of about 25,000–30,000 lbs. being necessary. Four washes, about 40,000 lbs. of water, are required to leach out the glycerol from such a batch. The first wash water contains 10 to 12 per cent of glycerol, and is sent to the glycerin works. The second, third, and fourth waters are put on a fresh batch, only the last wash being made with fresh water. In this way, there is no cause for evaporating glycerin water containing less than 10 per cent of glycerol. When the plant is working satisfactorily the water evaporated averages 15 per cent of glycerol.

After the glycerol has been obtained, the lime soap is carried by a conveyor and introduced slowly into the soap kettle containing a boiling solution of soda ash. After the lime has been replaced by the soda, a stage which can be noticed by the nonappearance of small lumps on the paddle, a small amount of caustic soda is added, and shortly after the soap is salted out. The contents of the kettle are allowed to rest, when  $CaCO_3$  settles out at the bottom as a heavy sludge, and the soap gathers on top, a salt solution containing an excess of alkali forming an intermediate layer.

Although Krebitz claims that the lime sludge will settle out and occlude or entangle but 4 to 7 per cent of soap, it has been impossible, so far, to prevent the occlusion of less than 9 to 12 per cent of soap. Of course, this soap must be recovered. At first this constituted quite a serious problem, because the lime sludge could not be filtered without leaving 2 to 3 per cent of soap in the lime cake. Attempts to wash out the soap by a series of washings and filtration were unsuccessful, because so much soap was present as to fill up the pores of the filter cloth, making filtration slow and unsatisfactory. Attempts to boil up the sludge with a little water and resalt out the soap were unsuccessful, because on salting out, the lime sludge settled to the bottom carrying most of the soap with it again. By continued experiment, it was found that the addition of enough water with heat and vigorous agitation caused the soap to go into solution, and on allowing the mass to settle the lime sludge, occluding but 3 to 5 per cent of soap, went to the bottom, the soap rose to the top, and could be pumped off and so recovered. The lime sludge could then be easily filtered, and only 1 to 1.5 per cent of soap is lost in the lime cake. This loss, though small, may perhaps still be reduced.

The quality and color of the finished soap obtained

<sup>1</sup> Presented before the 52nd Meeting of the American Chemical Society, Urbana-Champaign, April 18–21, 1916.

by the Krebitz process compares favorably with the soap produced by any other process. The amount of lime found in the finished soap depends on the number of washes or changes made in the kettle. Usually there was never less than 0.2 per cent of lime and it may run as high as 0.5 to 0.7 per cent lime. The process, however, claims that only a few thousandths of one per cent should remain in the finished soap.

At the present time a yield of about 95 per cent glycerol is being obtained by this process. This, compared to the yield of 60 to 80 per cent obtained by the recovery of glycerol from the soap lye in the case of soapmaking by boiling the glycerides with caustic soda, would give the Krebitz process a decided advantage. Moreover, we must recall that soap lyess contain at best but 5 to 8 per cent glycerol, depending on the way in which the changes of soap lye are worked up, and at the same time hold in solution much common salt, some caustic soda, soda ash, and organic impurities; whereas the Krebitz waters contain 12 to 15 per cent glycerol and are comparatively free from impurities, thereby making purification more simple and giving less water to handle and evaporate. Soda ash is cheaper than caustic soda, and since soda ash is used in place of caustic soda another material saving is made.

Without doubt, the Krebitz process would be preferred at this time, because of the high price of glycerol, but were glycerol 15 to 20 cents per lb. instead of 55 to 60 cents per lb. there might be a shadow of doubt as to whether it would be preferred to the soap-lye process taking into consideration the manifold operations prior to the soapmaking proper, and the work necessary to recover all the entangled soap from the lime sludge.

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#### THE DETERMINATION OF BENZOL IN COKE-OVEN GAS BY BURRELL'S VAPOR APPARATUS

By LOUIS C. WHITON

Received April 18, 1916

The method for determining benzol and its homologues in gas as proposed by the Laboratory of Gas Investigations, U. S. Bureau of Mines,<sup>1</sup> has been tried in this laboratory with a view to determining the efficiency of benzol scrubbers utilizing coke-oven gas. The extraction of benzol, toluol and solvent naphtha has become at once such a profitable and important addition to a by-product coke oven's equipment that a rapid method of determination of scrubber efficiency seems imperative. The customary method of absorption of the vapors requires from 12 to 24 hrs. time and in this period many dollars worth of benzol and toluol may be lost, due to faulty operation of the scrubbers. Furthermore, especially when starting up a plant, conditions may have automatically been improved, without the operator's knowledge, toward the end of the test, which would mean that a change in operation as indicated by the test would perhaps be a disadvantage rather than otherwise.

The method as described in THIS JOURNAL did

<sup>1</sup> THIS JOURNAL, 7 (1915), 669.

not give the details of operation, which are extremely essential if accuracy is to be expected when determining such small traces of benzol vapors as are contained in debenzolized coke-oven gas.

Briefly, the apparatus as described by Burrell and Robertson, of the Bureau of Mines, consists essentially of a bulb about 6 in. long with a slight constriction in the center. The upper portion of the bulb contains glass wool mixed with phosphorus pentoxide to extract all the moisture from the gas. Connected with this bulb is a mercury manometer and an entry and exit tube with a ground glass 3-way cock. The air is first evacuated by means of a vacuum pump, the gas to be tested is sucked in and the 3-way cock turned when the gas is under barometric pressure. The entire bulb is then placed in liquid air or in a mixture of CO<sub>2</sub>-snow mixed to a consistency of slush with alcohol or acetone. It is allowed to remain there 10 min., the temperature being approximately -78° C. The benzol freezes out at this temperature and the CO<sub>2</sub>, O<sub>2</sub>, CO, H<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, and C<sub>2</sub>H<sub>4</sub>, which have a high vapor pressure at this temperature, are evacuated by means of the vacuum pump, the cock turned to seal the system and the apparatus brought up to room temperature. The partial pressure of the benzol vapor is registered on the manometer and this result divided by the barometric pressure times 100 indicates the per cent benzol.

There were several difficulties which had to be overcome in order to term the above a practical method for commercial work.

1—The readings on the manometer ranged from 10 mm. for benzolized gas to 1 mm. for debenzolized gas. With an ordinary manometer it is difficult to read much closer than 1 mm., which was beyond an allowable error.

2—In a vertical position it was impossible to surround the apparatus with the CO<sub>2</sub>-alcohol slush with economy in the use of the material which withal, as a commercial proposition, is expensive.

3—The P<sub>2</sub>O<sub>5</sub> in the glass wool soon ceased to be a good dehydrator and with the suggested construction of the apparatus it was impossible to charge it again with P<sub>2</sub>O<sub>5</sub>.

These difficulties were overcome to a certain extent in the following manner:

I—The mercury manometer was connected by means of a short, heavy piece of rubber tubing and was placed at a 10 to 1 slant, *i. e.*, 10 on the hypotenuse to 1 of altitude. This was placed on a firm gauge stand and leveled with spirit levels both ways. The gauge then gave a reading ten times the actual pressure. Thus it was possible to determine the pressure within 0.1 mm. which was sufficiently accurate.

II The bulb was laid horizontally in a trough with a notch at the end through which the stem of the apparatus could pass. In this position it could be more easily surrounded with carbon dioxide slush without danger of breakage of the bulb and with greater economy in respect to the slush. This trough was 8 in. long, 2 1/2 in. deep and 2 1/2 in. wide, with a hinged cover and double walls with the air evacuated. It was



found difficult to make this vacuum chamber absolutely tight so a petcock was soldered on and frequently the vacuum was attained again by means of the pump. This trough saved considerable cost in CO<sub>2</sub> and alcohol, preventing the former from being melted by the heat in the room to a considerable extent and enabling one to collect all of the alcohol after the determination by allowing the CO<sub>2</sub> to vaporize off.

III—The P<sub>2</sub>O<sub>5</sub>, which soon ceased to be active in respect to water vapor, necessitated cutting the tube leading from this bulb and connecting the two pieces by means of rubber tubing. In this way fresh P<sub>2</sub>O<sub>5</sub> and glass wool could be easily inserted.

Several other points of operation may be of interest. An ordinary Geryk vacuum pump, single stroke, was used and found effective. It might be well to state the well-known method of making CO<sub>2</sub> snow economically. A cylinder containing 50 lbs. CO<sub>2</sub> at high pressure is inverted to an angle of about 45° and the snow which issues forth when the valve is opened quite wide is caught in a canvas bag about 12 × 18 in. in size. The snow keeps well in a cardboard box.

It was found that more constant results were obtained by bringing the bulb up to room temperature after immersion in the freezing mixture, by means of inserting it in water for 10 min. A more careful control of the temperature can thus be maintained.

Although this article is intended only to give certain suggestions for the operation of Burrell and Robertson's apparatus it might be of interest to show some results obtained with it using coke-oven gas, to supplement the results obtained at the Bureau of Mines on Pittsburgh illuminating gas.

	Gas A (duplicates)		Gas B (duplicates)	
Bar. pressure, mm.....	742.0	742.0	741.0	741.0
Partial press. benzol vapors.....	5.4	5.2	1.8	1.9
Per cent benzol in gas.....	0.729	0.702	0.243	0.256

These are typical determinations made by this machine. Benzol scrubber efficiency does not call for absolute benzol determinations, comparative results before and after scrubber being sufficient. Therefore it is not necessary to have the manometer as carefully leveled as otherwise. Efficiency of scrubbers with the above results averaged would be determined thus:

$$\left( \frac{1.00}{5.3} \times 1.85 \right) \times 100 = 65.1 \text{ per cent}$$

The extreme results on the above tests would indicate 66.7 and 63.7 per cent efficiencies, which is as good as can be expected with this apparatus.

The result using this method as a determination of absolute benzol, toluol and solvent naphtha is somewhat lower than that obtained by absorption methods and averaged 24 per cent less than the amount obtained in actual practice. Benzol it is known has a sufficiently low vapor pressure at -78° C. to assert that it is completely condensed; about toluol there appears to be some doubt, and about solvent naphtha (a mixture of xylol and higher homologues of the benzene

series) there appears to be little known and with reason as its composition varies in different plants.

With an actual recovery during the period of one month of 2.20 gals. per net ton of coal carbonized of benzol + toluol + solvent naphtha, the average of many results determined by this apparatus indicated an amount equal to 1.70 gals. per ton coal or 22.7 per cent low. The recovered hydrocarbons in practice consisted in the following:

HYDROCARBON: 90% Benzol	Crude Toluol	Solvent Naphtha
Per cent recovered..... 67.5	19.3	13.2

This would seem to indicate that all of the benzol, part of the toluol and little if any of the solvent naphtha was condensed at the temperature of -78° C.: but this is merely a suggestion as it has not been as yet thoroughly investigated.

In conclusion it might be added that this method is more difficult of operation than it appears. The apparatus is delicate and the conditions as stated above must be rigidly adhered to in order to obtain consistent checks. As a method for determining benzol scrubber efficiency it is of some value; as a method of absolute determination of benzol, toluol and solvent naphtha it is of doubtful value, giving results apparently 24 per cent lower than those obtained in actual practice. Furthermore, the operation of the method requires a man skilled in handling such apparatus.

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## AN AUTOMATIC PIPETTE<sup>1</sup>

By ALEXANDER LOWY

Received March 28, 1916

Fig. 1 shows the entire pipette with the modified stopcock adaptable to any given volume. Fig. 2 shows the position of the stopcock while the liquid is being drawn up. Line *AB* is the mark of graduation. *H* shows the chamber below stopcock and *G* the chamber above the stopcock. *F* is a cylindrical bore through the stopcock connecting chambers *G* and *H* during the process of suction. *E* is a cylindrical bore ending back of *F* at an angle of 90°, of which *C* is a continuation and ends at a slight elevation at *D*. Fig. 3 shows the position of stopcock after it has been turned clockwise 90° to that shown in Fig. 2. *D* shows place closed by thumb. In this position channel *C* is connected with chamber *H* through opening *E*. In this position channel *G* is shut off from channel *H*.

With suction applied at end of chamber *G* (Fig. 2), the liquid is drawn up through chamber *H* until it just passes the graduated mark *AB*. The thumb is then placed on *D* so as to close opening *D* air-tight. The stopcock is then rotated clockwise through 90° thus bringing opening *E* (the continuation of tube *C* and *D*) to line of graduation *AB* and directly in contact with the upper opening of chamber *H*. The thumb is then released. Air pressure now forces the exact

<sup>1</sup> Patent applied for.

measured volume of liquid out of chamber *H*. Any excess liquid drawn up beyond line *AB* will be entrapped in either bore *F*, or in bore *F* and in chamber *G*. This excess is returnable by revolving the stopcock counter-clockwise through 90°.

The advantages of this pipette may be summarized as follows:

1—It enables the operator to automatically control an exact measured volume of liquid drawn into the pipette.

2—It obviates the necessity of adjusting, maintaining and manipulating the exact volume of the liquid once it has passed the graduation mark, placed

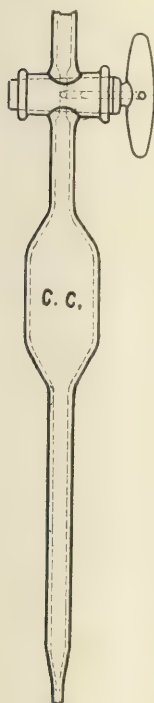


FIG. 1

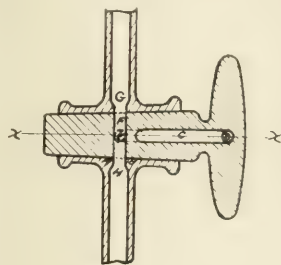


FIG. 2

Section at Y-Y

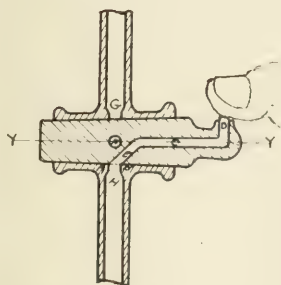


FIG. 3 - Section at X-X

where the stopcock meets the lower end of the valve of the pipette.

3—It permits the discharge of the exact measured volume of liquid from the pipette.

4—It is exceedingly easy to manipulate.

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### THE DETERMINATION OF AIR, WATER VAPOR AND NITROUS OXIDE IN MIXTURES OF THESE THREE CONSTITUENTS<sup>1</sup>

By G. A. BURRELL AND I. W. ROBERTSON

Received May 19, 1916

The authors of this report had occasion recently to examine some samples of nitrous oxide (dentists' "laughing gas") for the presence of water vapor and

<sup>1</sup> Published with the permission of the Director of the Bureau of Mines.

air. The mixture was first liquefied by means of liquid air, the air being then withdrawn with a Töpler mercury pump, and measured. The residual gas was subjected to a temperature of  $-78^{\circ}\text{C}$ ., the nitrous oxide being then withdrawn and measured. Finally the partial pressure of the water vapor was measured. This analysis is one of the many gas analyses that can be performed by means of the apparatus shown in Fig. 1.

The apparatus is first exhausted of its air by means of a Töpler mercury pump, and the sample of "laughing gas" is introduced at atmospheric pressure. Next the bulb *A* is immersed in a Dewar flask containing liquid air. After about 10 min. the air is withdrawn from the mixture through the pump and measured. The vapor pressure of the air at the temperature of liquid air is of course very high, and the air can be readily removed from the mixture. The vapor pressure of nitrous oxide is 1 mm. at a temperature of  $-144.1^{\circ}\text{C}$ .,<sup>1</sup> hence its pressure at the temperature of liquid air is practically negligible.

After the air has been removed and measured, the bulb *A* is immersed in a mixture of solid carbon dioxide and acetone. This mixture gives a temperature of  $-78^{\circ}\text{C}$ .. The bulb *A* is exposed to this temperature for about 10 min., and the nitrous oxide is withdrawn through the pump and measured. The normal boiling point of nitrous oxide is  $-88.7^{\circ}\text{C}$ .<sup>2</sup> so it can be readily removed from the mixture at a temperature of  $-78^{\circ}\text{C}$ . On the other hand, the vapor pressure of water is practically nil at a temperature of  $-78^{\circ}\text{C}$ . so that it freezes and remains in the bulb *A*.

After the nitrous oxide has been withdrawn and measured, the Dewar flask containing the solid carbon dioxide and acetone is removed from around the bulb *A*. The frozen water vapor then vaporizes and exerts its partial pressure on the mercury in the manometer tube *C*. This pressure is, of course, proportional to the percentage of water vapor present.

The results of the analysis of three samples of gas taken from the same tank follow:

CONSTITUENT	PERCENTAGE ANALYSES OF NITROUS OXIDE				TOTAL
	Air	N <sub>2</sub> O	H <sub>2</sub> O		
Sample 1.....	2.0	95.9	2.0		99.9
Sample 2.....	2.1	95.6	2.0		99.7
Sample 3.....	2.0	96.2	2.0		100.2

BUREAU OF MINES, WASHINGTON

<sup>1</sup> G. A. Burrell and I. W. Robertson, "The Vapor Pressures of Sulfur Dioxide and Nitrous Oxide at Temperatures below Their Normal Boiling Points," *J. Am. Chem. Soc.*, **37** (1915), 269.

<sup>2</sup> G. A. Burrell and I. W. Robertson, *Loc. cit.*



FIG. 1

Apparatus for the  
Determination of Air,  
Water Vapor and Ni-  
trous Oxide in Mixtures  
of the Three



## ADDRESSES

THE METALLURGY OF THE RARER METALS<sup>1</sup>

BY J. W. RICHARDS

Received June 14, 1916

There are many metals which may be called "the rarer metals." Among them the most interesting by far, to the metallurgist and to the economist, are those metals whose compounds are relatively cheap but which command a high price because of the difficulty of their reduction. These are the metals whose market price may at some time be reduced one-half, three-quarters, perhaps nine-tenths, by improved methods of reduction, and the discussion of how this might be accomplished and to what uses these metals at such low prices might be put, is interesting to the border of fascination.

If this article were being written thirty years ago, aluminum would be one of the metals to be discussed. It is now out of that class, but in 1886 it was one of the rarer metals, selling at \$10 per lb., although its ores were "as common as dirt." At that time you could buy a ton of bauxite ore containing 0.6 ton of alumina or 0.3 ton of aluminum, for \$5.00, while the 0.3 ton of aluminum was being sold for \$3,000, at wholesale. Or, eliminating the purely chemical work, 0.6 ton of chemically purified alumina could then have been bought for \$50, while the aluminum it contained was worth on the market 60 times that amount. Such were the metallurgical conditions in the aluminum industry thirty years ago, and so attractive were they to experimenters and inventors that the genius of the profession expended its best talents on the problem, with the result, in less than ten years, of reducing the market price to less than one-tenth its former figure.

The silicon industry furnishes another example in point. Silica is the most abundant and the cheapest material in nature, yet silicon was selling in 1900 as a chemical curiosity at *over \$100 an ounce*. Imagine the stirring up which my metallurgical wits received, when in 1902, Mr. Tone, at Niagara Falls, showed me a barrel full, 100 lbs. perhaps, of silicon made in his electric furnace, and asked me what uses it could be put to. At the present time, 10 c. per lb. is a good market price for silicon, which is often sold by the carload.

It is such seeming fairy tales as these which constitute the fascination of those metals which are abundant in nature but whose high cost rests on the difficult and costly methods of reduction employed. Such opportunities exist for our rising generation of chemists and metallurgists to make themselves famous and, incidentally, rich—but they will find their fame more of a reward than their riches.

Among the metals at present of high price, but which by improved metallurgical processes might be made very cheaply, are beryllium, boron, magnesium, calcium, strontium, zirconium, molybdenum, barium, titanium, chromium and cerium (mixed metals of the cerium group).

## BERYLLIUM

Commencing with one of the light, alkaline-earth metals, its ore is not so rare as is ordinarily supposed. Most non-mineralogists link it with beryl, and think of the latter as a very pretty and very expensive gem—the emerald. But the emerald is only the clear green or aquamarine stone, while massive beryl, looking like massive green quartz, is much more common, and is even abundant in some localities. The beryl crystals of Acworth, N. H., are sometimes as large as a barrel, and the massive beryl at this locality is quarried like feldspar. Its composition is:  $\text{SiO}_2$ , 67;  $\text{Al}_2\text{O}_3$ , 19; and  $\text{BeO}$ , 14 per cent.

It is difficult to say what the price of this material would be

if it was desired by the ton, but it should not be expensive. When chemically treated, both the  $\text{Al}_2\text{O}_3$  and the  $\text{BeO}$  which it contains could be separately obtained.

Up to the present, no one has succeeded in isolating the metal except by reducing a halide salt of beryllium by potassium or sodium (Bussy, Wöhler, Debray, Menier, Reynolds, Nilson and Peterson, Kruss and Morah), or by electrolysis of double chloride, bromide, or fluoride of beryllium and sodium or ammonium (Borchers, Warren, Lebeau, Liebmann).

These methods are tedious and costly for two reasons: *First*, they require the conversion of the beryllium into an anhydrous halide salt, which is a difficult chemical operation; *second*, the electrolysis sets free the halogen, which is very destructive to electrodes and apparatus. It is not to be expected that beryllium can be made cheaply until someone masters the direct electrolysis of the oxide, dissolved or suspended into a more stable melted salt. This is by no means an impossibility; a similar solution was found for the aluminum problem, and systematic, determined search would in all probability find the answer for beryllium. In such a case, the cost of the metal would depend only on the cost of beryllium oxide, being probably not more than 20 c. per lb., plus the cost of the oxide. Since  $\text{BeO}$  is only 36 per cent Be, it would require 3 lbs. of oxide to give one of metal; if the oxide cost 10 c. per lb., the total cost of the metal should not exceed 50 c., by such a supposititious process. Dealers in rare chemicals will charge you, at present, \$300 per oz. for a specimen of it.

Lebeau has produced beryllium bronzes by reducing directly, in the electric furnace, a mixture of beryllium oxide, copper oxide and carbon: 0.5 per cent of beryllium makes copper hard and sonorous, 1.5 per cent makes it yellow, and 5 per cent makes a fine, golden yellow bronze.

Beryllium, like any other rare metal, must find uses which justify its cost. Being white, malleable and unchanged in air, its specific gravity, 1.64, would make it particularly useful for objects where great lightness and permanence in air is the first consideration and cost secondary. So far we practically know nothing about its tensile strength or rigidity, about how it might be strengthened or stiffened by small additions of magnesium or aluminum or even of zinc, or copper, or manganese, or some other metal. We do not yet know the mechanical properties of its fine bronzes, except that they are somewhat similar to aluminum bronze, but in what respects they might be superior or perhaps unique, is unknown. Finally, the metal may easily possess special properties, now unknown, which may render it particularly useful for some specific purpose. Its specific heat, for instance, is the highest of any useful metal, and its latent heat of fusion must be abnormally high, possibly 300 calories, and its latent heat of vaporization probably higher than that of any known element, except carbon or boron. Such characteristics might give it special uses in electrical instruments, or for physical apparatus, where its cost would not exclude its use. Altogether, beryllium is a metal which will well repay extended metallurgical research and minute physical and chemical study of its many unique properties.

## MAGNESIUM

The metallurgist has been coquetting with magnesium for half a century, and has not, as yet, made a fraction of the progress which he should have made. We can get its oxide cheaply and in abundance, its salts are not very difficult to prepare, we know their properties to a considerable extent, we know almost all the properties of the metal which bear on its isolation, and yet the industry lags and halts as if there were no such thing as modern metallurgy. To prepare by tedious methods the anhy-

<sup>1</sup> Presented at the 8th Semi-Annual Meeting of the American Institute of Chemical Engineers, Cleveland, June 14, 1916.

drous double chloride, and then to electrolyze it about as Matthiesen did fifty years ago, is nearly all that can be said with certainty about its present metallurgy. At any rate, using magnesium oxide costing a few cents per lb., the metal sells for about as many dollars per lb., and yet there is a great scarcity of the metal.

Dr. W. M. Grosvenor, in a recent paper before the American Electrochemical Society, summarizes the present methods of production and the uses of the metal. Happily he also suggests the great field open for improvement, especially for radically new metallurgical methods of production. With magnesium in its salts costing less than 8 c. per lb., he places the actual cost of the metal at \$1.00 per lb. leaving over 90 c. per lb. for the cost of its extraction. "Brethren, these things ought not so to be." Speaking with the enthusiasm born of past achievements in electrometallurgy, along entirely analogous lines, a modern, up-to-date attack on this problem ought to result in producing magnesium at 25 c. per lb.

The point of attack should be undoubtedly to reduce the oxide directly. The halogen salts are hygroscopic, and the halogen is destructive of the reducing apparatus. It is almost certain that proper research will enable the electrometallurgist to feed magnesium oxide (MgO) directly into an electrolytic bath of fused salts, and take magnesium or magnesium alloy from it. The pure metal will float on almost any fused salt, but its alloy with heavier metals may be made such as to sink, and many of its alloys have immediate useful applications.

Dr. Grosvenor makes suggestive remarks about the reduction of magnesia by carbon. If the boiling point is only 1200° C., then a process of reduction similar to that of zinc oxide might be practicable if we could (1) find a retort material which will stand the temperature required (1800 to 2000° C.), and (2) condense the vapors without contact with air. Fortunately, magnesium does not form carbide at high temperatures, so that its reduction is simpler by that much. Dr. Grosvenor speaks of a chemical process which will use cheap raw materials, a moderate amount of fuel, and give a fair efficiency of reduction. With all expenses added, he estimates a cost not over 35 c. per lb. This may be true, but whether it materializes or not, he and his colleagues have the right vision of the possibilities, I may even call them the probabilities, of this field; they are truly "absolutely fascinating."

While the world war lasts, with its enormous demand for magnesium for military purposes, the price will remain in the dollars per lb. But experience in this line is being rapidly accumulated, and improvements are undoubtedly rapidly succeeding each other, although keen competition is keeping them secret as far as possible. After the war's close, with normal industrial conditions reappearing, magnesium will undoubtedly sell at a price which will take it out of the class of the rarer metals and put it among the common ones. As the price goes down its industrial uses will increase in geometric proportion, and instead of production being expressed in thousands of lbs. per year it will reach thousands of tons. This will be another of the by-products of the great war's stimulus to metallurgical industry.

The possibilities held out to the metal industry by reasonably cheap magnesium are extremely interesting. The stiffening of magnesium to produce strong alloys with specific gravity not over 2, has not been properly studied. It is quite possible that alloys analogous to *Dur-alumin* may be discovered, as strong as soft steel and only 30 per cent of its weight, which will find extensive use in aeroplanes and dirigibles. Such alloys may also largely displace aluminum alloys, which are used by thousands of tons annually in the automobile industry, with a saving of one-third in weight, which will compensate for a higher first cost. The metallurgical uses of magnesium will also be greatly extended by its lower price, such as for deoxidizing brass, bronze,

nickel and Monel metal, since it is a much stronger deoxidizer than aluminum. In fact, aluminum has blazed the way into numerous uses for which magnesium, as soon as it becomes cheaper, will compete and replace its older sister. With supplies of magnesium ore as plentiful as those of aluminum ore, and the metallurgist awake to his responsibilities and producing the metal cheaply, there will inevitably be a large future for magnesium as one of the common metals of every day life.

#### CALCIUM, STRONTIUM, BARIUM

These form a trio of highly interesting elements, common enough in nature, but all scarce and of high price because of the metallurgists' lack of efficient and cheap methods of reduction. With burnt lime, CaO, one of the cheapest of common materials, strontium sulfate, a mineral found in considerable abundance, and barium sulfate, so common as heavy-spar that it is used as an adulterant for some cheap paints, the metallurgist is again faced with the demand for cheap methods of reduction. And yet, although calcium is sold at a few dollars per lb., strontium and barium cost several dollars per oz. Here is a twofold need: *First*, cheap production; *second*, a thorough study of these metals to find out their specific properties and their particular uses. Which should be undertaken first is an interesting topic for discussion. Historically, the metallurgist has usually produced the metal first and then studied its properties and possibilities; at present, with these metals already at hand, metallurgical activity might be greatly stimulated by extensive studies of the properties, alloys, and chemical uses of these elements. Our present information in this direction is fragmentary and partly unreliable as far as it goes. A Carnegie research scholar, or even the Bureau of Standards, by disclosing to us some of the unknown properties of these elements, might stimulate the experimenter to renewed efforts to find cheaper methods of reduction.

CALCIUM, at the present time, is the best known of these three elements. The method of electrolyzing its fused chloride and lifting the metal away from the surface, as an irregular stick, has been fairly successful, and since the chloride is not difficult to dehydrate, the whole operation is not very expensive. Calcium is therefore, at present, perhaps a *semi-rare* metal, which could be produced much cheaper even by present methods if made on a large scale to fill a large demand. The method of production is easily susceptible of minor improvements, and the chlorine is a valuable by-product to the manufacture. The principal hitch at present is in finding the uses for a large production of calcium. Here is where extensive study of the properties and possible uses of calcium would greatly stimulate the metallurgical industry. With a specific gravity of 1.85, its possible alloys with other light metals should be exhaustively studied; quite possibly some of them are strong, resistant to air and water, perhaps even to acids. Calcium tarnishes easily in the air, and magnesium also, but it is quite possible that some alloy of the two does not tarnish, and may have valuable mechanical properties. Another large possible use is as chemical purifying agent in melting and casting metals. Calcium-silicon-aluminum alloy has already found application as a deoxidizing agent in steel, because while aluminum oxide and silicon oxide and their combination with each other are infusible at steel-melting temperature and therefore are eliminated slowly from the metal, calcium oxide forms with these an easily fusible slag, which easily rises out of the molten metal. It is quite possible that a small addition of metallic calcium may in a similar manner reduce the amount of sulfur and phosphorus in steel, because it is either as calcium sulfide or calcium phosphate that these elements are eliminated in refining steel. Other metals and alloys, whose properties are damaged by sulfur or phosphorus, may be similarly refined or improved. The alloys of calcium with copper, tin, bronze, brass, Monel metal, and other commercial alloys have not been studied, until they are, no



one knows how many useful mixtures may exist with particular properties of industrial value. The question of adding calcium to the light, stiff aluminum alloys, for instance, is worthy of attention, but has not been touched.

STRONTIUM is a silvery white, very soft metal, with properties similar to calcium, density 2.54. Its ores cannot be called rare minerals, and it is a rare metal, therefore, only because of the difficulty of its isolation. It is chemically very active, and electrochemically extremely hard to manage. It has about the same specific gravity as its fused salts, so that it neither rises nor sinks in any of them quickly; it seems also to redissolve in its melted salts with great velocity, so that very high current density is required to obtain any metal at all. Its surface tension appears to be abnormally high, so that it separates out in more or less minute globules which are highly indisposed to running together into one mass. What an attractive subject this forms to the electrochemist who really wants to meet difficulties and taste the joys of overcoming them. And then, one may well ask: "To what purpose?" Here again we do not know, but we can feel confident that in the innumerable list of possible combinations of metals strontium might have properties different from any other element, which would lead to its employment on a large scale. These are all questions of the future which form the undiscovered country open to the investigator and chemical pioneer. We may well thank our stars that the world of science still holds unexplored areas to tempt the adventurous investigator and to reward the *wanderlust* of the metallurgical pioneer.

BARIUM is common in its compounds and almost unknown in itself. Under electrolytic conditions where calcium comes out *en masse*, and strontium separates as small globules, barium is obtained only as a fine powder. Its density is 3.75, but its salts are heavier than the corresponding strontium and calcium salts, so that the fine powder may sink or swim, largely according to the temperature. And yet the fused barium salts are very decent and manageable salts, easily obtained anhydrous and melting cleanly. Their electrolysis, however, is nearly the most difficult task that the electrometallurgist can take up. But it should be taken up and mastered, because a metal so common in its compounds could be obtained in large quantities if uses for it were developed, and if our modern electrometallurgists are worthy successors of Faraday, Bunsen and Castner, they should vigorously attack the problem of its cheap extraction. Even if their end was not reached, they would be whetting their metallurgical wits upon the finest of chemical whetstones, and their experiences would be of value to themselves as well as to other lines of electrometallurgy.

#### BORON

As an intermediate element, semi-metal, cheap and abundant in its compounds, yet almost unknown as an element, boron is very interesting. Although quoted at several dollars per oz. yet there are possibilities of it being made for  $x$  cents per lb., where  $x$  may be anything over 25. It is only the prophetic prescience of the enthusiastic metallurgist, however, that can discern the goal in the distant future.

Boron occurs in nature as its oxide, Sassolite, containing 31 per cent of boron, as borax, containing 11.5 per cent of boron, and as colemanite, containing 18.9 per cent of the metal. These sources are comparatively abundant, the oxide being found in volcanic districts, borax near dried up lakes, and colemanite (calcium borate), being literally a waste product of the borax mining, for which uses have only recently been developed.

Gay-Lussac and Thenard, Wöhler and Sainte-Claire Deville reduced the oxide by potassium or sodium, other chemists by phosphorus, magnesium, aluminum and calcium, while Duncan reduced boron chloride gas by hydrogen. Chemically, its reduction does not appear to be of extraordinary difficulty. Electrochemically, Davy electrolyzed fused boracic acid, Gore potas-

sium boro-fluoride, and Faraday fused borax. All describe having isolated boron. Quite recently, Weintraub has decomposed boron chloride by hydrogen in a high tension arc, and obtained purer boron and in larger quantity than any previous investigator. His classical paper is in the *Transactions of the American Electrochemical Society*, 16 (1909), 165.

The properties of the pure boron obtained by Dr. Weintraub are exceedingly interesting. Its fusing point is extremely high, between 2000 and 2500° C.; it was fused in a boron nitride crucible under the pressure of its own vapor. Its boiling point is near to its fusing point; it has considerable vapor tension as low as 1600° C. It has a conchoidal fracture, and is nearly as hard as the diamond. At room temperature it is electrically almost a nonconductor, but at 500° C. its conductivity has increased 2,000,000 times; at 1000° C. its conductivity is of the order of that of the metals. Applying moderate voltages to a cold piece, it soon warms up and makes itself a good conductor. Such extraordinary properties suggest its use for many interesting electrical contrivances, which are enumerated by Dr. Weintraub.

Other uses of boron, which have not yet been thoroughly investigated, are in the formation of boron steels and boronized copper. The former were investigated by Guillet, in France, with irregular results; in some respects, at times, the effects were similar to that of vanadium in the famous vanadium steels, at other times the results were different. The uncertainty may have been due to irregular composition of the ferro-boron alloy used. A great amount of investigation should be done on this line, first in making a reliable quality of ferro-boron, and second in using it systematically in various qualities of steel. The question of boronized copper is in a still greater state of uncertainty. Boron or even boron sub-oxide ( $B_2O$ , or perhaps, boron saturated with  $B_2O_3$ ) added to melted copper enables a perfect copper casting to be obtained, of practically 100 per cent electrical conductivity; a trade product sold as boronized copper has similar effects in producing sound copper castings. These results are only the beginning of an extensive field of investigation of the effects of small amounts of boron on metals and metallic alloys. They will certainly lead to important metallurgical discoveries and improvements.

In metals and alloys boron can act chemically, as a purifying or refining agent to remove oxygen, nitrogen and perhaps sulfur, phosphorus, and dissolved oxides, while in larger amount it acts metallurgically as an alloying element. In the latter respect it forms true alloys, such as the ferro-boron alloy, which is an article of commerce. The possibilities of extensive use in molten metals and alloys are great, but mainly dependent upon systematic metallurgical research in properly equipped laboratories.

The production of the metal and its alloys also needs expert attention. For use in steel, a good uniform quality of ferro-boron is needed, and the manufacture of this in satisfactory uniform quality has not yet been mastered. Some years ago, the Pacific Coast Borax Company offered a prize of \$500 to be awarded by the American Electrochemical Society, for a practical electric furnace method of producing ferro-boron directly from calcium borate (Colemanite), a waste product of the borax mines. A few years later the prize money was returned by the Society to the Company, as not having been earned, although several attempts were made for it. For use in copper, brass and bronze, cupro-boron alloy answers as well as having pure boron. One method of making this is being tried, and the product is giving some very satisfactory results. Improved and more certain means of getting boron into copper are needed, and could probably be found by a moderate amount of careful investigation. As for pure boron and the fascinating possibilities dependent on its remarkable properties, Dr. Weintraub's method makes the product, but at considerable expense, and a cheaper, easier method is a great *desideratum*. If such is found, boron

will certainly occupy an important place among the useful metals.

#### CHROMIUM

This element is also common and abundant in nature, and rare and expensive as a metal. Chromite, containing 34 per cent of chromium, costs normally \$20 to \$25 per ton, while the ferro-chromium alloy produced from it sells at \$100 to \$550 per ton, according to the percentage of chromium and carbon contained. But pure chromium, carbon-free, is produced only by reduction of chromium oxide by aluminum, and commands 75 c. per lb. The use of chromium in steel is rapidly extending to all varieties of extra hard and high-speed steel, but the use of pure chromium is limited by the high cost of its production and our lack of knowledge of how to handle it and of its possible useful effects. For example, chromium electroplating is white and durable, and for many purposes may be superior to nickel and almost equal to platinum plating, but the technique of always getting perfect plating has not been satisfactorily mastered. Cobalt-chromium alloys have been made which have some of the remarkable properties and uses of high-speed tool steel (Stellite alloy of Mr. Haines). This is an excellent example of totally unexpected and valuable physical properties being discovered by systematic investigation. These alloys, however, must be made from pure chromium, and not from ferro-alloy. How many other remarkable alloys yet remain to be discovered by patient and intelligent investigation, no one knows or can even guess.

As for the methods of reduction, ferro-chromium alloy carrying high carbon (6 to 8 per cent) is produced quite cheaply in crucibles, cupola furnaces, blast furnaces, or electric furnaces. Low-carbon ferro-chromium commands three to five times as high a price, because of the difficulty of decarbonizing the raw product. It is very much to be hoped that tests will be made in the electric shaft-furnace to see if it is not possible to produce directly from the ore a low-carbon product. The thing has been done in the case of pig iron, producing a low-carbon product which is called pig steel; there is no inherent impossibility in similarly mastering the conditions for producing directly the low-carbon ferro-chromium. The present prices of the two products, \$100 and \$500 per ton, respectively, would warrant great efforts in that direction.

Similarly, chromium is not a difficult metal to reduce to the metallic state, but it is a difficult question to find the proper flux, and to keep carbon out of it. Goldschmidt reduces it by aluminum; electrolysis of its fused salts is difficult because of their high melting points. If electrolysis of aqueous solutions of chromium salts could be satisfactorily controlled, so as to produce heavy deposits, this might open the door at once to cheap and pure chromium. Electrolysis of molten relatively fixed salts in which chromium oxides are dissolved (similar to the Hall aluminum bath) is not a hopeless proposition. The chromium would be plated solid, however, on chromium cathodes, since the working temperature would be below the melting point of chromium.

The metallurgy of chromium is full of attractive possibilities, and the usefulness of pure chromium in the field of alloys is only beginning to be scratched; the scratching, however, is proving very much "worth while."

#### TITANIUM

Our friend, Mr. A. J. Rossi and the Titanium Alloy Manufacturing Company of Niagara Falls are the *alpha* and *omega* of the titanium industry. Nearly 15 years ago my first introduction to Mr. Rossi was in the historic barn, at Niagara, the cradle of so many of the Niagara Falls industries. Mr. Rossi was running the electric furnace and Mrs. Rossi was in the little laboratory, making the necessary analyses.

Everyone knows of the enormous masses of titanic iron ore in northern New York and Canada, which contains so much

iron and so little sulfur and phosphorus, that every blast furnace would be glad to get it if it was not for the titanic oxide which makes it so unworkable that you could not give it to them. Mr. Rossi tried first to extract the iron only, throwing away the titanium in the slag, but that was not profitable. He then turned to producing ferro-titanium alloy, for use in steel and cast iron, and by indomitable perseverance has made that a success. A finely written booklet of over 100 pages, published by his company and to be had for the asking, tells the whole story, so why take up time to rehearse it here? Get the booklet and read it. In addition to titanium treatment of steel, to de-oxidize and denitrogenize, this company also makes a specialty of titanium-treated aluminum bronze, also of titanium-treated bronzes and brasses of various compositions.

With titanic iron ore carrying 10 to 15 per cent of titanium as cheap as iron ore, and if iron-free material is required, rutile, 60 per cent titanium, at 5 to 7 c. per lb., there is no lack of cheap raw material. If uses are found for pure titanium, however, some other than the electric furnace must be used to reduce it, because, in absence of iron, titanium carbide would result. The methods for producing pure titanium are, like its prospective uses, still in the future, but they nevertheless are worth study and work. One can buy titanium metal now at about the price of silver, but if the problem were properly faced it could probably be made as cheaply as chromium.

#### MOLYBDENUM

Molybdenum sulfide,  $\text{MoS}_2$ , 60 per cent molybdenum, looks almost exactly like graphite, and is about as widely distributed. Normally, it can be purchased as 90 per cent concentrates at 25 c. per lb. This would make the raw material for 1 lb. of molybdenum cost nearly 50 c.; the selling price of the metal is about \$2.00. This leaves a large margin to pay for reduction. In fact, \$1.00 per lb. of contained molybdenum ought to return the reduction works a good profit.

However, the principal need of the molybdenum industry is a better utilization of its sources of raw material. The deposits have not been, in general, properly prospected or opened up, and then not properly worked. They are usually low-grade propositions, with 5 to 10 per cent of molybdenite disseminated through hard rock. This calls for careful study of crushing and concentrating methods, so as to minimize waste and loss. In most cases, the actual treatment falls far short of this, and possibly half the molybdenite in the ore is lost. The producers of the concentrates are being paid high prices for their material, but the market is limited and dull. If molybdenite were sold cheaper, there is little doubt that ferro-molybdenum, 50 to 85 per cent molybdenum, could be sold at half its present price, and the uses of molybdenum in steel correspondingly increased. New uses have also been found, such as the molybdenum wire so useful in electric resistance furnaces. This wire is scientifically very useful in that it resists the alloying action of many liquid metals even at very high temperatures. Dr. C. G. Fink, of the Edison Lamp Works, has studied these notable physical and chemical properties, and has described them in the *Transactions of the American Electrochemical Society*, 17 (1910), 229.

#### ZIRCONIUM

We may mention this element, which, as metal, is rare enough, but whose oxide has recently been found in considerable abundance. The familiar mineral Zircon is the silicate, containing nearly 50 per cent of zirconium, but it is found only in limited amount. In the last ten years the oxide Baddeleyite has been found in large quantities in Minas Geraes, Brazil, running 75 to 95 per cent pure, giving 50 to 75 per cent of the metal. This source is now so common that it sells at 4 to 5 c. per lb., and is being used in large quantities as a refractory material, on account of its high melting point ( $2000^\circ \text{C}.$ ), high resistance to all kinds of slags, low thermal conductivity and low coefficient of expansion.



The metal, however, is almost an unknown quantity. It has been obtained by the action of potassium or sodium on the anhydrous fluorides. Fused, it is white, density 6.4, melting point  $1500^{\circ}\text{C}$ ., hard enough to scratch quartz. Ferro-zirconium has been made in the electric furnace, and used in small amounts in steel, with rather indefinite results. And yet, if some very useful properties of zirconium were discovered, the metal could undoubtedly be prepared at a reasonable price—only a fraction of the \$5.00 per oz. now asked for it as a chemical curiosity. How it is to be obtained cheaply is one more of the interesting questions confronting the metallurgical pioneer.

#### CERIUM

There is a peculiar interest attaching to this metal and its close associates, from the fact that hundreds of tons of fairly rich cerium material is lying on the waste heaps of the incandescent mantle factories. The thorium ore used by these factories is Monazite—a phosphate of the cerium earths plus thorium silicate. On extracting the thorium, the residue is worthless for mantle fabrication. It is known as "Commercial Cerium Carbonate," and contains cerium, lanthanum, neodymium, praseodymium, samarium, gadolinium, yttrium, ytterbium, a little thorium, and considerable alkalis, iron, phosphoric acid and silica. By treatment with acids, precipitation of the rare earths, and ignition, a chocolate-brown mixture of oxides of the rare earths is obtained, in which cerium oxide predominates, and which contains nearly 50 per cent of metallic cerium. When this mixture is reduced directly, without further separation, to the metallic state, an alloy of the rare earth metals is obtained which is known as mixed metal (Mischmetal), or impure or commercial cerium. The composition of mischmetal naturally varies, but may be taken as approximately 30 to 50 per cent of cerium, 15 to 25 per cent of lanthanum, 10 to 15 per cent of the didymiums, up to 20 per cent of the yttrium metals, and 1 to 5 per cent of thorium.

An immense amount of laboratory and practical work has been expended on the production of mixed metal and of purer cerium. Professor Muthmann and his students in Munich, and Alcan Hirsch in the United States deserve particular mention for their articles, in *Liebigs Annalen* (1902 to 1910), and *Transactions of American Electrochemical Society*, 20 (1911), 1-102, respectively. Dr. Aufer von Welsbach was the pioneer in the commercial manufacture and use of mischmetal. Annoyed by the sight of heaps of the cerium residues around his mantle factories, he experimented with their reduction to mischmetal and with the possible uses of the latter. Finding that it gave off sparks when scratched he conceived the idea of using it in automatic lighters, but found that it sparked far too feebly and unreliably to be practical. He then thought that if he purified the cerium it might give sparks more freely, but on making the purest cerium he found it to spark less than the impure metal. Turning in the opposite direction, he took mischmetal and added to it alloying metals not of the rare earth class, and found that they increased the sparking property. Iron, for instance, when increased to 30 per cent gave an alloy with remarkable spark-giving properties, such as make it most efficient and reliable in automatic lighters. This has formed the basis of the "pyrophoric alloy" industry, since although other metals have similar effects the 30 per cent iron alloy is probably the best sparking alloy, for general use, so far made.

The electrolysis of fused cerium salts, double chlorides or double fluorides, to give the melted mixed metal is carried on on a large scale in Austria at Treibach, in Germany near Berlin, and was commenced in the United States, in 1916, near New York City, by Mr. Hirsch and his associates. The technique is not easy to master, and all the works keep their operations as secret as possible. The principal difficulties are the re-solution of deposited metal, metal fog, and scattering of the metal as fine globules or "metal-mush" through the electrolyte, making it

difficult to unite the metal to one melted mass. Since the latter trouble is largely due to surface tension, a study of this property, particularly how it can be diminished, might help in overcoming the difficulty. As an example of the opposite effect, the cupelling of lead on a bone ash muffle depends absolutely, for its success, on the surface tension of the molten lead. But, metallic tellurium in quite small percentage decreases the surface tension of the lead so greatly that the metal wets the cupel and cupellation is rendered impossible. Arsenic, on the other hand, increases the surface tension of melted lead, and is therefore purposely added, about 0.25 per cent, to lead being made into lead shot, in order to make rounder shot. A physical study of such effects on cerium might well assist in overcoming the scattering of the metal in globules in the electrolytes. Another direction in which improvement might be made would be the careful study of the eutectics of mixtures of cerium salts with barium salts, so as to find an electrolyte of lower melting point in which the losses by re-solution of deposited metal would be less than they are at present. Another possible improvement would be the finding of an electrolyte which would dissolve cerium oxide or the mixed oxides directly, and give metal by electrolysis. Such a bath has been discovered for aluminum oxide, and a long experimental search for a similar bath for the cerium oxides would be amply justified.

The possibility of using the 30 per cent iron alloy as a melted cathode, and enriching it in cerium by electrolysis, might be considered. If we had the fusing point curve of cerium-iron alloys we could draw some useful conclusions in this direction. The addition of small amounts of other metals to the bath, so as to produce other useful cerium alloys directly, might facilitate the electrolytic operation. Further experience with the process, particularly by those familiar with the electrolysis of molten baths for sodium, magnesium or aluminum, will very probably lead to considerable improvements and reductions of cost.

The uses of cerium and particularly of its alloys are sure to increase, and may attain considerable proportions. It has been proposed by Borchers as an addition in small quantity to aluminum, to improve its properties. But the large use will always be the pyrophoric alloys, which have so largely replaced matches. Before the European war, over 3000 workers were employed in Austria in this industry of pyrophoric alloys and automatic lighters. Mistakes were made in the early days of the industry, and some alloys put into lighters which crumbled to pieces by the time the apparatus reached Australia, but continual improvement was being made, until a satisfactory substitute for matches was attained. The improvement most needed in the pocket lighting apparatus is to be able to dispense with alcohol or similar liquid; a wick impregnated with a solid combustible which can be ignited by a pyrophoric alloy, would give a great impetus to this art.

The author apologizes for making this paper so largely critical and prophetic. If it has sounded too prospective in tone, the excuse must be that it is inherent in the subject. Some of these elements are among the most common in nature, yet they remain so rare in practical life that they are still chemical curiosities. But the chemical curiosities of one age have frequently become the chemical commonplace of the next age, and even within a generation some of us have seen this happen, under our own eyes. Let us then be foresighted, forehanded, and anticipate possible developments a little by such a general review as has just been given, so that when some wonderful changes and improvements are made in the next few years we may have the satisfaction of knowing that we glimpsed their shadows sometime before they arrived, and may even have assisted in hastening their arrival.

LEHIGH UNIVERSITY  
SOUTH BETHLEHEM, PENNSYLVANIA

RESEARCH<sup>1</sup>

By ARTHUR L. WALKER

Research does not necessarily mean delving into abstruse problems that it is impossible for the average man to understand, neither does it mean work that is entirely governed by university regulations. Research is diligent investigation that will as a result improve our knowledge and condition whether it is in abstruse science or in the nature of an advance in the Arts which will add to the world's welfare and the usefulness of mankind. It covers a multitude of fields and may be carried on in numerous ways.

I remember a few years ago when I attended the initiation ceremonies of our sister chapter at Yale, George Borup was one of the initiates who had accomplished his work about as far away from the center of civilization as it is possible to get. But what could be more useful than the diligent investigation which helped to discover a way to an unknown portion of the world, in this case the North Pole, which had been the goal of many explorers and the cause of much suffering for nearly a century.

A practical engineer approaches the study of a new problem, whether it is the examination of a property, the design of a plant, the development of the science, or a study of conditions with the idea of improvement, in a true scientific spirit. He obtains facts, physical, chemical, economic, etc., and he must assemble these facts in a logical manner in order that deductions and conclusions may be arrived at upon which he can base his recommendations, his designs, or the theories which he uses as a foundation for the improvement.

The wonderful development which in the last few years has been made in lead smelting operations is due to careful investigations of the theory of smelting operations and the chemistry involved therein, as well as to the study of the theory of roasting ores preparatory to blast furnace operations. This work extended over a period of many years and was conducted at several plants in the Far West, Southwest, and in Mexico. It is gratifying to know that the investigator who conducted this work is a graduate of our School of Mines and this society has seen fit to recognize his services by admitting him into Sigma Xi this evening. I refer, of course, to Arthur S. Dwight.

In another field of work our colleague, Robert M. Raymond, has distinguished himself as an investigator of the conditions which surround mine development and mining operations. His success has won for him international fame of a high order, and we are glad to welcome him as one of our *Brothers in Zealous Research*.

While it can be truly said that the university is not the only place in which research can be conducted, it must be admitted that conditions which surround university life and university work are such that it should be the place where work of an investigative nature can be most successfully and effectively accomplished.

There never has been a time in the history of the world when the systematic investigation of problems, the solution of which will give us what we want or what is really necessary, has attracted so much attention. Never until the present has there been a time in the history of this country when the question of systematic investigation has commanded any attention at all from the people at large.

The various nations of the world are realizing that in order to protect themselves they must not lay on their oars and let others do the work of investigation which may result in the manufacture of what all the world needs. They too must work and improve and manufacture all products that they are dependent on, in order to be prepared for any unforeseen emergency, and be independent when that time arrives.

In this country we are beginning to awake to a realization of the extent of our dependence on others, and our attention is now brought to the fact that we should prepare to manufacture what we need. There are reasons why it has not been deemed necessary, in the past, for us to consider this question. The wonderful natural resources of the country have been conducive to lax methods; but we now begin to realize that these resources should be conserved, the products which have formerly gone to waste should be utilized, and that a study should be made as to how we can manufacture that which even the wealth of our resources does not provide.

While we as a nation have not considered the question of research as carefully as we should, and there has been a lack of the spirit of research as it is understood from the university standpoint, there has been no lack of diligent investigation, which has resulted in the enormous improvements which have added to the world's progress and the comforts of mankind.

Among the leading nations it is an undeniable fact that that nation which is supposed to have conducted the greatest amount of pure research is the nation which has shown the least amount of initiative in connection with the great discoveries of the world. And it can also be said, without boasting, that our own nation, which, up to the present, has done the least amount of pure research, has contributed more than any other to the great discoveries of the world. And as we look at the list of nations we see that the amount of pure research undertaken and original discoveries made are inversely proportional. This is an important consideration, something which should be thought of now and remembered in the future.

All of our large manufacturing establishments are either operating research laboratories on a large scale or are making plans for laboratories which will give them facilities for conducting research. Our universities are establishing laboratories on very much more extensive lines than heretofore thought of, and the question of a very large research laboratory for the government is being discussed. This wave of enthusiasm is quite recent, but if the work is properly conducted and co-ordinated it is bound to result in great benefit to this country, and to the world at large.

It has been said that a university cannot compete with the industrial laboratories of our large corporations. Probably this has been more or less true in the past, as the situation is such that the investigator comes in actual contact with the operations at the industrial corporations and thereby sees a great deal which aids him in the work he is performing. But a greater reason than this is that in most of our university laboratories the investigators are so tied down by routine work that they cannot devote a sufficient amount of concentrated time to investigation. On the other hand, the works laboratories are at a great disadvantage in that there is a large amount of duplication in spite of the fact that, at the present time, there is a freer interchange of ideas than ever before. The advantages which the university laboratories should have compared with the works laboratories are: (1) complete absence of secrecy; (2) the universal character of the work which can be done; (3) the facilities open to all; (4) the reduction of the expense of investigation; (5) the fact that unsuccessful work accomplished is more apt to be recorded and the data open for future reference.

In the advance copies of papers to be presented at the meeting of the American Electrochemical Society, in Washington, during the end of this month, on the subject of industrial research, some of the most distinguished scientists have expressed their opinion from professional, university, government, and corporation standpoints. The keynote of these expressions is "cooperation," but how cooperation can best be obtained is not definitely determined or agreed upon.

Undoubtedly all of our research laboratories at the present

<sup>1</sup> Initiation address before the Society of Sigma Xi, Columbia University, April 18, 1916.



time, whether they be in university or industrial plants, are operating under great disadvantages, either for lack of space or facilities in the case of the university laboratories, or for lack of time in the case of industrial laboratories. Will not these difficulties be properly solved by the creation of an industrial development laboratory under the auspices of some large university like Columbia? With the proper technical staff unhampered by excessive academic duties, work could be conducted in such a laboratory with a thorough knowledge of what is being done in the field.

Professional men with problems to solve could have them investigated, large corporations who have not the time to undertake investigations, and small concerns which have neither the requisite time nor the money for research could confidently avail themselves of the facilities offered by such a laboratory, and even the government might find it advantageous to utilize it for certain classes of work.

The magnitude of an undertaking of this character is enormous, but so would be the beneficial results obtainable in a proper industrial development laboratory, conducted on scientific, professional, and business lines. As Dr. Whitney facetiously suggests, to this laboratory could be brought "the poorest furnace slag to be quickly tried for farm fertilizer, tested in cements, made into glass, ground into paints, calendered into writing paper, blown into thermal insulation, turned into asbestos, put into dynamite, or injected into medicine."

No matter how much we may progress in research or industrial development work, let us remember that this work should not be controlled in such a way that the initiative the people of this nation now possess is made subservient to every-day plodding and investigation work.

COLUMBIA UNIVERSITY  
NEW YORK CITY

## CURRENT INDUSTRIAL NEWS

### COAL-MINE FATALITIES IN THE UNITED STATES, 1870 TO 1914

Detailed information concerning coal-mine fatalities in the United States from 1870 to the close of 1914 is given in *Bulletin 115* recently issued by the Bureau of Mines, Department of the Interior. In this bulletin more than 52,000 fatalities at coal mines have been classified by cause of accident, State, and calendar year. For the first time all of the States are placed on a calendar-year basis from the beginning of inspection in each State to the close of 1914. This report is a diagnosis of the mine-accident hazard and contains information that will be used as a basis of the study of accident prevention by operators, State and Federal officials and insurance companies.

Part I of the bulletin is devoted to the coal mines of the United States, in which the United States is treated as a unit by calendar years and by causes. It contains detailed information concerning accidents due to falls of roof, haulage, explosives, and electricity; a complete list of mine disasters in which five or more men have been killed since 1839; complete production figures, number of men employed and data relating to mining methods. There is also a study of mine accidents as related to machine mining, in which four groups of mines are maintained, namely, those in which 1 to 20 per cent of the coal is machine mined; 20 to 40 per cent machine mined; 40 to 60 per cent machine mined; and 60 per cent and over machine mined. These groups are tabulated by States and by years covering a period of 18 years, and include the number of men employed; number killed and fatality rates per 1,000 employed for each group of machine mines according to the foregoing classification.

The bituminous coal mines of the United States are treated independently of the anthracite so that fatality rates for the bituminous mines may be obtained.

Part II takes up the mine-accident question by States. Under each State is given a brief paragraph on the area and distribution of the coal fields; character of the coal beds; mining methods; reportable accidents and the organization of the inspection service. Data are given showing the production, number of men employed, number killed, number of machines in use in each State, and the percentage of coal mined by hand or shot off the solid, as well as the amount of coal mined per man, per day and per year. There is also under each State a list of the mine disasters that have occurred therein.—A. H. FAY.

### QUALITATIVE AND QUANTITATIVE ESTIMATION OF GUM ARABIC

The most characteristic qualitative test for gum arabic is the precipitate with basic lead acetate. Mixtures of copper

sulfate and caustic soda and of neutral ferric chloride and alcohol are of value as confirmatory tests. Basic lead acetate is conveniently made by the prolonged boiling of 40 g. crystallized lead acetate dissolved in 250 cc. water, with excess of litharge. The quantitative method adopted makes use of an alcoholic copper acetate-ammonia solution made up as follows: 50 g. copper acetate are dissolved in water, excess of ammonia added and the solution made up to 1000 cc., using water and alcohol in such proportions that the final solution contains 50 per cent alcohol. For each determination a 50-cc. portion of a gum arabic solution representing 0.25 g. of gum arabic was pipetted into a beaker, an equal volume of alcohol added and then 25 cc. of copper reagent, with constant stirring. The precipitate was allowed to settle, filtered on tared paper, washed with 50 per cent alcohol containing ammonia, then 70 per cent and finally 95 per cent alcohol. It was afterwards dried to constant weight at 105° C., ignited and the ash weighed. The amount of ash is deducted from the original weight and the difference called "net gum arabic." The amount of moisture in the gum originally must be allowed for; this is determined by drying in a current of hydrogen at 105° C. The method seems to give accurate results.—A. McMillan.

### ZINC ORES

The last two numbers of the *Bulletin of the Imperial Institute, London*, says the *Mining World*, contain an interesting paper on the known occurrences of zinc ores in all parts of the world. Although containing a good deal of information of a familiar character, the paper gives a good and complete account of all well-known sources of supply. Of special interest at the present time is the information in regard to the deposits within Germany itself and in adjacent countries from which Germany could, in future, draw supplies in the event of her being cut off from the mines in allied countries. The paper concludes with notes on the valuation and smelting of zinc ores and the chief products yielded.—M.

### MOTORS AND CAPSTAN CONTROL GEARS

The *Times Engineering Supplement* gives a résumé of the dimensions and other particulars of small-power motors for both continuous and single-phase alternating current from a list published by the British Thomson-Houston Company, of Rugby. The machines are made in two types. In one, standardized for 0.02 to 0.5 h. p., the continuous current motors are shunt wound up to 0.1 h. p., and compound wound up to 0.5 h. p.; and those for alternating current are of the split-phase, induction type with rotating field, the primary winding being placed on the rotor and connected direct to the line while the secondary winding is on the stator. The machines of the second type,

which are made in two forms, one for alternating and the other for direct current and are rated between  $\frac{1}{200}$  and  $\frac{1}{18}$  h. p., are designed with series characteristics and are suitable for cases in which the exact load to be connected is known. The same firm is also issuing a list describing control gears for electric capstans and winches which are designed to ensure that the motor is started up in the quickest time compatible with safety. The gear includes a pedal switch and an accelerating unit consisting of a series of contactors or electrically operated switches. The pedal switches, which do not carry the main current, but when depressed close the operating coil circuit of the first or shunt contactor, causing it to close and complete the motor circuit through the starting resistance, are made in two forms. One is intended for service in unexposed positions and the other for places where the switch is likely to be exposed to heavy rain or sea water or to be injured by vehicles passing over it. In the second form, the plunger passes through a water-tight gland and the pedal portion, when not in service, can be disengaged from the operating mechanism and dropped down flush with the ground. The switches are made in various capacities up to 25 h. p. and for circuits up to 550 volts.—M.

#### KIESELGUHR FROM AUSTRALIA

According to a report in the *Mining Journal*, there is at present a large demand in the United Kingdom for kieselguhr (infusorial earth) for use in the manufacture of dynamite, for metal cleaning and for sugar refining. The Imperial Institute, London, lately suggested to the Australian authorities that various samples of Australian diatomite should be forwarded for technical examination. Samples were sent from Victoria, New South Wales, Western Australia and Tasmania. Those from Victoria and New South Wales proved to be of most promising quality. In particular, samples from the Lilliecur deposits, northwest of Ballarat in Victoria, found special favor.—M.

#### EUROPEAN BEET-SUGAR PRODUCTION

According to an estimate of the European beet-sugar production for 1915-16, the total yield is put down at 5,190,387 tons. Germany is credited with 1,500,000 tons, Austria with 1,011,400 tons, France with 140,000 tons, Belgium with 100,000 tons, the Netherlands with 230,000 tons, and Russia with 1,588,872 tons.—M.

#### ELECTRICAL CHARGING-WAGONS FOR COKE OVENS

According to the *Journal of Gas Lighting and Water Supply*, an installation of electrically driven wagons for charging coke ovens has been applied to a battery of 60 coke ovens, which can be kept charged by one man instead of 10 or 12 by the old system. The coal bins are not in a direct line with the axis of the track over the charging hoppers but through small curves down to 5 meters radius. The charging-set comprises 3 wagons of 3 tons capacity each. Each wagon is 4 meters long by 1.2 meters wide and 1.7 meters high and is divided into two parts with the usual drop bottoms. Between the two hoppers is the driving motor of 4 k. w. capacity which, together with the starting and the other switch gear, is enclosed in a dustproof compartment. Power is taken from an overhead trolley wire and the motor is controlled by a lever. After the three wagons have been filled at the coal bins, they are sent along in succession under their own power towards the ovens, the operator following on the last. When the wagons reach the coke-oven platform, the motors are switched off automatically and breaks applied by means of stops projecting from the track. These stops are placed by the operator at the particular oven it is desired to charge. The wagons are brought into the correct position and emptied. The operator then sends them along to the coal bins on their own power, closes the top of the filled oven and arranges the stop at the next oven to be filled.—M.

#### NEW SOURCE OF POTASH

In a recent number of the *Journal of the Society of Chemical Industry*, Mr. R. H. Ellis gives the results of an analysis of banana stalks. It was found that the ash contained no less than 45.9 per cent potash while soda was practically absent. The dried matter of the stalk is as rich in potash as kainit. The author calculates from his analysis that one ton of banana stalks would yield 188 lbs. of dried material containing 13.7 per cent of potash [ $K_2O$ ] or 54 lbs. of ash containing 47.5 per cent or 25 lbs. of pure potash. If one considers the very large quantity of banana stalks at present classed as waste material, it is evident that municipal authorities should investigate whether this material could not be advantageously used as a source of potash.—M.

#### RESEARCH IN ILLUMINATING APPLIANCES

The Illuminating Engineering Society, London, says *Nature* (Vol. 97, No. 2429), has been considering the encouragement of researches of special utility at the present time and, at the annual meeting held recently, a report was submitted by the Committee on Research. A number of problems were mentioned and among these the following were included: researches in the quality of glassware required for illuminating purposes; the study of lighting appliances (globes, shades, reflectors, etc.); investigation of the conditions of illumination required for various industrial processes. Attention is also directed to the need for a series of standard colors of specified tints and reflecting value, the standardization of so-called artificial daylight, and the prescription of a standard method of testing the permanence of colors, all of which problems are of interest in relation to the dyeing and coloring trades. The list submitted includes some thirty sections and it would appear that the study of the subjects will afford work for many years to come.—M.

#### QUEENSLAND SHALE OIL

At last, says *Gas and Oil Power*, the shale beds in Western Australia are to be exploited. A first-class man and a modern plant have been secured from America so that the enterprise starts under good auspices. The derrick is the largest in Australia and is said to be better than any other oil derrick in the world. The cost of the experiment will be about \$100,000 and the bore is a state monopoly. Originally the Ronia bore, which was put down in search of oil or natural gas, was begun as long ago as 1907 but, after a depth of 3000 feet had been reached, it was found that the spot located was not the right one. The new bore is about half a mile from the original hole. It was begun in November last and put down some 300 to 400 feet when the official opening took place. The expert says that he expects to strike oil at about 4000 feet.—M.

#### RAMIE FIBRE EXPORTED FROM KUIKIANG

Ramie fiber, says a consular report, is produced chiefly in Hupeh province though some is grown in the province of Kiangsi, notably in the Juichang district. The first crop is cut at the end of June and between then and November, two other crops are taken from the same roots, one in July-August and another in October-November. The fiber is divided into three qualities according to its length: (1) 30 to 40 in.; (2) 20 to 30 in.; (3) below 20 in.; this latter is purchased by the Japanese. The fiber is tied up in bundles bound together by a rope of ramie. It receives no treatment except in sorting for length but shippers at Hankow and Shanghai use hydraulic presses for treating the fiber. Japan, Belgium and France are the principal consumers, and shipments are made by Chinese dealers on account of foreign firms. The quantity exported in 1914 amounted to 100,883 cwts., being 15,024 cwts. less than that exported in 1913. The falling off is attributed to diminished shipments owing to the outbreak of the war and the absence of German buyers for the European market.—M.



### PAPER PULP INDUSTRY

According to the *Paper Maker*, exhaustive trials of New Zealand timbers—mainly from the West Coast of the South Island—have recently been made and samples sent out of the Dominion to be tested by experts in Canada and elsewhere. These have satisfactorily proved that New Zealand timbers are eminently fitted for conversion into paper pulp and then into the paper used for newspapers. A company is about to be floated, which has secured the water rights of a large watershed as well as many thousands of acres of virgin bush covered with suitable timber, and much is looked for by experts from this new industry. Similar experiments on a substantial scale have been instituted by the Victorian (Australia) State Ministry regarding the production of wood pulp. The government printer uses, at least \$400,000 worth of paper annually and the demand for private consumption is also considerable. There is, then, ample opportunity for the opening up of a large industry if it can be shown that Australian woods can produce the raw material.—M.

### UTILIZATION OF WASTE PRODUCTS—IRON SLAGS

A fruitful direction, says *The Times Engineering Supplement*, in which national economy can be effected is the application of discarded refuse to industrial purposes. History affords numerous examples of the accumulation of enormous quantities of practically indestructible waste products forming unsightly heaps which scientific progress has ultimately shown to possess an intrinsic value. Among such collections are the great banks of slag produced in the manufacture of iron. Many unsuccessful attempts have been made to use up this slag in the manufacture of bricks, slabs, and cement but, at last, a practical method adopted in Germany for some years is being introduced and developed in England. A brick-making plant is working in full swing in South Wales and another one to utilize the slag banks in the neighborhood of Cleator Moor is being built. Again, the modern methods of road construction required to meet the demand of motor traffic have provided an increasing market for tar macadam for the manufacture of which broken slag is peculiarly suitable, and molded slag blocks are used both in Great Britain and in the United States in the construction of pavements.—M.

### RUSSIAN BENZOL PRODUCTION

According to the *Oil and Color Trade Journal*, the cessation of the importation of benzol from Germany and other countries and the pressure of the strong demand of the Russian chemical industry have increased the production of this article in Russia during the last year and a half. The quantity produced in 1915 was a little over 9647 long tons, against 806 for 1914 and 113 in 1913. At the beginning of the war in the Donetz basin, which was the chief and practically the only source of this product hitherto in Russia, only 3 installations with 358 coking furnaces out of 1,082 at work were provided with benzol-producing equipment. During the first year of the war new concerns gradually sprung up with benzol factories and, at the end of last year, there were over 1,200 furnaces fitted for production of benzol and about 800 more were under construction. The quantity produced, however, does not nearly supply the demand of the market, which grows with the increase of chemical industry. The quantity produced in 1915 does not correspond to the capacity of the Russian equipment, some elements being able to work only up to 60 per cent of their capacity through want of labor, fuel, etc. In the Kuznetz basin there are large reserves of coking coal, and furnaces are being built with benzol-producing equipment. It is, however, questionable whether the demand can be supplied even with these latter furnaces producing material at an early date.—M.

### DRY-POWDER FIRE EXTINGUISHERS

A committee was recently formed, says the *Journal of Gas Lighting and Water Supply*, one of the members of which was Dr. J. A. Harker, F.R.S., of the National Physical Laboratory, London, to conduct experiments to test the value of dry-powder fire extinguishers as compared with water and other first-aid appliances for extinguishing fires caused by bombs. The broad conclusions arrived at may be given from the report which has been issued. The substances tested were a particular form of dry-powder extinguisher, water and liquid extinceturs. In one case, a supplementary test was carried out with sand. It seemed that, while none of the agents employed had any material effect on the burning of the bomb itself, the spread of the fire caused was greatly limited and in some cases totally extinguished by the application of water whereas, after the application of the dry powder, the fire continued to burn and seemed to be checked only temporarily. Dry-powder extinguisher generally contains as its main constituent bicarbonate of soda, which on being heated gives off carbon dioxide but, according to the report, it is regarded as doubtful if the quantity produced is sufficient to have any material effect in the case of small fires. Water was found to be far more effective and it appeared that a given volume of water applied as a jet from an extincetur was more effective than the same amount applied in buckets. The application of sand was, weight for weight, found to be less effective than the dry powder. In view of the results, the committee are confident that by far the best extinguishing agent is a plentiful supply of water applied in the manner most convenient.—M.

### HIGH-EFFICIENCY LAMPS

The new high-efficiency gas-filled lamp introduces variables not hitherto encountered in the photometry of incandescent electric lamps. On account of the comparative broadness of the filament spiral and the dissymmetry of the filament mounting, says the *Engineer*, there is considerable irregularity in the distribution of the light about the vertical axis. Consequently, when the lamp is rotated, as is commonly done in rating lamps at the factory, the light as seen in the photometer flickers so excessively as to render accurate measurements of candle power practically impossible without the use of an auxiliary apparatus. However, as is sometimes done, if two mirrors inclined to each other be placed at the back of the lamp, the flickering is so much reduced as to permit accurate candle power measurements even at very low speeds of rotation.—M.

### OIL-PRODUCING NUTS AND SEEDS

The report of the committee on "edible and oil-producing nuts and seeds" of West Africa just issued affords, says *Nature*, an interesting glimpse of the way in which the British Government has changed its attitude towards science and industry since the war broke out. The exports of oil seeds from British West Africa in 1913 were valued at \$35,140,000 and of this Germany took no less than \$18,345,000 chiefly in the form of palm kernels, the crushing of which for oil and cake she had practically monopolized. With the outbreak of war, the West African exporters were deprived of their best customer and a new British industry in the crushing of palm kernels has been set on foot. The committee, which has issued the report, makes four recommendations with a view to keeping the industry in British hands and two of these are to be put into force immediately. The first is the imposition of an export duty of \$10 per ton on all palm kernels exported from West Africa to ports outside the British Empire; the second is a recommendation for further coöperation between the West African Branch of Agriculture and the Imperial Institute, London, with a view to continuing investigations on the palm oil.—M.

## SPANISH CHEMICAL AND COLOR IMPORTS

The *Oil and Color Trade Journal* gives the following figures for the imports in chemical and color materials into Spain for the years 1914 and 1915, the figures denoting quantities in metric tons:

	1915	1914
Alkaline carbonates, borates and silicates.....	3,213	2,022
Caustic soda and potash.....	135	53
Mineral manures, ammonium sulfate.....	123,353	100,277
Superphosphate of lime and slag.....	116,897	63,013
Indigo and cochineal.....	70	184
Dye extracts (vegetable).....	3,653	5,832
Colors, artificial, dry.....	1,221	339

—M.

## BORNEOL IN AMBER

In a paper read recently before the French Academy of Sciences, M. Reutter gives an account of his studies on several samples of amber. Of the samples examined, all were found to contain free borneol, the alcohol present in rosemary and spike lavender oils. The residue from ambers of Italian origin—one from Sicily, the other from Bologna—was found after extraction with ether and alcohol to be amorphous while that from German amber treated in the same way, was crystalline. Amber of Italian origin contains 1 to 16 per cent succinic acid whereas German amber contains 65 to 80 per cent of the same acid.—M.

## SICILIAN SULFUR PRODUCTION

The figures of the Sicilian Sulfur Consortium giving the production of sulfur for the month of February, 1916, which are the latest official statistics, show a marked decline in the output. Sales, on the other hand, exceed those of the previous year, thus producing a reduction in the stocks. The production for February was 16,865 metric tons as against 24,799 for the corresponding month of 1915, while shipments for the month were 53,023 tons as against 35,121 in 1915. There were marked increases in the exports this year to the following countries: France, Great Britain, Greece, Turkey, Spain, Portugal and South America. Stocks in hand at the end of February were 258,766 tons as against 365,330 tons last year, being the lowest for sulfur stocks in Sicily since the consortium took over the industry.—M.

## DETECTION OF CADMIUM

A 20 per cent solution of ammonium perchlorate in solution of ammonia of sp. gr. 0.90 is a sensitive reagent for cadmium which it precipitates as a white, crystalline double perchlorate of formula  $\text{Cd}(\text{ClO}_4)_2 \cdot 4\text{NH}_3$ . In applying the test to the mixed sulfides of Cu, Cd and Bi as precipitated in the 2nd group, the precipitate is dissolved in nitric acid and the solution treated with excess of ammonia. Bismuth hydrate is filtered off and the blue filtrate treated with the perchlorate reagent which precipitates the cadmium even when five times as much copper is present.—M.

## TRADE OPENINGS IN SOUTH CHINA

The British Consul at Kiung-chow (Hoi-how) reports that generally speaking the whole of the import business of Kiung-chow is done through importing firms in Hongkong, the center of supply for the South China market. Firms, therefore, who desire to place their products on the market and are not in a position to send out travelling agents of their own to push their sales direct, should endeavor to get into touch with importing firms in Hongkong through the Chamber of Commerce there or through the firm's own home offices. There is a good demand in South China for hardware, small lamps, fancy globes and cheap novelties of every description. The Germans have hitherto been very active in the following (among other) lines: sulfate of soda, brass electroplated lamp bowls, lamp glasses, burners, lamp frames (gilded), wicks, hanging lamps, imitation gold varnish, soaps (laundry and toilet) and plate glass (silvered and unsilvered).—M.

## INDIAN STATISTICS

Vol. I of agricultural statistics for India, 1913-14, which deals with British India, shows a noteworthy steadiness of agricultural operations during recent years. In the last decade, the total area cropped—the areas sown with rice, millets, wheat, sugar, cotton, jute and oil-seeds—suffered slight fluctuations. The cropped area, which has been irrigated and the area devoted to food-crops have both increased, the former by 30 per cent. In the whole of India 80 million acres are sown with rice—an area which is ten times the acreage of Japan. The area under wheat, which measures 29 million acres, is only exceeded by the wheat acreage of the United States, while that devoted to the production of cotton, *viz.*, 25 million acres, covers a space equal to about two-thirds the cotton area of the United States. About one-eighth of the India area is cropped more than once a year. The exceptions to the general increase found are indigo and opium, the area for the cultivation of which has declined by about one-half since 1909. Recently the area devoted to cinchona was increased by one-tenth, this increase being due to a great extension of the cultivation in Bengal, the acreage having declined in Madras, which is the other chief growing district. Nearly half of the sugar cane is produced in Agra where the area under cultivation is being increased. One-third of the cropped area in Madras and the United Provinces, one-half in the Punjab and three-fourths in the district of the Sind depend upon irrigation, canals, tanks or wells for their water supply.—M.

## BOARD OF TRADE

During the month of June, the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles. Firms which may be able to supply information regarding these things are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall St., London.

Aluminum plates for domestic use	Filters, wine, vacuum apparatus, similar to Seitz make
Asbestos pulp	GLASS AND GLASSWARE:
Asbestos, metallic yarn, three-ply	Amber disinfecting bottles
Asbestos sheets	Fruit preserving bottles
Balances, pocket, cheap	Square screw cap bottles
Balls, hollow or solid, in brass or copper, 1/2 in. to 5/8 in. in diameter	1-oz. bottles for boot cream
Boxes, tin, round, with mirror top	Gelatin, leaf, thin for process printing
Boxes, pill, cardboard	Handles, bone and metal, for shaving brushes
Brushes, tooth, xylonite, transparent	Hinges, cabinet, small, 1/4 in. to 1/2 in.
Candles in 1 lb. packets	Kapok
Cane pulp	Locks, small
Capsules, metallic	MACHINERY AND PLANT FOR:
Casein for glueing three-ply wood	Making condensed milk
Cases, cigarette, tortoise shell	Cutting corks
Casks for soft soap in 28-lb. and 56-lb. sizes	Making capsules
Catgut, raw	Making dominoes
Celluloid, bangles and rings	Extracting tapioca
Cement, white for manufacture of tiles and Mosaic	Making paraffin wax candles
CHEMICALS	Making ice
Acetic anhydride	Electrolytic production of hydro-gen
Alum	Dating and stamping cans
Arsenate of copper	Crushing seeds
Benzyl alcohol	Making buttons
Beta-naphthol-7-sulfonic acid	Refining oil
Borax	Ore, Caledonian, chrome
Calcium phosphate	Paper, carbon
Magnesium acetate	Paper, steel blue
Oxalic acid	Paper, tissue, pink
Sodium phosphate and permanganate	Ponade
Tetrachlorethane	Prussian blue
Triacetin	Rings, gas mantle, magnesia or fire-clay
White zinc oxide	Rivets, boot electro-brassed
China and earthenware cheap household goods; dinner, tea and toilet sets	Starch Dextrine
Cork dust	Tea
Cutlery Penknives	Tubing, voice, flexible, metallic, as used in steamships
Pocket knife	Tar, pine
Razors, ordinary	Twine
Drugs Saponine	Whole bone, thin
Dyes Aniline for soap, dark brown, nut brown, maroon, purple, dark green, navy blue, pink, leather stains	Willow
Electric apparatus, 2- and 3-cell flash lamp batteries	Wire ropes, east steel, flat, width, 90 x 100 mm, thickness, 18 x 16 mm, breaking strain, 55 tons

—M.



## SCIENTIFIC SOCIETIES

### A MASTER'S COURSE IN CHEMICAL ENGINEERING

By WILLIAM H. WALKER

The splendid new buildings of the Massachusetts Institute of Technology, located in Cambridge on the banks of the Charles River, were formally dedicated last month, and will be occupied at the opening of the school year next September. The greatly increased facilities for both instruction and research in all departments makes possible the execution of a number of plans for improvement which have been under consideration at the Institute for some time. Of these none is more important than a new Master's Course in Chemical Engineering, including a School of Chemical Engineering Practice, which is now fully organized.

It is unnecessary to rehearse to the readers of *THIS JOURNAL* the rapid rise, within the last decade, of Chemical Engineering as a profession. The curve of progress has turned even more sharply upward since the beginning of the European war, and the recognition of the importance of the chemically trained man in industry grows more generous every day.

The current journals are full of pertinent articles on the urgent necessity of preparedness—both military and industrial—and we need here but call attention to the fact that while the economic conditions which must obtain when the war is over are still unknown to us, there will under any condition be a most urgent call for men to maintain that place in the world's industry and commerce which the United States is now rapidly assuming.

To meet this demand there must be provided men of the broadest possible training. They must be well grounded in science, trained in the application of its principles to daily problems, have acquired engineering points of view and angles of approach, and have developed business perspective with relation to chemical industries. In short, there must be produced the *potential* chemical engineer. When a man has acquired a solid foundation in science, has become an accurate observer, an exact and logical thinker, and has developed a love for the application of this knowledge to the investigation and solution of the many problems which industrial practice presents, he has done marvelously well; but he still lacks much that goes to make the successful chemical engineer.

While it is true that the resourcefulness in applying theory to practice, the training in the solution of industrial problems, the general business perspective and self-reliance, which in time complete the man's education and make him a *creative* engineer is obtained in its entirety only by years of experience, there is much which other engineering branches have accomplished to render more quickly available the scientific education of the embryonic engineer. Without well-equipped mechanical and electrical laboratories it would be a long and difficult step to pass from the small apparatus and light load of a physics laboratory to the heavy responsibilities of a power plant. But in operating and testing the commercial-sized units with which mechanical engineering laboratories are easily equipped, a measure of self-confidence and an appreciation of responsibility are obtained not otherwise possible. In addition to all this the student translates for himself the fundamental principles of physics as exemplified in the laboratory into the application of these same principles in units and processes of commercial size and value.

But analogous facilities have never been available for instruction in Chemical Engineering. The important and oft-times controlling difficulties inherent in carrying on a chemical process on a manufacturing scale, are not present when this same process is conducted in a chemical laboratory. To

duplicate the apparatus which has been designed and built for factory operation is possible, and in many cases well worth while. But in order to study its performance the apparatus must be operated—a process for which it was designed must be carried out. This procedure is obviously expensive and at best limited in its scope. A student cannot acquire the self-reliance necessary to operate a high pressure digester holding 25,000 gallons of acid by experimenting upon one of a few liters capacity. He cannot learn how to meet difficulties incident to handling a filter press, an electric furnace, a multiple-effect evaporator, a rotary kiln, and so on, if he has access only to such apparatus as the laboratory can provide. That experience which means power to execute comes only from contact with commercial-sized apparatus operating under the conditions imposed by practice.

Neither can the student obtain that training in the application of the principles of science to the problems of chemical industry on which successful industrial research so largely depends, without an opportunity to live with chemical processes which are being conducted on a large scale. It is true that the research chemist must be able to visualize the hitherto unaccomplished fact, but, on the other hand, the undreamed accomplishments of the future, while using methods and equipment now unrealized, will also undoubtedly, to a large extent, employ the apparatus and the processes of to-day, although along new and varied lines. A familiarity with what does and does not succeed in present practice is the best foundation for that soundness of judgment so essential in every research worker, and most especially in those who are to direct and guide the activities of our industrial research laboratories.

In view of the difficulty of developing the type of engineer outlined without greater breadth of method and of contact than is possible in our educational institutions alone, it is generally recognized that the industries themselves have a duty to perform in this regard, and that without their coöperation educational accomplishment must remain imperfect. On the other hand, no satisfactory scheme involving industrial coöperation with educational institutions has hitherto been proposed, and the conception and inauguration of such a scheme cannot but represent an educational advance of the first order. Within the last few years a comprehensive plan of great promise for the more adequate training of chemical engineers along these lines has been originated and developed by Mr. Arthur D. Little, a member of the Corporation of the Institute of Technology, and chairman of the Visiting Committee for the Department of Chemistry. The plan has been enthusiastically adopted, and is based upon the idea of a close coöperation between the Institute and certain selected manufacturing organizations in representative industries. It involves radical changes in the Institute curriculum for chemical engineering, and the location of a part of the Institute's instructional activity in the manufacturer's plant. As Mr. Little points out in his report to the Corporation of the Institute, "any chemical process on whatever scale conducted, may be resolved into a coordinated series of what may be termed 'unit-actions,' as pulverizing, mixing, heating, roasting, absorbing, condensing, lixiviating, precipitating, crystallizing, filtering, dissolving, electrolyzing, and so on. The principles underlying each of these unit-actions are the same, however different the materials operated upon may be. Thus in a gas absorbing system, the laws of counter-current absorption which control the action of an ammonia scrubber do not differ from those involved in making sulfite digester acid. The number of these basic unit operations is not very large and relatively few of them are involved in any



NEW BUILDINGS OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY

particular process. The complexity of chemical engineering results from the variety of conditions as to temperature, pressure, concentration, etc., under which the unit-actions must be carried out in different processes, and from the limitations, as to materials of construction and design of apparatus, imposed by the physical and chemical character of the reacting substances. It is possible to so select a relatively few industries that there will be represented by them all of the important unit-actions of chemical industry."

Experience has shown that when proper provision is made, the performance of a piece of apparatus may be studied without materially interfering with its output. Thus the principles of multiple-effect evaporation or of countercurrent lixiviation can best be understood by making properly designed tests upon a working plant involving these unit-actions. In other words, it is possible, under careful regulation, to use a manufacturing plant as a chemical engineering laboratory, and not cut down its production or influence adversely the quality of product. Some of the advantages of such a method of engineering practice over a laboratory equipped only for instruction, are:

1—A first-hand knowledge of the machines with which the plant is equipped, operating under conditions imposed by practice, the processes involved being considered as unit-actions; the factors which control their efficient performance; and a general knowledge of the cost of chemical apparatus in its relation to cost of installation and operation.

2—A study of the unit operations of the plant and the process which is being carried on, as examples of the application of the principles of science to industry; their interpretation in terms of physics, chemistry and mechanics.

3—A general knowledge of modern methods of factory management and control, obtaining thereby some familiarity with the problems presented by the human element in industry.

4—The education which comes from taking part in the work of the plant; in acquiring some degree of self-confidence in handling industrial processes and large sized apparatus.

To carry into execution Mr. Little's idea, a School of Chemical Engineering Practice has been organized, which will increase in scope as experience is acquired. For the present it consists of five Stations selected to furnish opportunity in specific fields of broadest general importance in Chemical Engineering. Each station will include a small instructional laboratory, drafting room, and conference room and will be provided with a projection lantern, such special library, drawings, and models as may be needed. It will be in charge of a director, who will be a member of the Institute faculty.

STATION A—Located with the Eastern Manufacturing Company, Bangor, Maine. Here will be studied:

(1)—That most important application of the principles of electrochemistry to reactions taking place in solution, namely, the decomposition of common salt, with the formation of hydro-

gen, caustic soda and chlorine. The unit operations here available for study are electrolysis, multiple-effect evaporation with separation of a crystalline precipitate, caustic soda purification and concentration; absorption of gas of low partial pressure; agitation of both heavy and light liquids; and sedimentation of sludge.

(2)—The manufacture of bleached spruce pulp by the sulfite process. This is a high pressure-temperature reaction under careful analytical control, which involves most interesting equilibria.

(3)—The manufacture of poplar pulp by the soda process. In this process a study of the losses of soda through the cycle of operations is a most instructive one. It involves precipitation, sedimentation, filter press separation, systematic lixiviation and washing, and a determination of the soda lost in furnace flue gases by the Cottrell electrostatic separation principle.

(4)—The boiling, bleaching, and beating of rags for paper stock, and the manufacture of bond and ledger paper. This is both beater and tub sized, and is partly drum and partly loft dried. The opportunities for chemical engineering study here are obvious.

STATION B—Located at Everett, Mass., with the New England Gas and Coke Company. Without going into detail, the opportunities here offered are readily appreciated. The Company operates large by-product coke ovens and water-gas plants, with all the apparatus incident to the recovery of naphthalene, benzol, toluol, tar, ammonia, etc. Every opportunity is here presented to study those high temperature reactions of hydrogen with various hydrocarbons which have become so important in recent years.

STATION C—Located at Niagara Falls with the Carborundum Company. High temperature electrochemistry is here represented in all its phases. Powerful electrical furnaces of both the resistance and arc types are in operation making a variety of products. The apparatus for pulverizing, with accurate separation, is here seen at its best, systems of sieving and screening, hydraulic classifying, and pneumatic separation being in constant operation.

STATION D—Located at Stamford, Conn., with the American Synthetic Color Company. At this plant will be studied the chemical engineering of organic chemistry. Fractional distillation, sulfonation, alkali fusion, nitration, reduction, crystallization, with all the necessary apparatus, are but a few of the operations here available.

STATION E—Located near Allentown, Pa., with the Atlas Portland Cement Company. Large scale operations involving crushing and grinding in many types of machines are here offered. The chemistry of combustion and furnace control is nowhere studied to better advantage than in the mammoth kilns of this plant.

To obtain the greatest good from such splendid opportunities it is clear that this school must be a part of a consecutive and



consistent course of study. Not only must an adequate scientific foundation be laid before undertaking this Chemical Engineering Practice, but provision must be made for taking advantage of the directness of purpose and enthusiasm for further scientific study which the factory work will create. This is accomplished by providing a Master's Course in Chemical Engineering of five years' duration, including the entire summer between the fourth and fifth years. The first three years are identical with those of the four-year Bachelor's Course in Chemical Engineering as now offered at the Institute. At the end of the third year the student will elect either to finish the regular course of four years, receiving therefor the Bachelor's degree, or to spend two years and the intervening summer in study and receive both the Bachelor's and Master's degrees. From those students who elect this Master's Course, including the School of Chemical Engineering Practice, the faculty will select those whose attainments and character, as shown by their previous record of scholarship and by other information, are such as to indicate that the course can be creditably pursued.

At the middle of the fourth year the men so selected will be divided into five groups, and one group sent to each of the five stations for a period of six weeks. (Experience may prove that this is too short a time to accomplish the greatest good.) At the end of each six-week interval the groups will change stations, so that by September 1st each group will have occupied each station. After from three to four weeks' vacation these men will all return to the Institute for the fifth year of advanced work—graduating the following June. It must be kept in mind that the students going out into these industries do not go as employees of the industry, but as students in the School of Chemical Engineering Practice. It is intended that the work in the plant shall be wholly educational, and the men are to be under the control and direction, not of the plant organization, but of the director of the station—a member of the educational staff of the Institute. While it is intended to give the men as much industrial experience as possible, having them take shifts in the ordinary routine of the factory, such work will be directed throughout to secure the maximum educational result, and the interpretation of the experiences and results of work in the plant will be accomplished by conference and drawing room exercises which will take up no small fraction of the time spent in each station. It is expected in this way to avoid the weakness and inefficiency of previous schemes of cooperation by making no attempt whatever to have the student an economic asset to the industry, but planning his whole activity for its educational return to the student himself. An educational feature of great potential value to the industries which we shall hope to develop at these stations, and for which their equipment will be especially well adapted, is a type of extension course for the benefit of the foremen and selected employees. In these courses will be taken up the theory of the processes employed, and a study of the plant from the point of view of current practice in analogous industries. It is believed that these courses will react for greater efficiency not only among the employees, but the students making up the school.

To secure this high educational efficiency from the contact of the student with the industry, it will be noted that the student has completed substantially the equivalent of a four years' course in Chemical Engineering before entering the School of Practice. This will make possible the full appreciation of the significance of every fact and the interpretation of every experience in the light of fundamental principles.

The work of the fifth year is advanced in character, broad in scope, and almost wholly elective, the purpose being to take advantage of the students' enthusiasm and to allow him to specialize in the line in which he has found by experience that he has the greatest aptitude and interest.

But the plan is a cooperative one, and while it is confidently expected that in the work carried on by these students entirely for its educational value, there will result an accumulation of data, much of which will be of service to the industry concerned, yet this prospective return is not figured as an asset of the plan. As a return for the use of the factory as a chemical engineering laboratory the Institute proposes to establish and direct for each Company concerned, a research organization devoted entirely to the solution of its individual problems. While a laboratory will be maintained at each station, the extensive research facilities of the Institute will be available for work of a special character, and the faculty of the Institute will function as a Consulting Staff.

The earning power of industrial research is now too firmly established to require any argument to demonstrate the possibilities for cooperative service which the plan possesses. It is earnestly hoped that in it may be found an effective method by which science may be more closely linked to industry, for the lasting benefit of both.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY.  
BOSTON, July, 1916

### FIFTY-THIRD (ANNUAL) MEETING AMERICAN CHEMICAL SOCIETY, NEW YORK CITY, SEPTEMBER 25 TO 30, 1916

A meeting of the American Chemical Society will be held in conjunction with the Second National Exposition of Chemical Industries, September 25 to 30, inclusive. A Council meeting is called for Monday afternoon and Monday evening. A general meeting follows on Tuesday morning, and on Tuesday afternoon it is hoped to have a public meeting in the large hall at the City College, with addresses by the President of the Society and by prominent men bearing upon "Chemistry and the National Welfare." On Tuesday evening a general "get-together" meeting or smoker will be held by the New York Section, complimentary to the parent Society, to which visiting chemists will be invited. On Thursday evening the Electrochemical Society will give a smoker, to which the members of the American Chemical Society will be invited, and on Friday evening a subscription banquet will be held in one of New York's large hotels.

Meetings of Divisions will be held on Wednesday, Thursday, Friday and Saturday mornings.

One of the special features of the meeting will be general conferences on special subjects in which the chemists of the country are now interested. The idea of these conferences is to have some important topics such as:

Glassware and Porcelain	Oils and Motor Fuels
Steel Alloy Metals	Convertibility of Plant
Paper and Its Utilization	Medicinal Chemicals
Dyestuffs and Their Relation to	Munition Factories
Industrial Alcohol, Acetone and Formic Acid	

The discussions will be started by well-known specialists in these lines. No set program is planned for these conferences, but it is believed from past experience that chemists interested in these various lines will get together, and many interesting points will be brought out which will be of mutual interest. The topics for these conferences have not as yet been determined upon, and suggestions are desired from members of the Society. These suggestions will all be placed before the Program Committee, and some six or eight topics selected therefrom. It is anticipated that two conferences will be in session each afternoon at the same time, one in the lecture hall of the Grand Central Palace, where the Second National Exposition of Chemical Industries will be held, and one in the lecture hall of the Chemists' Club.

The Divisions of Biological Chemistry, Physical Chemistry, and Industrial Chemistry will hold a joint symposium on colloids on Wednesday and Thursday mornings. On Wednesday morning the symposium will be of a theoretical nature, in which

the Industrial Division will not take part. On Thursday morning the symposium will be composed of industrial applications of colloid chemistry. A symposium on occupational diseases is also planned and is to take up part of one of the morning sessions of the Industrial Division.

### REVISION OF OUR CHEMICAL STATISTICS

By BERNHARD C. HESSE

In THIS JOURNAL, 7 (1915), 58, it has been pointed out that our chemical statistics need revision; a general plan or outline of plan thereof was then presented. At the Seattle Meeting of the American Chemical Society in September, 1915, a committee was appointed to devise some practical and practicable way of obtaining such revision and of putting it into useful and serviceable effect. The organization of that committee was not completed until June, 1916. The reason for this delay is that service upon this committee entails a large amount of very difficult and most tedious labor, and men hesitate to assume such added responsibilities. Successful execution of this plan calls for coöperative thinking and planning on the part of all members of the A. C. S., of all our other technical and chemical societies and associations, and of all those engaged in chemical pursuits of any industrial or commercial aspect in this country.

Inspection of the lists of European countries for the past twenty years, so far as they relate to chemicals and allied materials, shows that these lists have been very greatly expanded and indeed much more so than our own.

In general, each European country seems to arrange its list with a view of telling its own people the most about other peoples and of telling other peoples as little about their respective affairs as is convenient, particularly in those items which are capable of high diversification. For example, the German list divides 120,000 short tons or \$54,250,000 (= 21.5 c. per lb.) of coal-tar dyes into 4 items only; photographic chemicals totaling 3,080 short tons or \$2,000,000 (= 32.5 c. per lb.) are lumped into one item, and 1,320 short tons or \$5,300,000 (= \$2.00 per lb.) synthetic pharmaceuticals also take up but one item. These 6 items total 124,400 short tons or \$61,550,000 and average \$495 per ton (= 24.7 c. per lb.) and cover fully 1800 different articles of manufacture, only few of them closely related; 123 short tons of various alkaloids and their salts of a total value of \$1,750,000 or \$14,220 per ton (= \$7.11 per lb.) make up one export item.

On the other hand, Switzerland, in its lists, is more diversified as to its imports from Germany than Germany is in its list of exports to Switzerland; in fact, Switzerland seems to enter and report trade-marked or proprietary synthetics and the like as such; our own lists do this in isolated cases only.

German statistics for the calendar year are published within the first 5 weeks of the succeeding year; our own reports are two or three months later.

On its face, it seems plausible that if we are now to diversify our domestic chemical industry rapidly and with the fewest false steps and commercial or industrial calamities, we should be advised in some authoritative manner as to the nature of our domestic market as it is now and may develop to be in the future. If under these conditions we do not properly develop our markets and our domestic manufacture we at least cannot reasonably raise the defense that we did not do better because we had no way of determining what our country's needs were and therefore could not intelligently plan our independence from foreign supply-sources. I am encouraged in a belief in this utility and benefit by the rather large number of inquiries that have been made of me personally, orally and by letter, within the past 20 months, for information as to the domestic

consumption of this, that or the other imported article and in only the fewest instances have I been able to dig up an answer that filled the bill. It seems to me that there can be no debate on the general proposition that the more we know about our market requirements the more likely are we to build up a domestic industry. Add to this the fact that at comparatively little added expense our Federal Government, through one or more of its Departments, can gather and promptly publish such added information, and it seems to me to be conclusive that the chemists of this country should get together, make up a list of such specific added items concerning which they need information and indicate such further diversifications of items as promise to them the greatest help in the future. We can rest assured that the number of different chemical materials and products that this country will use and continue to use will be not at all diminished in the future but, quite on the contrary, will be greatly and very likely rapidly increased. The longer we put off such diversification of our lists the harder the task of future diversification will become; it will certainly not become any easier. Such a request for added information has nothing in common with asking for a subsidy or a bonus or added tariff protection; it is simply a request to be better informed as to the requirements of the public so that we may more intelligently work towards our nation's industrial independence of foreign supply-sources; in so helping us the public will be helping itself.

In presenting to the proper authorities a request for added information we must make as reasonably sure as possible that whatever is presented is not half-baked but is as mature as circumstances and conditions will permit, that it meets with and embodies the views of the great majority of those likely to be affected by this information and that there is a reasonable stability to the list; such request should be in as definite, final form as possible.

Clearly, the constructing of such a request is by no means whatever the duty of any one man or of any small group of men; it is a duty in which every person in the country engaged in the making, selling and distributing of articles of this class fully shares; in fact it is everybody's business. The committee of the American Chemical Society can act merely as a clearing-house for requests and then put them into a form that will be likely to receive the sympathetic attention and enlist the active coöperation of the officials who must supervise the details of gathering and publishing such material.

As Chairman of this special committee of the American Chemical Society, I have prepared a consolidated list (List I) of articles used or produced in or by chemical industries as they appear in the most diversified commercial reports of Austria, France, Germany, Great Britain, Italy, Sweden and Switzerland; italicized entries are to be found in the most diversified U. S. lists; black entries are additional items in our own U. S. lists as given in *Monthly Summary of Foreign Commerce of the United States* and *Quarterly Statement of imported merchandise entered for consumption in the United States*. In noting these entries it must be remembered that not all those entries appear separately; in many cases they are separated, but in the majority of cases they are lumped in with a large number of other items and segregation into values is not feasible and generally impossible; this is also true of List III.

In working with List I it must be borne in mind that in few cases only has any alphabetical arrangement been attempted for the reason that in the original lists little or no regard to alphabetical arrangement is had; the items seem to be arranged according to some commercial connection, real or assumed, between the various items. Further, that extreme niceties as to logic of classification cannot be considered by those who, in the final event, must gather the information; that repetition must be avoided and no material can be reported more than once.



LIST 1 ARTICLES PRODUCED IN OR BY CHEMICAL INDUSTRIES TAKEN FROM MOST DIVERSIFIED LISTS ISSUED EUROPEAN (ROMAN TYPE). IMPORTED MERCHANDISE ENTERED FOR

I.—MAKET, OIL, FRUITS, INDUSTRIAL PLANTS, FRUIT & PLANT JUICES  
 Beans, soja, vanilla  
 Malt, excl. malt & ground  
*Rapeseed*  
 Castor beans  
 Poppy & sunflower  
 Linseed & meal  
 Cocoa, crude  
 Palm kernels  
 Licorice root  
 Kopra  
 Hemp seed  
 Hops  
 Madroerroot, Quercitron & other dye plants  
 Sugar-beet-seed  
 Opium  
 Strychnine & its salts  
 Kino  
 Aloe & other fruit & plant juices

II.—VEGETABLE PRODUCTS FOR INDUSTRIAL OR MEDICINAL USES  
 Cinchona bark  
 Rhubarb root  
 Gentian root  
 Chocolate  
 Curcuma  
 Cudbear  
 Caraway, Iceland moss & other crude lichens; Tamarinds, stick-cinnamon;  
 flowers, etc., for medicinal uses.  
 Insect powder & flowers  
 Tea for caffeine  
 Vegetable waxes in natural state  
 Wood for wood pulp, etc.  
 Wood charcoal & powder, charcoal briquettes  
 Wood, flour & excelsior  
 Roots for distillation. Roots for medicinal use

III.—DYEWOODS & TANNING MATERIALS  
 Logwood  
 Fustic, Brazil wood  
 Cam-wood  
 Orchil  
 Ground or fermented dyewoods, Quebracho & other woods, in blocks; ground  
 Algarobilla, Dividivi & other n. s. p. f.  
 Valonia  
 Nutgalls  
 Myrabolans  
 Sumach  
 Catechu (brown & yellow) Gambier (crude or refined)  
 Oak bark  
 Coniferous barks  
 Mimosa, mangrove, maleito & other tan-barks  
 Oak, pine & chestnut-extracts  
 Nutgall extract  
 Quebracho-extract  
 Sumach-extract  
 All other tanning extracts

IV.—RESINS, LAKES, VARNISHES & PUTTIES  
 Lakes, dry or pulp  
 Turpentine resins  
 Kauri & other copals  
 Damar, akaroid & other resins, oilbanum & other soft resins; gum-resins  
 Gum-lac  
 Gum, chicle  
 Guayule  
 Shell-lac  
 Acacia, ocajon, cherry, cutera & bassora-gums  
 Extract Persian berries  
 Tragacanth  
 Scammony  
 Oil varnishes, Bird-lime ex linseed oil  
 Spirit varnishes, Shellac-putty  
 Lacquers (non-spirit) asphalt varnishes, coach varnishes  
 Sealing waxes  
 Putty & putties n. s. p. f.  
 Asbestos paints, asbestos pigments, asbestos putty

V.—CAOUTCHOUC & CAMPHOR  
 Caoutchouc, crude or refined  
 Gutta percha, crude or refined  
 Balata, crude or refined  
 Insulating compound  
 Rubber, scrap or waste  
 Caoutchouc substitutes  
 Camphor & manna

VI.—ANIMAL & VEGETABLE FATS & OILS  
 Hog lard  
 Lard, neutral compounds & substitutes  
 Oleomargarine  
 Goose-fat, beef marrow, etc.  
 Grease: enflourage, soluble

Prime beef tallow  
 Beef & mutton tallow  
 Lard, fat, waste, stearin pitch  
 Fish, whale & seal oil  
 Fats, etc., from fish, whale & seal  
 Horse fat, deer tallow, etc.  
 Rape oil  
 Colzae oil  
 Linseed oil  
 Peanut oil  
 Sesame oil  
 Olive oil  
 Lavat & sulfur oil  
 Cottonseed oil  
 Wood tar oils  
 Castor oil

OIL: Almonds (sweet)  
 Birch tar  
 Cajuput  
 Chinese nut  
 Cinnamon  
 Citronella  
 Cod  
 Cod liver  
 Eucalyptus  
 Hempseed  
 Origanum (red & white)  
 Poppyseed  
 Beech, bone, corn, poppy, sunflower and other fatty oils  
 Fat-salt in tins, bottles, etc.  
 Cocoa butter  
 Cottonseed stearin  
 Palm oil (palm butter, -fat, etc.)  
 Palmkernel oil & fat  
 Coprae oil, fat & tallow  
 Vegetable tallow  
 Vegetable ivory  
 Olein  
 Margarine  
 Edible vegetable tallow  
 Ole. Cakes: Corn  
 Cottonseed  
 Cotton & linseed  
 Mustard  
 Peanut  
 Rapeseed  
 Soya bean  
 Oil cake meal  
 Oleostearine

VII.—ANIMAL PRODUCTS  
 Extract, meat  
 Egg-yolk  
 Egg-albumen  
 Bees & other insect waxes, honeycombs  
 Gelatine  
 Spermaceti  
 Fish glue, agar-agar  
 Glue  
 Glue-size  
 Glue-waste  
 Bones, horns, hoofs, etc., not for cutting purposes  
 Horn-waste for fertilizer  
 Galalith  
 Oil cloth  
 Linoleum  
 Bone & other animal blacks; bone-ash  
 Dried blood

VIII.—STARCH, SUGAR  
 Potato starch green or dry  
 Rice starch  
 Corn, wheat & other starches  
 Starch gums, dextrins, burnt starch, paste, adhesives & gluten-meal  
 Beet sugar  
 BEET-SUGAR: Flats, sticks & cubes  
 Ground & lump  
 Ground refined  
 Loaf & brown  
 Confectioners'  
 Raw, solid or liquid  
 Cane sugar  
 Cane sugar, raw, solid or liquid  
 All other solid & liquid sugars  
 Sugar (cane & beet) tank bottoms, syrups, etc., up to 1000  
 Sirups & molasses  
 Glucose (syrup)  
 Starch, fruit & other fermentable sugars, burnt sugar  
 Caramel, solid & liquid  
 Grape sugar  
 Invert sugar  
 Maple, sugar & syrup  
 Milk sugar

IX.—ALCOHOL, VINEGAR, YEAST & MINERAL WATER  
 Alcohol, in barrels  
 Alcohol in bottles  
 Vinegar of all kinds  
 Methylated spirits  
 Wine yeast  
 All other yeasts  
 Mineral waters, artificial, etc., incl., bottles

X.—MINERAL & FOSSIL RAW MATERIALS  
 Alumin  
 Clay, common, pottery, fire & pipe  
 Kaolin & china clay  
 Burnt clay, chamotte, Fayence etc  
 Yellow, ochre, bole, Sienna & Verona earths  
 Other earth-colors, artificial oxide iron, crude  
 Chalk, white, crude  
 Purified  
 Graphite, crude, ground & washed  
 Pumice, Traptid, crude, ground, washed or in bricks or tile  
 Emery, crude, ground or washed  
 Mineral abrasive, polishes, & cleansers, crude, ground, or washed  
 Enamels & glazes  
 Kieselguhr, quartz-sand, fire-stones  
 Lime, slaked, limestone or lime mortar  
 Magnesia  
 Magnesite, native or burnt  
 Witherite, native or burnt, strontianite  
 Lime phosphates (Apatite, phosphorite, coprolite, etc.)  
 Gypsum; gypsum-superphosphate  
 Puzzolan, etc.  
 Portland & Roman cements  
 Gypsum cement  
 Keene's cement  
 Ground lime; tripolith  
 Asbestos, crude  
 Venetian chalk, crude, ground or burnt  
 Talc, crude, ground or burnt  
 Mica, crude  
 Barytes & Celestite  
 Feldspar, ordinary  
 Fluorspar, crude; Cryolite, natural  
 Boracalite & Tincal  
 Monazite-sand  
 Mantles (gas, oil, etc.)  
 Fuller's & other earths & bituminous shale

XI.—ORES, IRON, SLACS  
 Antimony ore & matte  
 Antimony regulus  
 Arsenic ores  
 Bauxite, concentrates  
 Lead-ores  
 Cerium-ore  
 Chrome-ores  
 Cobalt-ore  
 Iron-ores  
 Gold-ores  
 Corundum  
 Copper-ores inclusive of pyrites cinders  
 Copper regulus  
 Kainite  
 Kieserite  
 Manganese-ores  
 Nickel-ores  
 Platinum-ores  
 Pyrites (Pyrrhotite, marcasite, etc.)  
 Silver-ores  
 Tungsten ores  
 Zinc-ores  
 Zinc sulfide  
 Tin-ores  
 Uranium, molybdenum & other ores n. s. p. f.  
 Uranium oxide  
 Gas-purifying masses containing iron or manganese; slags, slag felts, slag wools; ferrocyanide, sludge; ashes, pyrites-cinder, etc.

XII.—FOSSIL FUELS  
 Anthracite, bituminous & cannel coal  
 Lignite  
 Peat, peat-coke & peat fuels  
 Coke  
 Coal-briquettes  
 Culum  
 Lignite-briquettes  
 Coke-like residues & artificial fuels  
 Carbon electrodes  
 Incandescent lamps, carbon or metal filament  
 Carbons, formed & crude; vegetable carbon

XIII.—MINERAL OILS & OTHER FOSSIL RAW MATERIALS  
 Asphaltum & bitumen  
 Lubricating & vaseline oils  
 Crude petroleum; pitch & natural liquid asphalt  
 Heavy gasolines, turpentine substitutes

Gas oils  
 Dead oils  
 Refined petroleum  
 Crude gasoline  
 Benzene, gasoline, ligrom, petroleum ether & similar refined light-oils  
 Lignite, peat and shale-oils & other not otherwise specified mineral oils, tars & pitches  
 Paraffin, crude & refined  
 Soft paraffin  
 Solid asphalt & asphalt bricks  
 Asphalt mastic, pitch, resin & wood cement  
 Ozocerite & mountain-pitches, crude  
 Refined ozocerite, ceresin  
 Pitch & black wax  
 Pitch-like petroleum residues heavier than water  
 Marine glue pitch  
 Shale-pitch; lignite tar, peat tar, wood tar, birch tar  
 Oil & water-gas tar  
 Gas liquor

XIV.—COAL TAR OILS & PRODUCTS  
 Coal tar  
 Carbolineum  
 Coal tar pitch  
 Benzol, toluol, cumol, etc.  
 Anthracene, carbolic, cresole & other heavy coal-tar oils & asphalt-naphtha  
 Solvent-naphtha  
 Naphthalene  
 Anthracene  
 Phenol, crude or refined  
 Lime carbolate  
 Pyridine bases  
 Cresol, crude carbolic, 100 per cent  
 Arsenic  
 Anilin; Oil & salts  
 Dimethylanilin  
 Benzyl chloride  
 Naphthol, naphthylamin  
 Naphthol compounds  
 Anthraquinone, nitrato benzol, ioluidin, resorcin, phthalic acid & other coal-tar products

XV.—WAXES  
 Prepared bees, & other insect waxes  
 Prepared vegetable waxes; vegetable wax waste

XVI.—SOAPS AND FAT PRODUCTS  
 Ordinary soft soap; oils & fluid fats, Turkey-red oil; liquid Creolin & like cleansers; soap substitutes in barrels  
 Hard soaps; Creolin & like hard cleansers; soap substitutes & evaporated lyes not elsewhere specified  
 Cake soaps; liquid soaps, soap powders, papers & other soap substitutes  
 Soap: Castile  
 Medicinal  
 Toilet, perfumed  
 Toilet, unperfumed  
 Stearin, palmitin  
 Tapers, candles & night-lights  
 Phonograph plates & rolls of wax or ceresin  
 Crude glycerin  
 Refined glycerin  
 Soap waste lyes  
 Paraffin ointment, vaseline, vaseline ointment, lanolin & lanolin preparations  
 Rosin-soaps  
 Washing powder & fluid  
 Degreaser  
 Axle-grease  
 Other lubricants made from fats or oils  
 Shoeblackening, solid  
 Yellow shoe polish  
 Polishes made of fats, oils, soaps; alumina soap, artificial polishes  
 Stearin, palmitin, etc., formed

XVII.—CHEMICAL & PHARMACEUTICAL PRODUCTS  
 Abram salts:  
 12-15 per cent K<sub>2</sub>O  
 More than 15-19 per cent K<sub>2</sub>O  
 Abram salts n. s. p. f.  
 Actanilid  
 Acetates, all other n. s. p. f.  
 Acetone oil  
 Acetphenidine  
 ACID:  
 Acetic  
 Acetylsalicylic  
 Arsenic  
 Arsenious  
 Benzoic & sodium benzoate  
 Boric  
 Chlorsulfonic

U. S. (ITALICS); ADDITIONALS CONTAINED IN "MONTHLY SUMMARY OF FOREIGN COMMERCE OF THE UNITED STATES" AND "QUARTERLY STATEMENT OF CONSUMPTION IN THE UNITED STATES" (BLACK)

## ACID (Continued):

**Chromic**  
*Citric*  
*Formic*  
**Glycerophosphoric**  
*Hydrochloric* (nitrohydrochloric)  
*Hydrofluoric*  
*Lactic*  
*Nitric*  
*Oxalic*  
*Phosphoric*  
**Prussic**  
**Pyrogallic**  
*Salicylic* & sodium salicylate  
*Sulfuric*  
Non-fuming  
Fuming  
For fertilizers  
Spent  
*Tannic* & gallic  
*Tartaric*  
**Valerianic**  
Acid, Anhydrides  
*Acetic*  
Sulfuric  
Alkali & other metals not specified  
Alkaloids, all other, their salts & compounds  
**ALUM:** soda, potash or ammonia chrome, iron or copper  
**ALUMINUM:** Acetate  
Chloride  
Hydrate, artificial  
Oxide, artificial  
Sulfate  
Sulfite  
Sulfocyanide  
Ammonia water  
**AMMONIUM:** Carbonate  
Chloride  
Fluoride  
Nitrate  
Perchlorate  
Persulfate  
Phosphate  
Sulfate  
**Amyl acetate**  
nitrite  
Anilin compounds, not dyes  
**ANTIMONY:** Fluoride  
Oxalate  
Regulus or metal  
All other compounds  
n. s. p. f.  
**Antipyrrene**  
**Antitoxins**  
*Arc carbons*  
*Argols, crude or refined* (soda or potash)  
Artificial & natural mineral water salts  
Artificial balsams, extracts & waters, not perfumes  
**ARSENIC:** Metal  
Sulfide  
Compounds, all other  
n. s. p. f.  
**Aspirin**  
**Baking powder**  
**BARIUM:** Chlorate  
Chloride  
Hydrate  
Oxide  
Nitrate  
Peroxide  
Sulfide  
Beetroot potash  
Benzoates n. s. p. f.  
Bismuth salts  
**Borax**  
**Bromine**  
Bromides of potash, soda, ammonia  
Bromides n. s. p. f.  
Bromoform & Iodoform  
Bromine, organic compounds  
n. s. p. f.  
**Caffeine**  
**CALCIUM:** Carbide  
Chloride & liquors of  
Nitrate (air)  
**Tartrate**  
Carbon bisulfide  
Carbon tetrachloride  
Carborundum  
Carborundum discs  
Carborundum paper  
Carborundum, other manufactures of  
Carbides n. s. p. f.  
Carnallite, 9-12 per cent K<sub>2</sub>O  
Casein & non-edible casein preparations  
Chemical products, n. s. p. f. for photographic, cleansing & other uses  
Chloral hydrate  
Chlorates n. s. p. f.  
Chlorine compounds, organic  
n. s. p. f.  
Chloroform

**CHROME:** Acetate  
Chloride  
Oxide (hydroxide)  
**Chromous chloride**  
**Cobalt oxide**  
Cobalt salts n. s. p. f.  
*Cocaine, crude or refined*  
*Cyanides* (potash or soda)  
**Cellulose**  
Collodion & collodion  
Copper sulfate (copper & ferrous sulfate)  
Creosote, wood-, peat & tar  
*Cryolite*  
*Cyanides* (potash or soda)  
Disinfectants  
**Eggonine**  
Egg albumen, dried & powdered; albuminous materials  
Epsom salts  
Ethyl bromide  
Ethyl chloride  
Ethyl iodide  
Ferrosilicon with 25 per cent Si or more  
Fertilizer salts inclusive of potash fertilizer with 30 per cent K<sub>2</sub>O  
**Filter tubes**  
Fluorides  
Fluosiilicates  
Formaldehyde  
Formaldehyde-sulfoxylates  
Fruit & plant juices containing ether or alcohol  
**GASES, COMPRESSED:** Acetylene  
Hydrogen  
Nitrogen  
Oxygen  
All other  
**LIQUEFIED:** Acetylene  
Ammonia  
Carbon dioxide  
Sulfur dioxide  
All other  
*Gelatine*  
Gelatine capsules  
**GLUE:** Crude  
Other than egg  
For printing rolls  
**GOLD:** Chloride  
All other salts of  
**GREEN:** *Schweinfurth* & similar  
**Guaia-col carbonate**  
Hydrogen peroxide  
Hypochlorites n. s. p. f.  
Industrial chemicals n. s. p. f.  
Inorganic  
Organic  
Inorganic chemicals for medicinal use n. s. p. f.  
Insecticides  
**IRON:** Acetate  
Chromate  
Lactate  
Mordant  
Sulfate  
Sulfide (artificial)  
Iodine  
Iodides of potash, soda & ammonia  
All other  
Lactates n. s. p. f.  
**LEAD:** Chromate  
Nitrate  
Oxide (litharge) with or without gold & silver  
Peroxide  
Red oxide of  
Sugar of  
Sulfate  
All other salts n. s. p. f.  
Licorice extracts  
Crude or refined  
Medicinal  
**LIME:** Acetate & gray acetate  
Chloride of & bleach liquors  
Citrates of  
**MAGNESIA:** Carbonate, artificial  
Chloride & liquors of  
Manganese chloride  
Medicinal & pharmaceutical preparations, n. s. p. f.  
**MERCURY:** Metal & alloys thereof  
Chlorides  
Metalloids n. s. p. f.  
Methyl-ethyl ketone  
Morphine & its salts  
**NICKEL:** Oxide  
Sponge  
Sulfate  
Nicotine  
Nicotine, salts of  
Nitrates of thorium, cerium & rare earths  
Nitrates n. s. p. f.  
Opium alkaloids  
Organic chemicals for medicinal use, n. s. p. f.  
Oxides n. s. p. f.  
Perchlorates

Persulfates  
**Phenolphthalein**  
Phosgene  
*Phosphorus, red & yellow*  
Phosphorus hydride  
Phosphorus sesquisulfide  
Photographic chemicals n. s. p. f.  
Photographic dry plates & films  
**POTASSIUM (OR POTASH):** Arsenate  
Bitartrate  
Carbonate  
Caustic, solid or liquor  
Chlorate  
Chloride  
Chromate & bichromate  
Magnesium sulfate  
Manganate & permanganate  
Nitrate  
Oxalate  
Phosphate  
Prussiate yellow or red (sodium)  
Sulfate  
Sulfide (soda)  
Sulfocyanide  
Salts, all other n. s. p. f.  
Proprietary medicines  
**Quinine, its salts & compounds**  
Rochelle salts  
Saccharine  
Salicylates n. s. p. f.  
**Salicine**  
Salt  
Salt brines & bitters  
Santonin  
Saponine  
Selenium sludge  
Sheep-dip  
Silk, artificial  
Nitro  
All other  
**SILVER:** Bromide  
Chloride  
Nitrate  
All other salts  
All other compounds  
**SODIUM (OR SODA):** Acetate  
Aluminate  
Arsenate  
Ash, crude and refined; boiler scale preparations containing soda ash; washing soda  
Bicarbonate  
Bisulfate (nitre cake)  
Caustic solid or liquid  
Chlorate  
Chromate or bichromate  
Crystals (soda)  
Hydrosulfite  
Hyposulfite  
Nitrate  
Nitrite  
Peroxide  
Phosphates  
Silicofluoride  
Sulfate (salt cake)  
Sulphhydrate  
Sulfide  
Sulfite & bisulfite  
**STRONTIUM:** Carbonate (artificial)  
Chloride  
Oxide  
Sulfides, all other n. s. p. f.  
Sulfuric acid  
Sulfur, Spence metal  
Synthetic or artificial foods or nutrients  
Tartar emetic  
Terpene hydrate  
Thorium, cerium & zirconium, all other salts of  
Thymol  
Tin, chlorides of  
Oxides of  
All other salts of n. s. p. f.  
Tungsten dioxide  
**UREA**  
Water glass (potash or soda) liquors  
Water glass (potash or soda) solid  
Welsbach mantles, scrap  
**ZINC:** Chloride  
Sulfate  
Salts, all other n. s. p. f.  
All other chemicals & pharmaceutical products  
**XVIII: DYES & DYE WARES**  
Cochineal  
Lac-dye  
Animal kermes, cochineal, carmine, sepia  
Bleacher's blue  
Coal-tar dyes  
Aniline dyes  
Azo dyes  
Sulfur dyes  
Azuline, fuchsine & rosein dyes  
Naphthalene dyes  
Anthraene dye, other than alizarin red

Alizarin red  
Indigo vegetable & synthetic  
Indigo carmine & lakes of indigo & indigo carmine  
**Food & butter colors**  
*Prussian blues, chrome green & zinc-green*  
*Ultramarine & ultramarine lake.*  
Cobalt oxide  
**Litharge**  
**Orange mineral**  
White lead  
Blanc fixe  
Zinc oxide (white)  
Zinc dust  
**Lithopone**  
Zinc oxide (gray)  
Red cinnabar  
Copper oxide  
Logwood extracts  
Extracts of luscic, Brazil wood, Quercitron & other dye woods  
Chalk, white, washed, etc.  
Iron oxide, native & artificial (also yellow ochre)  
*Umber, Sienna & other n. s. p. f. earth colors*  
Dry, not prepared printing ink  
Lampblack  
**Blanco polish**  
Bronze & metal colors  
**Chrome colors**  
Copper pigments & other n. s. p. f. pigments & lakes, dry or pulp  
Colored printing inks; cheese colors, orseille extract, chlorophyll & other n. s. p. f. prepared colors  
**Printing ink, black**  
Lead, zinc, lithopone, iron oxide ground in oil, in tins or otherwise packed for retail; all other prepared colors  
Smalts  
Colors in color boxes, water-colors, etc.  
**Ink, ink-powder**  
Graphite, formed for retail  
**Earth, Van Dyke**  
Zinc chromate  
Lead & colored pencils or crayons; chalk crayons  
All other dyes & dye wares  
**XIX—ETHERS & ALCOHOLS**  
Acetic ether  
Amyl ether  
Butyric ether  
Ethyl ether  
**Ether, nitrous**  
Ethers of all kinds; cognac-oil  
Fusel oils; amyl, butyl, propyl alcohols  
Crude wood alcohol  
Crude acetone  
Refined acetone, wood alcohol & water solutions of formaldehyde  
Acetaldehyde, paraldehyde  
**XX—VOLATILE OILS, ARTIFICIAL PERFUMES, TOILET PREPARATIONS**  
Wood tar oil, caoutchouc oil; animal oil  
Turpentine oil, pine-needle oil, rosin spirit  
Orange, lemon, bergamot & other citrus volatile oils  
Camphor, anise, clove, laurel, elderberry, peppermint, rosemary, lavender & other volatile oils; menthol & menthol pencils  
Terpineol, heliotropin, vanilla, cumarin, anethol, benzaldehyde, & other perfume materials  
Synthetic perfumes  
Odoriferous fats, ointments & pomades  
Essence of Cologne  
Other ether & alcohol containing toilet waters, vinegars & preparations  
Ether & alcohol containing mouth & hair washes  
Toilet waters  
Powders, cosmetics, tooth & n. s. p. f. powders  
**XXI—ARTIFICIAL FERTILIZERS**  
Artificial guano, ground bones & flesh, animal manure  
Natural guano  
Bone-meal  
Thomas phosphate meal  
Superphosphates, etc.  
Calcium cyanamide  
**XXII—EXPLOSIVES, AMMUNITION, COMBUSTIBLES**  
Naphthotol, collodion cotton  
Gunpowder  
Cordite



## LIST I (concluded)

Dynamite & other explosives	Pig iron
Fulminates	Scrap steel
Hydro acid	Scrap cast iron
High explosives	Pig iron aluminum, chrome, manganese, nickel, silicon, & other non-malleable iron alloys
Propellants	-Cerium
Primers & the like, flobert munitions	-Molybdenum
Loaded cartridges	-Phosphorus
Matches, wood & paper	-Titanium
Matches, seat	-Tungsten
Fireworks: antimony, magnesium or zinc torches	-Vanadium
Pitch torches, fuses, etc	Aluminum crude in plates
XXIII—WOOD FIBER—CHEMICAL	Aluminum bronzes
PAPER	Lead, crude, lead scrap
Mechanical pulp	Zinc: crude & scrap
Straw, esparto & other fibers; paper stock	Drawn, rolled
Tracing, blue-print, gelatine, fly, ozone & test papers	Dust
Sulfate pulp	Tin, crude & scrap
Sulfite pulp	NICKEL: Metal & coins
Chemical pulp: bleached & unbleached	Alloys
Paper maché	Copper, crude
Sensitized paper	Copper coins, scraps, etc
Photographic paper	Copper rods, sheets, vessels & hollow-ware
XXIV—FIRE-BRICK & CLAY	Brass & similar alloys & scrap
PRODUCTS	Bronze & similar alloys & scrap
Firebrick: rectangular under 5 kg per piece	Yellow metal
Firebrick: rectangular over 5 kg per piece	Babbitt metal
Other fireproof materials of clay or clay-like materials; crucibles, muffles, capsules, tubes, cylinders & other hollow-ware except retorts; plates other than stone; crucibles of magnesia cement or soapstone	Radium & its salts
Earthenware: Vitrified & non-vitrified	Rhodium
Retorts	Ruthenium
Graphite crucibles, tuyeres, etc.	Selenium & its salts
Porcelain chemical ware	Sodium
XXV—METALS	Tantalum
Barium	Titanium
Bismuth	Type-metal
Calcium	Antimony, crude
Cobalt	Chrome, cadmium, tungsten & other non-noble metals adapted for fabrication, crude & scrap
Magnesium	XXVI—INDUSTRIAL WASTES
Pewter	Animal
Potassium	Vegetable
Fine gold: alloyed gold, crude or cast; gold bars	Iron
Gold ashes, scrapings or broken gold	Glass
Platinum, iridium, osmium, palladium, rhodium, ruthenium, unalloyed crude or cast	Tobacco
Fine silver, alloyed silver, crude or cast; silver bars	Wax
Silver scrapings	Cotton
	Lead
	Dried fruit
	Dyehouse
	Linen, hemp, jute
	Cautchouc
	Nicke!
	Silk
	Soapmakers'
	Wool
	Sugar
	Beet pulp
	Fertilizer
	Papermakers'
	Leather & hides
	All other

promises the easiest and most practicable mode of expansion for all concerned.

The labor expended in getting up the foregoing lists has been considerable and it has been exceedingly tiring work; it has resulted in bringing into relatively small compass information contained in four different languages and itself widely scattered; in spite of reasonable care I have, no doubt, overlooked some items and duplication may not have been avoided, but this should in no wise deter everyone interested from taking off his coat and getting down to work to see, firstly, if he himself and his interests are supplied with proper information and, if not, just what further information may be needed; then repeat that process for his section of the country, and then for the country at large, and forward that information in a letter (preferably typewritten) to the secretary of the nearest section of the American Chemical Society or American Electrochemical Society. Such letters should be written, well spaced, on paper of the ordinary business letter size (8 or 8 1/2 by 11 inches) and on one side of the paper only; the intention is to have these original letters suitably bound and appropriately indexed, and to have them accompany the final recommendation when, and if, it is presented to the officials in Washington. The work of the members of the local sections of the A. C. S., the A. E. S. and of this special committee, will be greatly expedited if each such letter were to be accompanied by seven (7) carbon copies to serve as working copies for the various committee members, and such effective coöperation will be more than repaid in speed and certainty. The final recommendation of this special committee must be backed up, as far as possible, by individual letters, otherwise the recommendations might very properly be looked upon as the personal opinions of only a few; that would not be fatal but it would be disadvantageous.

This special committee itself cannot possibly bring its plans to the attention of all interested; it must depend upon the coöperation of the members of the A. C. S. and the A. E. S. to bring this matter to the attention of local boards of trade, chambers of commerce or similar coöperative business organizations, and to the attention of individual concerns and corporations. Each member has his work to do, and this special committee counts with entire confidence upon a full performance.

Persons and corporations not members of the A. C. S. or the A. E. S. need feel no hesitancy whatever in taking active part in

Those who use the lists in their final form must be prepared to perform some mental labor in spelling out from such records the precise information they may want in any specific instance.

List I is based upon official documents (except U. S.) published before the outbreak of the present war.

On May 10, 1916, the British Government prohibited the exportation of a number of chemical substances from Great Britain. This list appeared in the May 31, 1916, issue of the *Journal of the Society of Chemical Industry*, pp. 620-622. It is more diversified than any single Government Commerce Report that I have found; it may give valuable hints as to those things that in time of stress assume an importance to a nation's life that is not accorded them in times of peace; since such list may foreshadow further expansion of commerce reports such parts as are not contained in the foregoing are now given as List II. Study of this list may very well suggest proper additions to our own commerce or similar reports.

The Tariff Act of the U. S. recites certain specific chemicals and also classes of chemicals and these may also suggest proper additions; some of the relevant entries in the Tariff Act of October 3, 1913, are given in List III. The Treasury Department makes returns under each of the heads of List III and this information might be kept separate and published or at any rate so much of it as may thus serve a useful purpose; it is to this point that special attention should be directed since it

## LIST II—EXPORTATIONS (CHEMICALS) PROHIBITED BY BRITISH GOVERNMENT, MAY 10, 1916

Aeroplane dope	Henbane & its preparations
Capsicum	Hexamethylene tetramine & its preparations
Capsicum-oleoresin	Hydrobromic acid
Carbon, Brazilian	Hydroquinone & mixtures containing it
Aluminum nitrate	Ipecacuanha root
Amidol & mixtures containing it	Manganese peroxide
Ammonia perchlorate	Methyl aniline
Ammonia sulfoxyanide	Methyl salicylate & its preparations
Anti-tetanus serum	Metol & mixtures containing it
Belladonna & its preparations	Naphthalene compounds & preparations
Belladonna alkaloids, their salts & preparations	Neosalvarsan
Bismuth nitrate	Nitrotoluol
Calcium sulfide	Novocain & its preparations
Cantharides	Nux vomica & its preparations
Chromium chlorate	Radium compounds
Chromium nitrate	Salipyrine
Cobalt nitrate	Salvarsan
Copper suboxide & mixtures containing it	Senna leaves
Cresol & nitrocresol	Stramonium leaves & seeds
Cyanamide	Sulfonal
Diethyl-barbituric acid (Veronal)	Theobromine—sodium salicylate
Dyes, coal-tar, all articles containing them	Triphenyl phosphate
Emetine & its salts	Trioxymethylene
Ergot of rye	Xylol, its preparations & compounds
Ether, formic	Scheelite
Gentian preparations	Selenium
Green oil	Vanadium
Halogen derivatives of aliphatic hydrocarbons	Mineral jellies

this work; write your suggestions to the secretary of the section of the A. C. S. or the A. E. S. nearest to you; there are 54 sec-

LIST III—CHEMICAL ENTRIES IN U. S. TARIFF ACT OF OCT. 3, 1913. (TREASURY DEPARTMENT RETURNS ARE MADE UNDER HEADINGS USED BELOW)

ACIDS:	Benzidin	Oil, (continued):	Vanillin	Manganese oxide & ore of
Arsenic	Binittrobenzol	Anise	Vanilla beans	Myrabolans
Arsenious	Binittrotolul	Bergamot	Tonka beans	Oleostearin
Boracic	Tolidin	Camomile	SODA: Benzozate	Orchil
Carbolic	Dianisidin	Caraway	Chlorate	Oils: Birch tar
Chromic	Naphthylamin	Cassia	Nitrite	Cajeput
Citric	Diphenylamin	Cinnamon	Bicarbonate	Coconut
Fluoric	Benzaldehyde	Cedrat	Caustic	Cod
Formic	Benzyl chloride	Citronella	Phosphate	Cod liver
Gallie	Nitrobenzol	Lemon grass	Hyposulfite	Cottonseed
Hydrochloric	Nitrotolul	Civet	Sulfide	Croton
Hydrofluoric	Naphthylamin—sulfocacids	Fennel	Chromate	Ichthylol
Lactic	Naphthol—sulfocacids	Jasmine	Bichromate	Juglandium
Nitric	Amidosalicylic acid	Juniper	Yellow prussiate	Palm
Oxalic	Binittrochlorbenzol	Lavender	Borate (borax)	Palm kernel
Phosphoric	Diamidostilbendisulfoacid	Aspic	Carbonate	Perilla
Phthalic	Metanilic acid	Limes	Sulfate	Soya bean
Prussic	Paranitranilin	Neroli	Salt	Olive oil
Pyrogallie	Dimethylanilin	Origanum, red & white	Sulfite crystals	Chinese nut
Salicylic	Cobalt, oxide of	Thyme	Talcum	Nut
Silicic	Colloidon	Valerian	Ground talc	Kerosene
Sulfuric	ETHERS: Sulfuric	Morphine sulfate	Steatite	Benzene
Tannic and Tannin	Amyl nitrite	All other opium alkaloids	French chalk	Naphtha
Tartaric	Amyl acetate	Cocaine	Arsenic	Gasoline
Valerianic	Ethyl acetate	Ecgonine	Sulfide of arsenic	Paraffine
Acetic anhydride	Ethyl chloride	Barytes	Cinchona bark	Spermaceti
Acetone	All other ethers & esters	Blanc fixe	Bauxite	Whale
Alcohol, wood	EXTRACTS OF: Nutgalls	Satin white	Beeswax	ORES OF: Gold
Alkalies, alkaloids & medicinal mixtures	Persian berries	BLUES: Berlin	Bismuth	Silver
Alumina hydrate	Sumac	Chinese	COPPER: Sulfate	Nickel
Alum	Logwood	Ultramarine	Acetate	Platinum
Alum cake	Chlorophyll	BONE: Dust	Sub-acetate	Paris green
Patent alum	Saffron	Ivory	Meal	London purple
Sulfate of alumina	Safflower	Vegetable	Ash	Phosphates, crude
Aluminous cake	Formaldehyde	Gas	Crude	Phosphorus
AMMONIA, Carbonate	Fusel oil	Lamp	Borates of soda, crude	Photographic films
Muriate	Amyle alcohol	CHROME: Yellow	lime, crude	Platinum metal & manufactures of
Liquid anhydrous	Gelatine	Green	Bromine	Plumbago
Sulfate	Glue	Ochre	Cadmium	POTASH: Crude or black salts
Nitrate	Isinglass	Sienna	CALCIUM: Acetate, brown or	Carbonate
Perchlorate	Agar-agar	Umber	gray	Sulfate
Apatite	GLYCERINE: Crude	Spanish Brown	Chloride, crude	Hydrate
Argols	Refined	Venetian Red	Carbide	Nitrate
Crude tartar	GUM: Amber	Indian Red	Nitrate	Muriate
Cream tartar	Arabic	Colcothar	Cement, Roman, Portland	Quinine sulfate & all chemicals
Rochelle salts	Sesamol	Litharge	& other hydraulic	alkaloids
Calcium tartrate	Camphor, crude, refined or synthetic	Orange, mineral	Cerium ore	Radium & its compounds
BALSAMS: Copaiba	Chicle, crude	Red Lead	Chromate of iron	Selenium & its salts
Fir	Dextrine	White Lead	Chromium, hydroxide	Salt
Canada	Burnt starch	Lead acetate	(crude)	Santonin
Peru	British gum	Lead nitrate	Anthracene	Sheep-dip
Tolu	Iodoform	Varnishes	Anthracene oil	SODA: Arsenate
Barium: Chloride	Potassium iodide	Whiting & Paris White	Naphthalene	Cyanide
Dioxide	Licorice extracts	Zinc oxide	Phenol	Sulfate (salt cake)
Carbonate, precipitated	Licorice root	Lithopone	Cresol	Bisulfate (niter cake)
Blackening, polishing powders & creams	Licorice root	Zinc sulfide (white)	Cobalt & ore	Ash
Bleaching powder	Coca leaves	Sulfate of iron	Cochineal	Silicate
Caffeine	Lime citrate	Cryolite	Sulfate of iron	Nitrate
Calomel	MAGNESIA: Calcined	Cudbear	Iron ore	Soya beans
Corrosive sublimate	Carbonate of	Divi-divi	Graecae & fats for soap-making	STRONTIUM: Oxide
Chalk, precipitated	Sulfate (Epsom salts)	Fulminates	Guano	Carbonate
Chloral hydrate	Menthol	Gambier	Basic slags	Strychnine & its salts
Salol	OIL: Cod	Graecae & fats for soap-making	Cyanamide	Sulfur
Phenolphthalein	Seal	Guano	Lime-nitrogen	Pyrites
Urea	Herring	Basic slags	Cup powder & all explosives	Talcum, steatite, French chalk
Terpin hydrate	Whale	Cyanamide	Gutta percha	Tanning extracts:
Acetanilid	Sperm	Lime-nitrogen	India rubber, crude, scrap & refuse	Quebracho
Acetphenetidine	Wool grease	Chlorate	Indigo	Hemlock bark
Antipyrine	Turkey red	Chromate	Iodine	Oak
Glycero-phosphoric acid	Linseed	Bichromate	Iridium, osmium, palladium, rhodium & ruthenium	Chestnut
Acetylsalicylic acid	Poppy seed	Nitrate	Iron ore	Nuts
Aspirin	Rape seed	Permanganate	Kierserite	Nutgalls
Guaiacol carbonate	Peanut	Red prussiate	Kainit	Terra alba
Thymol	Hempseed	Yellow prussiate	Casein	Tin ore & metal
Chloroform	Almond, sweet	SALTS OF: Bismuth	Lard	Tungsten ore
Carbon tetrachloride	Almond, bitter	Gold	Asphalt, bitumen	Turpentine, Venice & spirits
Benzol	Sesame	Platinum	Litmus	Uranium oxides & salts
Naphthol	Bean	Rhodium	Madder	Valonia
Resorcin	Olive	Tin	Magnesite	Wax, vegetable or mineral
Tolul	Orange	SOAPS. Perfumed toilet		Witherite
Kyloil	Lemon	Medicinal		WOODPULP: Mechanical
Toluidin	Peppermint	Castile		Chemical
Xylidin	Amber	All other		Bleached
Cumidin	Ambergris			Unbleached

tions in 32 states of the Union and the District of Columbia. There are no formalities and there is no need to stand on ceremony.

In addition to the foregoing list helpful suggestions may be obtained by consulting the weekly import and export lists that appear in the *Oil, Paint and Drug Reporter* of New York, and the daily lists of manifests of incoming steamers as they appear in the *Journal of Commerce and Commercial Bulletin* of New York; also the weekly and annual summaries of British foreign and domestic chemical trade as they appear in *The Chemical Trade Journal* may offer useful suggestions.

List IV gives the name and address of the secretary of each local section of the A. C. S. and the A. E. S., arranged alphabetically by states.

Should there be any changes in local secretaries from those given, the person addressed as indicated can be confidently counted on to forward such communication to his successor.

## WORKING SCHEDULE OF COMMITTEE

The present plan is for this special committee to begin its preliminary list November 1, 1916; complete it November 15, 1916; publish this provisional list in the *JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY*, December 6, 1916, and in *Metalurgical and Chemical Engineering*; begin its final draft February 14, 1917; close the final recommendations February 28, 1917; and present its recommendations to the proper authorities in Washington before March 15, 1917; this will leave 3½ months for Washington to make its decision and arrange for the



## LIST IV NAMES AND ADDRESSES OF SECRETARIES OF THE LOCAL SECTIONS OF THE AMERICAN CHEMICAL SOCIETY AND OF AMERICAN ELECTROCHEMICAL SOCIETY

## A. C. S.

*Alabama*  
W. H. BEERS, JR.  
2114 First Avenue  
Birmingham, Ala.

*California*  
B. S. DRAKE  
5830 Colby Street  
Oakland, Cal.

HENRY L. PAYNE  
223 West 1st Street  
Los Angeles, Cal.

*Connecticut*  
R. J. MARSH  
C/o R. Wallace & Sons Mfg. Co.  
Wallingford, Conn.

G. S. JAMIESON  
121 Linden Street  
New Haven, Conn.

*District of Columbia*  
H. C. MCKELVEY  
Bureau of Standards  
Washington, D. C.

*Georgia*  
J. S. BROGDON  
70 1/2 Peachtree Street  
Atlanta, Ga.

*Idaho*  
H. A. HOLADAY  
University of Idaho  
Moscow, Idaho

*Illinois*  
D. K. FRENCH  
2005 McCormick Building  
Chicago, Ill.  
GEO. D. BEAL  
University of Illinois  
Urbana, Ill.

*Indiana*  
H. W. RHODEHAMEL  
643 East 32nd Street  
Indianapolis, Ind.

*Iowa*  
W. G. GAESSLER  
Iowa State College  
Ames, Iowa  
PERRY A. BOND  
Cedar Falls, Iowa

*Kansas*  
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24 Federal Building  
Kansas City, Kans.

*Kentucky*  
P. L. BLUMENTHAL  
Agricultural Experiment Station  
Lexington, Ky.  
A. M. BRECKLER  
C/o Jones & Breckler  
Louisville, Ky.

*Louisiana*  
F. W. LIEPSNER  
310 Customs House  
New Orleans, La.

*Maine*  
L. M. BURGHART  
University of Maine  
Orono, Me.

*Maryland*  
F. M. BOYLES  
C/o McCormick & Company  
Baltimore, Md.

*Massachusetts*  
E. B. SPEAR  
Massachusetts Institute of Technology  
Boston, Mass.

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Department Agricultural Chemistry  
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Morse Hall  
Ithaca, N. Y.

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52 East 41st Street  
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Niagara Falls, N. Y.

H. H. TOZIER  
26 Jones Avenue  
Rochester, N. Y.

A. J. SALATHE  
Union College  
Schenectady, N. Y.

R. S. BOEHNER  
Syracuse University  
Syracuse, N. Y.

*North Carolina*  
F. E. CARRUTH  
West Raleigh, N. C.

*Ohio*  
E. K. FILES  
University of Cincinnati  
Cincinnati, O.

A. F. O. GERMANN  
Adelbert College  
Cleveland, O.

W. J. McCAUGHEY  
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325 Wyandotte Street  
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J. H. GRAHAM  
113 W. Manheim Street  
Germantown, Pa.

W. C. COPE  
U. S. Bureau of Mines  
Pittsburgh, Pa.

*Rhode Island*  
ROBY. F. CHAMBERS  
Brown University  
Providence, R. I.

*South Carolina*  
A. C. SUMMERS  
University of South Carolina  
Columbia, S. C.

*South Dakota*  
H. I. JONES  
Dakota Wesleyan  
Mitchell, S. D.

*Tennessee*  
PAUL C. BOWERS  
9 Garland Avenue  
Nashville, Tenn.

*Vermont*  
C. E. BURKE  
Burlington, Vt.

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W. A. BURROWS  
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*Washington*  
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University of Washington  
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L. F. AUGSPURGER  
University of Wisconsin  
Madison, Wis.

## A. E. S.

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I. M. MUIR  
239 W. 39th Street  
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## A. T. HINCKLEY

C/o National Carbon Co.  
Niagara Falls, N. Y.

## Pennsylvania

S. S. SADDLER  
39 South 10th Street  
Philadelphia

H. C. RAY  
University of Pittsburgh  
Pittsburgh, Pa.

## Wisconsin

O. P. WATTS  
University of Wisconsin  
Madison, Wis.

gathering of the added information, if any, decided upon with the beginning of the fiscal year 1917-18.

Delay, or failure in getting suggestions to the local sections will hamper the special committee. Points of view cannot be considered unless communicated. Everybody's cooperation is not only necessary but most cordially invited; if our list is not the best and most useful in the world to-day we must strive to make it so.

25 BROAD STREET  
NEW YORK CITY

## DEATH OF SIR WILLIAM RAMSAY

Sir William Ramsay died at his home, Beechcroft, at Hazlemere, Bucks, England, on July 23rd. He was born in Glasgow October 2, 1852. He received his early education in Glasgow Academy and University, and served as assistant in technical chemistry in the Young Laboratory as early as 1872. He later became assistant in Glasgow University, where he remained until 1880, at which time he became professor of chemistry in University College at Bristol. He later joined the faculty of the University College, London, as professor of chemistry, which position he occupied until 1913, when he retired as emeritus professor.

Sir William Ramsay has for many years held an undisputed position among the foremost scientists of the world and his scientific achievements are well known to the chemical profession. He was personally known to a large body of American chemists through his frequent visits to this country where he lectured at many of the leading universities and before the notable international meetings of the technical societies.

Of the many honors which he has received, probably the most notable is that of the Nobel prize in chemistry, which was awarded to him in 1904. Sir William was created a Knight in 1902. He was also a Commander of the Crown of Italy, a Knight of the Prussian Order Pour le Merite, an officer of the French Honor Legion, and an honorary member of the Royal Academies of twelve countries.

## RESOLUTIONS ADOPTED ON THE DEATH OF ELTON FULMER

The following resolutions have been adopted by the Northern Intermountain Section of the American Chemical Society on the death of Professor Elton Fulmer, of the Washington State College, Pullman, Washington:

WHEREAS, Professor Elton Fulmer has suddenly been taken from our midst by death, be it

*Resolved*, That we, the members of the Northern Intermountain Section of the American Chemical Society, express our deep appreciation of his work as pioneer and leader in the development of chemistry in the Northwest, his sterling character, and his devotion to high ideals.

*Be it further Resolved*, That we express to the family our deep sense of loss in the taking away of a fellow worker and friend, and extend to them our heartfelt sympathy.

(Signed) J. KOSTALEK  
J. S. JONES

## NOTES AND CORRESPONDENCE

### ON EFFICIENCY OF AIR DRYERS

*Editor of the Journal of Industrial and Engineering Chemistry:*

I have read with considerable interest the letter of Prof. W. K. Lewis on the Efficiency of Air Dryers,<sup>1</sup> wherein he refers to a discussion of this subject in the columns of the *Journal of Metallurgical and Chemical Engineering* in the years 1909 and 1910. Inasmuch as I was guilty of starting some of the discussion referred to, in the issue of April and May, 1910, I beg permission to say a few words further on the subject.

The discussion arose from a published report<sup>2</sup> of a test of a drying machine wherein an "efficiency" of 85 per cent was claimed by the late Mr. W. B. Ruggles.

I criticized the use of the word "efficiency" in the sense in which it was employed, and I take this opportunity to say that my criticism was directed solely to what I regarded as a misleading use of a scientific term, and that I very clearly recognize the valuable services of the late Mr. Ruggles to the practical art of drying.

Mr. Lewis finally arrives at the conclusion that it is desirable to express the results attained by drying machines in terms of "performance" rather than "efficiency," "Performance" as defined by Mr. Lewis being the actual heat consumption in terms of B. t. u. per lb. of water evaporated. With this I heartily concur and it really differs in no way from what I contended was the correct definition of "efficiency" in 1910. Such a statement of performance is exact and definite, and precisely expresses what a drying machine accomplishes towards the purpose for which it is designed, *viz.*, the evaporation of water by expenditure of heat. Further, the form of statement as proposed by Mr. Lewis makes it possible directly to compare the operation of two or more machines of different types. The "performance" as defined by Mr. Lewis is indeed a direct statement of energy expended and useful work performed thereby.

The difficulty pointed out by Mr. Lewis of stating the "efficiency" of multiple-effect evaporating apparatus is a real one and we may as well boldly face the fact that such apparatus (multiple-effect) really has an efficiency as heat using machinery of greatly over 100 per cent actually, and its theoretical "efficiency," as Mr. Lewis shows, is infinity. This is really only another way of stating the doctrine of conservation of energy. Ordinarily our utilization of energy is confined to one transformation from kinetic to potential or *vice versa*. Multiple-effect apparatus is one instance (practically almost a singular instance) where we are able to repeat the change cyclically. Hence a definite amount of heat can be made to evaporate an indefinite amount of water. Of course in practice the physical limits are somewhat sharply drawn at five or six cycles, but theoretically there is no limit to the quantity of water that can be vaporized by a given amount of heat.

Such, however, is not the case with "air dryers," which is the titular heading of Mr. Lewis' letter and which was the subject matter of the discussion of several years since, referred to by him.

The consumption of heat in an "air dryer" for evaporative purposes is a perfectly definite thing and just as definite as in the case of a steam boiler. We have to deal only with one possible transformation of heat from sensible to latent form and the work that can thereby be performed (as evaporation) is perfectly definite.

It is perhaps well to define an "air dryer," and by the term I understand a machine utilizing artificial heat to evaporate water from some solid substance, wherein air at substantially atmospheric pressure is usually the medium by which heat is

conveyed to the material to be dried and *always* the medium by which the vapor produced is removed from the material or machine. I believe this definition covers all practical types of atmospheric drying apparatus. It will be noted that it does not cover vacuum drying apparatus; but in all practical vacuum drying apparatus the evaporative possibilities of a given amount of heat are also definite and limited. The theoretical possibility of indefinitely repeated utilization shown by Mr. Lewis applies only to multiple-effect machines. As far as I am aware multiple effect has not been applied to drying, but only to the evaporation of solutions.

We see, therefore, that either in "air dryers" or in vacuum dryers (single-effect) the quantity of water that can be evaporated by a given amount of heat is quite definite—not only practically but as a theoretical matter, and hence it is quite possible to state the performance of all practical dryers as a percentage "efficiency."

It requires practically 1120 B. t. u. to evaporate 1 lb. of water from average normal temperature (I speak of course in round numbers) and any air-drying machine or vacuum dryer that evaporated 1 lb. of water for an input of 1120 B. t. u. would have an efficiency of 100 per cent.

In practice there are various losses, due to radiation, to heating the dried material to the discharge temperature and to heating the outgoing air to the discharge temperature—this last being usually the greatest. All the losses are unavoidable; all can be greater or less according to the type and perfection of the machine and on their balance depends the efficiency of the machine. My contention in the discussion of several years since was that any drying machine should be charged with the total heat supplied, whether in the form of steam or from direct combustion of fuel, and credited solely with the heat usefully expended in evaporation of water. This view is, I believe, entirely in accordance with Mr. Lewis.

The second example given by Mr. Lewis to demonstrate that there is no definite efficiency in air drying, appears to me quite irrelevant. The case is given of spreading material under a shed and allowing air to blow over it. Manifestly there is in this case no expenditure of artificial energy and it can have no relation to efficiency of fuel because fuel is in no way concerned. Nevertheless energy is expended and quite definitely; and the only reason we are not able to determine the efficiency of such a system is the impossibility of determining the factors. Could we determine with any accuracy the amount of air coming in contact with the material under such circumstances and the amount of (low-grade) heat brought into the system, also the drop in temperature and the increase in saturation (both of which would be very small), we should have in hand all the data necessary to determine the efficiency of the system.

Mr. Lewis' letter really treats of much more than the efficiency of air dryers and goes into the field of evaporation in general. While this is of equal interest, it appears to me that the two things are quite distinct, although they do indeed involve the common factor of evaporation of water. Nevertheless the other factors are so different that they had best be treated independently.

Mr. Lewis has himself clearly shown one reason for separate treatment, in pointing out that a theoretically perfect multiple-effect evaporator has an unlimited efficiency. I do not think this has been scientifically shown before, but we see in trade customs a dim realization that the standards applicable to drying machines, or in general single-effect machines, are not equally applicable to multiple machines. It is quite a common custom for manufacturers of drying machines to claim for their

<sup>1</sup> THIS JOURNAL, 8 (1916), 570.

<sup>2</sup> J. Met. and Chem. Eng., March, 1910.



machines a certain "efficiency," as a percentage. As I remember, this is never done with multiple-effect evaporators, but instead a certain evaporation per pound of steam supplied is specified. This it will be seen is practically identical with the "performance" proposed by Mr. Lewis.

As regards the last portion of Mr. Lewis' letter, treating of the evaporation of solutions, I frankly confess that I utterly fail to understand. He assumes a solution boiling under a definite pressure,  $p$ , which is less than the pressure,  $p_0$ , of the pure solvent at the same temperature. The vapor from the boiling solution is to be compressed isothermally and "can be introduced into the coils of the same effect from which the vapor itself came and there condensed at a temperature *differentially higher* (italics are mine) than that of the solution on the other side of the heating surface. The heat of condensation will thus be available for the evaporation of more water from the original solution."

Now the temperature of the vapor is that of the pure solvent boiling at the assumed pressure and is *lower* than that of the boiling solution, owing to the lowering of the vapor tension by the substance in solution. This vapor is compressed isothermally, that is, it remains at the same temperature, but it is required to give up its "heat of condensation" (? latent heat) to a solution at a temperature higher than its own.

Unless I have misread this passage, it looks like a flagrant violation of the second law of thermodynamics, and indeed involves the direct transfer of heat from a lower temperature to a higher.

I hasten to say this is not criticism and that my failure to understand the mechanism of the described process is undoubtedly due to my personal weakness in the science of thermodynamics.

BAYONNE, NEW JERSEY  
June 24, 1916

W. E. WADMAN

#### ACTIVE AND LATENT SOIL ACIDITY *vs.* IMMEDIATE AND CONTINUED LIME REQUIREMENT

*Editor of the Journal of Industrial and Engineering Chemistry:*

Recently there appeared an article in *THIS JOURNAL*, 8 (1916), 572, entitled "Immediate and Continued Lime Requirement *vs.* Active and Latent Soil Acidity," by W. H. MacIntire, of the University of Tennessee. In this article the inference is made that the present writer in a report in *THIS JOURNAL*, 8 (1916), 341, has not given sufficient credit or prominence to MacIntire's recognition of his so-called "Immediate and Continued Lime Requirement" as given in *THIS JOURNAL*, 7 (1915), 864. In regard to the statements that are made and the questions that are raised the writer deems it appropriate to state as follows:

Although possibly unknown to MacIntire, the writer published an article in *Science*, 42 (1915), 505, in which the distinction is made between *active* and *inactive* soil acidity. This article appeared in the issue of October 8, 1915, and MacIntire's article, in which he gave the expressions *immediate* and *continued lime requirement*, appeared also in the October, 1915, number of *THIS JOURNAL*. In the *Science* article, the writer used the term *inactive*, for which was later substituted the term *latent*, since that seemed more desirable.

It is well to note further that Veitch, in an excellent discussion of the nature of soil acidity in the *Am. Chem. Jour.*, 26 (1904), 659, used the terms *active* or *actual acidity* and *inactive* or *negative acidity* to designate different kinds of soil acidity. Veitch states that the total *active* and *inactive* acidity is estimated by his lime-water method. This distinction of Veitch is thus plainly a different one than that made by the writer in *THIS JOURNAL*, 8 (1916), 341, since the lime-water method does not estimate even all the acidity that is designated by the

writer as *active acidity*, to say nothing of the acidity designated as *latent acidity*.

Possibly other references could be given in which a recognition has been made of differences in the *activity* of the acids causing soil acidity. One of the most significant facts in regard to the various methods proposed for determining soil acidity is that the results by any one method are seldom the same as by any of the others. These differences have been recognized and attributed by some to differences in the nature and activity of the acids causing soil acidity. The writer used the term *active acidity* and recognized differences in *activity* of soil acids in *Wis. Sta. Bull.* 249, p. 15. This bulletin appeared eight months before MacIntire's publication in which was used the expression *immediate lime requirement*.

Perhaps the expressions chosen by MacIntire are superior to those chosen by the writer. If such is the case the criticism may be made that the writer should have changed his expressions in the subsequent publications after MacIntire's article appeared. The writer is as yet not convinced of this superiority, and even if this superiority is granted other difficulties arise as follows:

Determinations made lately indicate that MacIntire's method for his so-called *immediate lime requirement* does not indicate the same amount of acidity as the method given by the writer for *active acidity*. The methods thus clearly do not indicate the same point in the complete neutralization of the soil acids. The writer would thus have been open to serious criticism had he stated, subsequent to the publication in *Science*, that the method proposed measures the so-called *immediate lime requirement* as defined by MacIntire. In fact, the writer wishes to state definitely that the method proposed does not measure this *immediate lime requirement* as apparently defined by MacIntire.

Whatever practical or scientific meaning MacIntire may wish to convey by the expression, *immediate lime requirement*, it may be well to state clearly that the method (in which is used a solution of  $\text{Ba}(\text{OH})_2$ ) proposed by the writer for *active acidity* does not, and never was intended to indicate, in any way, the amount of lime that should be used under practical field conditions. It simply indicates the amount of acid substances present which are sufficiently active to react quickly with bases like  $\text{Ba}(\text{OH})_2$  or  $\text{Ca}(\text{OH})_2$ . The expression, *amount of active acidity*, has no connection or relation to the expression, *lime requirement*, in the sense in which the latter expression has been used in the past.

The writer confesses that he does not clearly understand what MacIntire means by *continued lime requirement*. It has not been possible to find a description of a laboratory method for the determination of this so-called *continued lime requirement* and hence had the writer appropriated the expression *continued lime requirement* in place of *latent acidity*, or stated that the two expressions mean the same thing, he would again have been open to serious criticism.

Further than mentioning that MacIntire had described a method in which a solution of  $\text{CaCO}_3$  in carbonated water is used, the writer purposely avoided either favorable or unfavorable comments. Since MacIntire did not present data, the relation of *immediate lime requirement* to *active soil acidity* could not be intelligently discussed at that time. The field was left clear, and as far as the present writer is concerned, MacIntire should have little trouble in getting full recognition for the merits of his work.

MacIntire states that he is unable to find in the writer's article in *THIS JOURNAL*, 8 (1916), 341, any data which indicate that soil acidity is due to true acids and not selective ion adsorption by colloids. The writer believes that this is entirely possible. For further explanations the reader is referred to an article by the writer entitled "The Cause and Nature of Soil

Acidity with Special Regard to Colloids and Adsorption," *Jour. Phys. Chem.*, **20** (1916), 457.

In the past several theories have been advanced regarding the nature of soil acidity; numerous methods have been proposed for determining a part or the whole of the acidity; and various names have been proposed for designating this or that part or kind of the acidity. MacIntire has seen fit to use the terms *immediate* and *continued lime requirement* for designating what he believes are certain soil conditions; the writer has seen fit to use the terms *active* and *latent* soil acidity for what he believes designate certain other soil conditions; and undoubtedly investigators in the future will see fit to use still other terms for designating what they may think are certain kinds of soil acidity, for it seems quite certain that no one as yet has a monopoly on the ideas regarding soil acidity or names that are suitable for designating certain aspects or phases of this subject. It seems reasonable to believe that investigators of this subject in the future will be as versatile and ingenious as those of the past.

In conclusion, the writer wishes to state that he has always entertained a high regard for the work of MacIntire and his associates and hopes this may continue in the future.

MADISON, WISCONSIN  
June 20, 1916

E. TRUOG

#### NOTE REGARDING DETERMINATION OF ALKALINITY OF ASH IN ANALYSES OF ORGANIC MATERIALS

It is frequently recommended that the alkalinity of ash of various food materials be determined in order to gain an idea as to the nature of the ash and the probability of adulteration of the sample.

In this connection there is room for considerable error in that sodium chloride may be dissociated, the chlorine driven off and the sodium appear at the end as sodium carbonate. Indeed, if care is not taken to avoid too high temperature or too prolonged heating all the chlorine may be thus driven off and the alkalinity of the ash is then no criterion as to organic combination of elements.

That chlorine is lost is shown by the following results obtained on corn syrup:

Sample.	Per cent chlorine by titration.	PER CENT CHLORINE IN ASH	
		Ashed with excess $\text{Na}_2\text{CO}_3$ .	Ashed straight
No. 1.....	0.180	0.180	0.065
No. 2.....	0.185	0.185	0.070
No. 3.....	0.190	0.190	0.071

In order to observe the effect of ashing pure granulated cane sugar to which a small percentage of salt had been added the following tests were made: Ten grams sugar was ashed with 0.025 g. salt (1 cc. of solution containing 2.5 g.  $\text{NaCl}$  in 100 cc.).

A—Straight ignition at lowest heat practicable.

B and C—Charred, extracted with hot water, char ashed, extract added, evaporated and heated to redness.

D—A few drops of sulfuric acid added and then sample ignited as A

Test:	A	B	C	D
Ash (added $\text{NaCl}$ ).....	0.25%	0.25%	0.25%	0.25%
Ash found.....	0.18	0.20	0.22	0.24
Alkalinity of ash as $\text{Na}_2\text{CO}_3$ .....	0.12	0.20	0.19	0.03

These results illustrate the point made above, *viz.*, that too much weight should not be placed on alkalinity of ash when it is possible that chlorides of the alkalies may have been present in the original material.

CLINTON SUGAR REFINING COMPANY  
CLINTON, IOWA, April 24, 1916

A. P. BRYANT

## PERSONAL NOTES

The Illuminating Engineering Society will hold a lecture course at the University of Pennsylvania, Philadelphia, from September 21 to 28, inclusive, immediately following the Annual Convention of the Society, to be held in that city.

This is the second time in its history that the Illuminating Engineering Society has decided to conduct a series of lectures, the first having been held in the fall of 1910, in cooperation with the Johns Hopkins University, Baltimore. Whereas the 1910 course emphasized the *science* of illumination, the new course will emphasize the *art* of illumination. This course will include about twenty lectures by men selected on account of their qualifications, to deal authoritatively with the several phases of the subject. The preliminary list of lecture subjects will appear in the September issue of *THIS JOURNAL*. Associated with the lectures will be an exhibition, at the University of Pennsylvania, of the latest developments in illuminating appliances, together with novel applications of light. In connection with the lecture course there will be organized an inspection tour which will include visits to manufacturing establishments, laboratories, lighting companies and notable installations. The price of tickets, which include admission to all lectures and functions connected therewith, has been fixed at \$25.00. The *Chairman* of the Sub-committee on Publicity of the Illuminating Engineering Lecture Course, is Mr. H. K. Mohr, Philadelphia Electric Company, Tenth and Chestnut Streets, Philadelphia.

The 1916 Directory of the American Chemical Society was issued July 1st. Members of the Society can secure copies by request to the Secretary, accompanied by twenty-five cents, and the statement that "The Directory will not be loaned or disposed of to any firm or individual for advertising purposes." This issue is revised to June 1, 1916, and shows a membership of 8057. The officers of the Society, of the divisions,

and of the local sections are listed separately on the first pages. Corporation members, honorary members, and life members are grouped separately immediately following the officers.

The National Fertilizer Association elected the following officers at their 23rd Annual Convention held in Hot Springs, Va.: *President*, Horace Bowker, New York City; *Vice-President*, W. D. Huntington, Baltimore; *Treasurer*, Irvin Wuichet, Dayton, Ohio (relected); *Secretary*, W. G. Sadler, Nashville, Tenn. (relected); *Assistant Secretary*, John D. Toll, Philadelphia.

The United States Civil Service Commission announces the following open competitive examinations: *Assistant Physicist* (Male) *Qualified in Physical Metallurgy*, on August 23, 1916; *Junior Chemist*, Departmental Service, and *Laboratory Apprentice* (Male), Bureau of Standards, on September 13, 1916; *Laboratory Assistant* (Male), Bureau of Standards, on October 11, 1916. Further information may be had from the U. S. Civil Service Commission, Washington, D. C.

The Thirtieth General Meeting of the American Electrochemical Society will take place this fall, in New York City, in the week of the Second National Exposition of Chemical Industries. Sessions will be held at the Chemists' Club, 52 East 41st Street, on September 28, 29 and 30, 1916.

Mr. F. L. Craddock has been appointed manager of the New York office of The Pfaunder Company, 110 West 40th Street, to succeed Mr. George M. Kendall, a notice of whose death appeared in the July issue of *THIS JOURNAL*. Mr. Craddock has long been associated with The Pfaunder Company, both as erection engineer and as salesman, and enjoys a wide acquaintance among the trade.



Mr. R. B. Kilmer has been appointed manager of the Chicago office of The Pfaunder Company, 1001 Schiller Building. Since casting his lot with The Pfaunder Company, Mr. Kilmer has been continually associated with the Chicago office and is well known to the Middle Western trade.

The following officers were elected by the American Society for Testing Materials at their annual meeting held recently in Atlantic City, N. J.: *President*, A. A. Stevenson, Philadelphia; *Vice-President*, S. S. Voorhees, Washington, D. C. *Executive Committee*: W. H. Bassett, Waterbury, Conn.; John Brunner, Chicago; G. W. Thompson, New York City; and F. E. Turneure, Madison, Wis.

Mr. Ralph L. Fuller, vice-president of Harshaw, Fuller & Goodwin, manufacturers of chemicals, has been elected president of the Cleveland Chamber of Commerce. Mr. E. R. Grasselli, second vice-president and treasurer of the Grasselli Chemical Company, is vice-president of the Chamber.

Prof. Frank H. Thorp, Massachusetts Institute of Technology, has resigned his assistant professorship of industrial chemistry and expects to devote himself in the immediate future to private business.

We learn from *The Engineering and Mining Journal* that Dr. Henry M. Howe, emeritus professor of metallurgy in Columbia University, has been appointed honorary vice-president of the Iron and Steel Institute of Great Britain. This distinction is held by only two other persons: Georgio E. Falck, of Italy, and D. Tschernoff, of Russia.

The University of Cincinnati, on June 19th, conferred the honorary degree of doctor of science on Prof. John Uri Lloyd, known for his contributions to chemistry and pharmacy.

In order to improve increased manufacturing space for the well-known Lee puncture-proof pneumatic tires, the Lee Tire & Rubber Company has just placed a contract with John W. Ferguson Company, of New York City and Paterson, N. J., for another building at their Conshohocken plant. The building measures 80 ft. by 120 ft. in plan and will for the present contain but two stories. The foundations and reinforced concrete columns on the first floor are designed, however, for several additional stories, with the idea of probable expansion in view. H. M. Haven and W. W. Crosby, of Boston, drew up the plans and specifications.

Dr. A. D. Emmett, assistant chief in animal nutrition, of the Illinois Agricultural Experiment Station at the University of Illinois, has accepted the position of research biological chemist in the Research Laboratory of Parke, Davis & Company, Detroit, Michigan. Dr. Emmett will assume his new duties on September 1st.

Richard K. Meade, chemical, mechanical and industrial engineer, Baltimore, announces that owing to need for increased facilities, he has removed his offices from 202 North Calvert Street to The Law Building, Courtland Street, Baltimore.

Frank H. Probert, a graduate of the Royal School of Mines in London, and for the past twenty years engaged in consulting mining engineering practice, has been appointed professor of mining in the University of California, as successor to the late Prof. Samuel Benedict Christy.

Prof. Arthur Green, F.R.S., lately of the tinctorial chemistry chair at Leeds University, England, has accepted the post of director of the research department of Messrs. Levinstein, Ltd., aniline dye manufacturers, Blackley, Manchester.

The Chemical Society, London, has removed from its list of honorary and foreign members the names of enemy aliens.

The employees of the Joseph Dixon Crucible Company, who joined the National Guard prior to its being called by the President and subsequently sworn into the Federal Service in June, 1916, will receive full pay while away doing military duty. These men will have their places kept open for them. This provision holds good until future developments make it necessary to change or modify it.

Herman & Herman, Inc., New York manufacturers and jobbers of chemicals, announce the removal of their offices, on account of increased business, to more spacious quarters, in the Robinson Building, 6 Church Street, cor. Liberty Street, New York City.

Mr. Henry Brunner, of Messrs. Brunner, Mond & Company, Ltd., died at his residence in Liverpool, England, on June 17th at the age of 78 years.

The new chemical laboratories recently erected in connection with Oxford University, England, were opened at the beginning of June.

Charles W. H. Kirchhoff, of New York City, editor-in-chief of *The Iron Age* from 1889 until 1910, died on July 22nd at his summer home, North Asbury Park, New Jersey, in his sixty-fourth year. Mr. Kirchhoff was the special agent of the U. S. Geological Survey for the collection of statistics of the production of lead, copper and zinc from 1883 to 1906. He was prominent for years in the mining industry, being at one time president of the American Institute of Mining Engineers. He was a member of the American Iron and Steel Institute, the Iron and Steel Institute of Great Britain, the American Society of Mechanical Engineers, the Verein Deutscher Eisenhuettenleute, the Century and Engineers' Clubs of New York City, and an honorary member of the Franklin Institute.

Dr. Leo H. Baekeland, of Yonkers, N. Y., and Prof. Julius Stieglitz, of the University of Chicago, were given the honorary degree of doctor of chemistry by the University of Pittsburgh at its recent commencement.

The Annual General Meeting of the Society of Chemical Industry was held in the hall of the University Union, Edinburgh, Scotland, on July 19, 1916.

Dr. William Simon, professor of chemistry at the College of Physicians and Surgeons, Baltimore, died at Eaglesmere, Pa., on July 19, 1916. He was born in Germany in 1844, and came to this country in 1870. The following year he opened the first chemical laboratory for instruction in Baltimore. Dr. Simon was a professor of chemistry in the Maryland College of Pharmacy from 1872 to 1902, in the College of Physicians and Surgeons, Baltimore, since 1880, and in the Baltimore College of Dental Surgery since 1888.

The American Institute of Mining Engineers extend an invitation to the members of the American Chemical Society to accompany them on their trip to the Southwest in connection with the Arizona Meeting of the Institute to be held on September 18-25, 1916. It is planned to make a special train tour of the Arizona Mining Districts and Grand Canyon. A pamphlet containing the itinerary and other information may be obtained from Mr. Bradley Stoughton, *Secretary*, American Institute of Mining Engineers, 29 West 39th Street, New York City.

The<sup>1</sup> Hoskins Manufacturing Company announce that the address of their Boston office has been changed from 613 Unity Building, 185 Devonshire Street, to 445 Tremont Building, 73 Tremont Street. The office will continue to be in charge of Mr. J. E. Hines.

The Sarco Company, Inc., New York, have appointed Newton-Johnson, sales engineers, as sales representative in Wisconsin and the northern peninsula of Michigan.

# GOVERNMENT PUBLICATIONS

By R. S. MCBRIDE, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

## PUBLIC HEALTH SERVICE

**Bread as a Food** CARL VOEGTLIN, M. X. SULLIVAN AND C. N. MYERS. Public Health Reports, 31 (April 14, 1916), pp. 935-43. The changes in the vitamin content of bread as related to the nutritive value are discussed with reference to the occurrence of pellagra. The following conclusion is reached: "The fact that the above-mentioned influences, which have undoubtedly reduced the vitamin content of the diet, made themselves felt a relatively short time before the rapid increase in the pellagra incidence in this section of the country, furnishes considerable evidence in favor of the vitamin-deficiency theory of pellagra."

**Establishments Licensed for the Propagation and Sale of Viruses, Serums, Toxins, and Analogous Products.** Public Health Reports, 31 (April 14, 1916), pp. 943-8. This is a list of establishments holding licenses under the Treasury Department for traffic in the above-mentioned articles.

**Some Fallacies Regarding Phenol.** MARTIN I. WILBERT. Public Health Reports, 31 (April 28, 1916), pp. 1046-51. This is a review with reports of observations on the influence of ethyl alcohol on the germicidal and on the toxic properties of phenol. "In conclusion, it may be again noted that the experimental work clearly shows that the addition of ethyl alcohol to phenol not only increases the solubility of phenol in water, but also increases rather than diminishes the antiseptic value of the resulting solution. Ethyl alcohol can be used to advantage as a substitute for glycerine in making antiseptic solutions of phenol.

"The experiments with animals clearly show that the addition of ethyl alcohol to solutions of phenol in water does not, in any way, inhibit the toxic action of phenol, but rather tends to facilitate absorption and thus hasten death."

**The Effect of Alcohol or Glycerin on the Toxicity of Phenol as Shown by Inoculations into White Mice.** LISTON PAINE. Public Health Reports, 31 (April 28, 1916), pp. 1052-4. This is an abstract of a report by this author.

**Pellagra: Laboratory Examinations in Connection with the Disease.** J. R. RIDLON. Public Health Reports, 31 (May 19, 1916), pp. 1231-41.

**Public Health Administration in Florida.** CARROLL FOX. Public Health Reports, 31 (June 2, 1916), pp. 1359-1407. This is a description of the administrative methods, personnel, arrangements, and activities of the Florida State Board of Health. It is of interest to administrative officials particularly.

**Cyanide Gas for the Destruction of Insects.** R. H. CREEL AND F. M. FACET. Public Health Reports, 31 (June 9, 1916), pp. 1464-76. This work has special reference to mosquitoes, fleas, body lice, and bedbugs and it also discusses the procedure for making cyanide fumigation.

## SANITARY LEGISLATION

**Manufacture or Storage of Acid Drinks and Foodstuffs in Zinc Lined and Galvanized Metal Containers.** Regulation of the Indiana State Board of Health, adopted July 2, 1915.

It specifically prohibits the use of zinc lined or galvanized metal containers with citric, tartaric or vegetable acids which will dissolve zinc.

**Adulterated or Misbranded Drugs.** New York City Department of Health regulation, adopted October 26, 1915, amending Section 116, which defines the terms "drugs," "adulterated," and "misbranded."

**Names of Ingredients of Proprietary Medicines to be Registered.** Regulation of the New York City Department of Health, adopted October 26, 1915, amending Section 117, which prescribes rules for the registration of composition of proprietary medicines.

**Regulation for the Registration of Proprietary Medicines.** New York City Department of Health regulation, as amended December 21, 1915. This gives further rules as to the registration of proprietary goods.

**Production, Care and Sale of Milk and Cream.** The following regulations on this general subject have been adopted recently including in each case definitions of the minimum quality of milk, cream, skimmed milk, and other milk products which are required in the localities affected. The page numbers in parenthesis refer to pages of Volume 31 of the Public Health Reports:

1—Hackensack, N. J. Regulation of the Board of Health, adopted December 28, 1915. (1115).

2—Leominster, Mass. Regulation of the Board of Health, adopted September 29, 1915. (1116).

3—Jackson, Mich. Ordinance, adopted April 27, 1915. (1222).

4—Lackawanna, N. Y. Ordinance, adopted February 1, 1915. (1276).

5—Kansas City, Kansas. Ordinance 13208, adopted July 29, 1915. (1338).

6—New York City Department of Health Regulation, adopted December 21, 1915, amending Section 155 of the Sanitary Code. (1347).

7—Portland, Oregon. Ordinance 30491, adopted May 26, 1915. (1507).

8—Portland, Oregon. Ordinance 30554, adopted June 10, 1915, defines buttermilk. (1512).

9—Sacramento, California. Ordinance 208, as amended August 19, 1915. (1515).

## GEOLOGICAL SURVEY

**Relation of the Wissahickon Mica Gneiss to the Shenandoah Limestone and Octoraro Schist of the Doe Run and Avondale Region, Chester County, Pennsylvania.** ELEANORA F. BLISS AND ANNA I. JONAS. Professional Paper 98-B, from Shorter Contributions to General Geology, pp. 9-34. Published May 20, 1916.

**Mineralogic Notes. Series 3.** WALDEMAR T. SCHALLER. Bulletin 610. 164 pp. "The results of the smaller, independent pieces of mineralogic research work carried out by the writer in the chemical laboratory of the United States Geological Survey from July 1, 1911 to December 31, 1913, are here assembled."

The following articles varying from a few pages to 35 pages each make up this bulletin: Koechlinite (bismuth molybdate); inyoite and meyerhofferite, two new calcium borates; kycubite, a new mineral; a dimorphous form of variscite; the crystallography of variscite; schneebergite; romeite; the natural antimones and antimonates; velardenite, a new member of the melitite group; the melitite group; the composition of cebolite; the crystallography of thaumasite; the chemical composition of tremolite; new occurrences of some rare minerals; gigantic



crystals of spodumene; the probable identity of mariposite and alurgite; the ambygonite group of minerals—fremontite (=natrambygonite); the crystallography of fremontite; the chemical composition of nephelite; large crystals of bloedite; alunite from Marysvale, Utah; the composition and relations of custerite; the composition of hodgkinsonite; crystals of pisanite from Ducktown, Tenn.; the refractive indices of strengite; the calculation of a mineral formula.

**Contributions to Economic Geology, 1915. Part I—Metals and Nonmetals Except Fuels.** F. L. RANSOME AND HOYT S. GALE. Bulletin 620. 360 pp. This bulletin is made up of 17 short articles, most of which have been previously announced in *THIS JOURNAL*.

**Geology and Coal Resources of Castle Valley in Carbon, Emery, and Sevier Counties, Utah.** CHARLES T. LUPTON. Bulletin 628. 86 pp.

**Natural Gas Resources of Parts of North Texas.** Bulletin 629. 125 pp. This bulletin includes the following three articles which report on work done in coöperation with the cities of Dallas and Fort Worth:

"Gas in the Area North and West of Fort Worth," by EUGENE WESLEY SHAW; "Gas Prospects South and Southeast of Dallas," by GEORGE CHARLTON MATSON; "Notes on the Gas Fields of Central and Southern Oklahoma," by CARROLL H. WEGEMANN.

**Geology and Underground Water of Luna County, New Mexico.** N. H. DARTON. Bulletin 618. 186 pp. This report includes a discussion of the mineral resources, the quality of water, and the general geological conditions of the district. Rock and mineral analyses from the region are also reported.

**The Caddo Oil and Gas Field, Louisiana and Texas.** GEORGE CHARLTON MATSON. Bulletin 619. 62 pp. Paper, 30 cents. The history, physiography, geology, and oil and gas resources of this region are discussed in detail.

**A Reconnaissance in Palo Pinto County, Texas (with Special Reference to Oil and Gas).** CARROLL H. WEGEMANN. Bulletin 621-E, from Contributions to Economic Geology, 1915, Part II, pp. 51-9. Corrected edition published April 17, 1916. This report includes a discussion of the history and development, topography, stratigraphy and report on tests for oil and gas. It recommends an exploration at a particular point by the drilling of a well. According to the results on this well the general conditions in the region can be interpreted.

**The Atlantic Gold District and the North Laramie Mountains.** A. C. SPENCER. Bulletin 626. 85 pp. This is a group of papers on conditions in Freemont, Converse, and Albany Counties, Wyoming.

**Ground Water in San Joaquin Valley, California.** W. C. MENDENHALL, R. B. DOLE AND HERMAN STABLER. Water Supply Paper 398. 310 pp. and numerous plates. The third section of this report (by R. B. Dole) which occupies over 100 pages is on the quality of water found in this region. It discusses in considerable detail the important question of quality, describes methods for collection of water samples and methods for field and laboratory assay, gives standards for water classification, and discusses the importance of various characteristics and methods of purification of water for different applications, such as boiler use, potable water, and others. Much of the discussion is of general interest to anyone concerned with the testing, purification, or industrial application of water supplies. Many analyses of water from this district are reported.

**Ground Water in the Hartford, Stamford, Salisbury, Willimantic and Saybrook Areas, Connecticut.** HERBERT E. GREGORY AND ARTHUR J. ELLIS. Water Supply Paper 374. 150 pp. and numerous plates and maps. This report is the result of an extended investigation made jointly by the United States Geological Survey and the Connecticut Geological and Natural

History Survey for the purpose of obtaining information as to the quantity and quality of water available in various parts of the State of Connecticut for municipal and private uses. The data presented are largely of local interest and include many analyses of water from these districts. The general method of attack upon the problem is of wider interest.

**Chromic Iron Ore in 1915.** J. S. DILLER. Separate 1, from Mineral Resources, 1915, Part I, pp. 1-6. Published April 10, 1916. "The production of chromic iron ore or chromite in the United States in 1915 amounted to 3,281 long tons valued at \$36,744, a gain of 2,690 tons and of \$28,029 over 1914. From 1880 to 1915, inclusive, the average annual production has been 1,229 tons, and the average price per ton has been \$14.82.

"The total imports of chromic iron ore in 1914 were 74,686 long tons, the maximum since 1908, valued at \$655,306. The imports in 1915 as compared with those in 1914 increased 1,769 long tons in quantity and \$124,755 in value, so that the average price per long ton increased from \$8.77 to \$10.20 in 1915.

"A fair price for imported ore in December, 1915, was \$25 to \$35 a ton for 50 per cent ore in full cargoes of about 7,500 tons. The retail prices ran as high as \$45 a ton, and one lot of 2 tons was imported at \$125 a ton. This was ground and packed in casks.

"The price at which chromic iron ore was sold on the Pacific coast during 1915 ranged from \$11 to \$18 a ton f. o. b. cars at point of shipment. On ore that contains more than 50 per cent chromic oxide a premium of 50 cents a ton is paid for each additional per cent unit of chromic oxide. The silica permissible in 50 per cent ore is limited to 8 per cent, and a penalty of 50 cents a ton is imposed for each additional unit in excess of that quantity.

"The price of bichromate of soda on January 1, 1915, was 4 $\frac{3}{4}$  to 5 cents a pound, varying with the quantity, and for bichromate of potash about 10 cents a pound. There has been a continuous advance in the price of these commodities since the spring of 1915, caused by the increase in the prices of raw materials and the uncertainty of receiving them and also by the unprecedented demand for bichromates, a demand due to the unusual conditions abroad. Domestic manufacturers are shipping bichromates freely to foreign countries, and owing to the lack of coal-tar dyes there is a large temporary increase in the use of bichromates in the textile industry at home.

"The price of chrome brick fluctuated during 1915 from \$50 to \$90 a thousand for standard sizes, and on account of freight is usually \$2.50 to \$3 a ton higher at inland cities than at the seaboard."

**Contributions to the Hydrology of the United States.** NATHAN C. GROVER. Water Supply Paper 375. 180 pp., and numerous plates. This is a consolidation of seven separate articles relating to water supply conditions. Only those portions in which water analyses are reported are of chemical interest. Such analyses are given only for the following districts: Sacramento Valley, California, Paradise Valley, Arizona, and Lasalle and McMullen counties, Texas.

**Fuel Briquetting in 1915.** C. E. LESHER. Separate 1, from Mineral Resources, 1915, Part II, pp. 1-6. Published May 6, 1916. "Little change was recorded in the fuel-briquetting industry in 1915. The manufacture of this type of fuel is still in its infancy in the United States and probably many years will elapse before it assumes large proportions. The production in 1915 amounted to about 222,000 short tons, valued at about a million dollars, and although there was a decrease, as compared with 1914, of 11 per cent in quantity and 10 per cent in value, the output exceeded that of all years prior to 1914."

**Sand-Lime Brick in 1915.** JEFFERSON MIDDLETON. Separate 2, from Mineral Resources, 1915, Part II, pp. 7-8. Published May 4, 1916. "The increase in the quantity of sand-lime brick

sold in 1915 over 1914 was 7,014,000 bricks, or 4 per cent, and the increase in value was \$76,592, or 7 per cent."

**Fuller's Earth in 1915.** JEFFERSON MIDDLETON. Separate 3, from Mineral Resources, 1915, Part II, pp. 9-12. Published May 6, 1916. "The fuller's earth industry continued to show progress in 1915, the product marketed increasing in both quantity and value. The increase in quantity was 6,920 short tons, or 17 per cent, and in value \$85,573, or 21 per cent, over 1914, the year of largest production and value prior to 1915. Imports of fuller's earth decreased in 1915, compared with 1914, 22 per cent in both quantity and value. Almost from the inception of the industry in this country the domestic production and value and the average price per ton have exceeded those of imports. In 1915 the quantity of domestic earth marketed was more than twice as great as that imported, the value of the domestic output was more than three times that of the imports, and the average price per ton of domestic earth was \$2.37 (nearly a third) more than that of the imported earth.

"Fuller's earth obtains its name from its original use in fulling cloth. Little domestic earth is now used in this country for that purpose, the principal use being in bleaching, clarifying, or filtering fats, greases, and oils. It is also used in the manufacture of pigments for printing wall papers, for detecting certain coloring matters in some food products and as a substitute for talcum powder."

**Geology and Ground Waters of Northeastern Arkansas.** LLOYD W. STEPHENSON AND ALBERT F. CRIDER. Water Supply Paper 399, with supplement discussing the **Chemical Character of the Water** by R. B. DOLE. 309 pp. The interesting section of the publication from the chemical standpoint is the supplement which includes a discussion of the characteristics of waters which are desirable for various uses, describes the treatment of the characteristic water of this region, and tabulates numerous analyses of these supplies.

**Petroleum Withdrawals and Restorations Affecting the Public Domain.** MAX W. BALL. Bulletin 623. 427 pp., with numerous large maps. Paper, \$1.10. This is a summary with accurate copies of orders of withdrawal, restoration, modification and classification, together with certain correspondence bearing on these questions, as affecting the policy of petroleum lands in the Public Domain.

**Some Manganese Mines in Virginia and Maryland.** D. F. HEWITT. Bulletin 640-C, from Contributions to Economic Geology, 1916, Part I, pp. 37-71. Published June 22, 1916. The minerals and nature of deposits with suggestions as to quantity, treatment, and handling of these ores in this district are discussed in considerable detail.

**Molybdenite and Nickel Ore in San Diego County, California.** F. C. CALKINS. Bulletin 640-D, from Contributions to Economic Geology, 1916, Part I, pp. 73-82. Published July 8, 1916. This report discusses the occurrence of molybdenite from the standpoint of further prospecting. It suggests the possibility of further development that will warrant commercial operations, but prospectors are warned against being too optimistic because of the rich showings at certain points on two accounts *first*, because of the apparent strong showing of small deposits; and *second*, because of the uncertainty as to the continuity of deposits.

The section on nickel ore discusses the character of ore showing probable origin and mineral characteristics of the material found in this region. The direction in which to look for further ore bodies is suggested, but the uncertainty of the problem is clearly set forth.

**Ozokerite in Central Utah.** HEATH M. ROBINSON. Bulletin 641-A, from Contributions to Economic Geology, 1916, Part II, pp. 1-16. Published June 13, 1916. This bulletin includes a discussion of the history of the discovery and development of

ozokerite with sections on its composition and properties, tests, form and content of deposits, origin, and statistics of comparison with foreign fields, imports, production, etc. Methods of concentration and the uses of this mineral are also set forth.

**A Reconnaissance of the Archean Complex of the Granite Gorge, Grand Canyon, Arizona.** L. F. NOBLE AND J. FRED. HUNTER. Professional Paper 98-I, from Shorter Contributions to General Geology, 1916, pp. 95-113. Published July 7, 1916.

**Gold, Silver, Copper, Lead, and Zinc in the Eastern States in 1915.** Mineral Resources of the United States, 1915, Part I, pp. 7-20. Published June 7, 1916. "This section of the Mineral Resources report deals primarily with the mines of the Eastern States from which gold, silver, copper, lead, and zinc were produced in 1915. For convenience in the collection of statistics the zinc and copper mines of eastern Tennessee are grouped with the Eastern States.

"The total value of the output of gold, silver, copper, lead, and zinc in the Eastern States was \$29,968,372 in 1915, a notable increase of \$18,530,665, or nearly 158 per cent, over the production in 1914. The total value is distributed among the various metals as follows: Gold, \$224,250; silver, \$51,990; copper, \$3,285,229; lead, \$32,775; zinc, \$26,374,128.

"The great increase in value is due largely to the increased output of the zinc mines, and, of course, to the increase in price of all the metals except gold and silver."

The report is principally devoted to a review, by states, of production and mines statistics.

**Asbestos in 1915.** J. S. DILLER. Mineral Resources of the United States, Part II, pp. 13-18. Published May 24, 1916. "The United States marketed a domestic production of 1,731 short tons of asbestos in 1915, valued at \$76,952. As compared with the production of 1914, this represents a gain of 484 tons, or 39 per cent, in quantity, and of \$57,987, or 306 per cent, in value. The great increase in value was due to the high grade of the material produced.

"The average annual production of asbestos in the United States (for the last 26 yrs.) from 1890 to 1915, inclusive, has been 1,470 short tons, ranging from a minimum of 50 tons in 1893 to a maximum of 7,604 tons in 1911. In 1911 and 1912, when there was a large production in Vermont, the total value of the output exceeded that of the production in 1915. But on account of the high grade of the Arizona asbestos the average value per ton in 1915 was \$44.46, against \$15.77 and \$19.98, respectively, in 1911 and 1912.

"The principal source of the asbestos sold in the United States is in Quebec, Canada, where also prices are controlled. The average price in New York has been gradually rising, especially for the higher grades, and the rise continues. Early in April, 1915, No. 1 crude was selling as high as \$500 a ton, and No. 2 at \$300.

"The principal source of the world's supply of asbestos is Canada. The United States, being Canada's nearest neighbor and having every facility for intercourse, has naturally become the greatest importer of raw material from Canada and the largest manufacturer of asbestos products.

"Unmanufactured asbestos is admitted to the United States free, but manufactured asbestos is dutiable at from 25 to 40 per cent *ad valorem*.

"The imports of manufactured asbestos from Canada in 1915 were nearly 34 per cent greater than in 1914; but it is not certain how much of the imported material remained in the United States for consumption and how much was reshipped to other countries.

"It is of interest to note that practically all of the imported unmanufactured asbestos came from Canada, but that manufactured products of asbestos were imported from 10 countries."

**Slate in 1915.** G. F. LOUGHLIN. Mineral Resources of the United States, 1915, Part II, pp. 19-31. Published May 25, 1916.



"The depression which began to affect the slate industry in October, 1914, continued throughout the greater part of 1915, and the total value of slate sold in the latter year decreased 13 per cent. For the first time since 1901 the total value of slate sold fell below \$5,000,000. Roofing slate decreased 5 per cent in quantity and 10 per cent in value. For the first time since 1898 the number of squares sold was less than 1,000,000 and for the first time since 1900 their value fell below \$4,000,000. Mill stock decreased nearly 15 per cent in quantity and 17 per cent in value, the lowest value since 1908. Blackboard material and school slates ("other uses") decreased nearly 31 per cent."

**Fluorspar in 1915; with a Note on Cryolite.** ERNEST F. BURCHARD. Mineral Resources of the United States, 1915, Part II, pp. 33-41. Published June 5, 1916. "The year 1915 was a record year in the fluorspar industry in the United States, the output exceeding that of the next highest year, 1912, by more than 20,000 tons or nearly 18 per cent.

"The total quantity of domestic fluorspar reported to the Survey as sold in 1915 was 136,941 short tons, valued at \$764,475, an increase in quantity of 41,825 short tons and in value of \$194,434, representing nearly 44 per cent of the quantity and about 34 per cent of the value of the product marketed in 1914. The average price per ton for the whole country, all grades of fluorspar, gravel lump, and ground considered, was approximately \$5.58 in 1915, compared with \$5.99 in 1914, a decrease of nearly 7 per cent. This value represents the selling price on board cars or barges at railroad or water shipping points; and with reference to the product from Colorado, New Mexico, and New Hampshire, the price reported for much of the spar includes the cost of a long wagon haul—\$1.50 to \$3 a ton. In Illinois the principal producing mines are near river transportation and many of the mines reporting from Kentucky are near a railroad, so that the cost of long wagon hauls has not entered to an important extent into the reported value of the fluorspar from those States.

"The imports of fluorspar into the United States entered for consumption in 1915 were 7,167 short tons, valued at \$22,878, as compared with 10,205 short tons, valued at \$38,943, in 1914. This represents a decrease of nearly 30 per cent in quantity and of about 41 per cent in value. The price assigned to the imports in 1915 averaged \$3.19 a ton, as compared with \$3.82 a ton in 1914, a decrease of 63 cents a ton or about 16.5 per cent. The imports of fluorspar in 1915 were equivalent to about 6.3 per cent of the domestic production of gravel spar, as compared with nearly 13 per cent in 1914.

"The market for the bulk of the fluorspar sold in the United States depends on the steel industry, and the demand for fluorspar fluctuates with the rise and fall in the production of steel. Gravel spar is consumed as a flux in basic open-hearth steel furnaces and to a smaller extent in other metallurgical operations. In both 1914 and 1915 the sales of gravel spar constituted between 83 and 84 per cent of the total marketed output of domestic fluorspar. Fluorspar is used also as a flux in blast furnaces, iron foundries, and in silver, copper, and lead smelters; in the manufacture of fluorides of iron and manganese for steel fluxing; in the manufacture of glass, enameled, and sanitary ware, and of hydrofluoric acid; in the electrolytic refining of antimony and lead; and in the production of aluminum. In the last process fluorspar is reported to be fused with bauxite and soda ash into a so-called artificial cryolite, to which more bauxite is added, and from this mixture aluminum is extracted in the electric furnace.

"No cryolite is produced in the United States, the entire supply used in this country being imported from Greenland.

"The quantity of cryolite reported to have been imported for consumption in the United States in 1915 was 3,940 long tons, valued at \$82,750, as compared with 4,612 long tons, valued at \$94,424, in 1914. The average price per ton declared in 1915

was apparently \$21 as compared with \$20.47 in 1914. Cryolite is now imported free of duty."

#### BUREAU OF STANDARDS

**Determination of Volatile Thinner in Oil Varnish.** E. W. BOUGHTON. Technologic Paper 76. 6 pp. Paper, 5 cents. "It has been shown that any of the methods described above give results which, though only approximate from a scientific standpoint, are satisfactorily accurate for practical purposes. The volatilization of the thinner, in some cases turpentine and in others mineral spirits, from drying films of freshly prepared varnishes was practically complete in 2 hrs. at room temperature (30 to 35° C.)."

**Regulation of Electrotyping Solutions.** ANONYMOUS. Circular 52, 2nd Ed. 42 pp. Paper, 10 cents. "The principal new information in this edition is that relating to the study of copper electrotyping baths, from which certain specific recommendations have been made. There are also included in this edition tables giving the density of acid copper sulfate solutions and tables showing the weight and thickness of the copper deposited from such solutions by definite current densities in specified periods of time."

#### CONGRESSIONAL COMMITTEES

The following Congressional Committee reports contain material of chemical interest:

**Uniform Standards of Classification for Cotton.** House Report 777, to accompany House Bill 15913 which proposes to authorize the Secretary of Agriculture to establish uniform standards of classification for cotton, etc.

**Mineral Resources of Certain National Forests.** House Report 772, 1 page. This report is to accompany House Bill 12885 which proposes to authorize the Secretary of Agriculture to permit prospecting, development, and utilization of mineral resources of certain national forest regions.

**Linseed Oil.** This is a Senate Report on hearings before the Sub-committee having in charge the Senate Bill 1289 which is intended to prevent manufacture, sale, or transportation of adulterated, mislabeled, or misbranded linseed oil, turpentine, or paint. 101 pages. Available only through the members of the United States Senate.

#### INTERNAL REVENUE COMMISSIONER

**Denatured Alcohol.** Treasury Decision 2326. This decision (Vol. 30, No. 18) gives formula No. 22 for denatured alcohol which is a special preparation for use in formaldehyde solutions. Available as a 1-page separate.

#### BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**Saving of Waste Paper Material.** ANONYMOUS. This is an unnumbered circular issued May 10th, describing methods for selecting, sorting, and disposal of waste paper, rags, and other paper-making material. It is of chemical interest only as indicating the sources and methods of handling waste materials which are useful in the paper trades.

**Statistical Abstract of the United States, 1915.** This is No. 38 in this series of annual publications. Available through the Superintendent of Documents, bound in paper, 50 cents. 740 pp. This publication is entirely tabular in nature consisting of summaries of statistics, among others including natural resources, agriculture, forestry, fisheries, manufacturing, mining, foreign and domestic commerce, consumption estimates, prices, financial statistics and other data collected by various Governmental agencies.

#### DEPARTMENT OF AGRICULTURE

The following articles in the Journal of Agricultural Research for May and June are of chemical interest:

**Test of Three Large-Sized Reinforced-Concrete Slabs under Concentrated Loading.** A. T. GOLDBECK and E. B. SMITH. Journal of Agricultural Research, 6 (May 8), 205-34.

**Effect of Climatic Factors on the Hydrocyanic-Acid Content of Sorghum.** J. J. WILLAMAN AND R. M. WEST. *Journal of Agricultural Research*, 6 (May 15), 261-272.

**Production of Clear and Sterilized Anti-Hog-Cholera Serum.** M. DORSET AND R. R. HENLEY. *Journal of Agricultural Research*, 6 (May 29), 333-338.

**Effect of Röntgen on the Tobacco, or Cigarette, Beetle and the Results of Experiments with a New Form of Röntgen Tube.** G. A. RUNNER. *Journal of Agricultural Research*, 6 (June 12), 383-389.

**Stimulating Influence of Arsenic upon the Nitrogen-Fixing Organisms of the Soil.** J. E. GREAVES. *Journal of Agricultural Research*, 6 (June 12), 389-416.

**Availability of Mineral Phosphates for Plant Nutrition.** W. L. BURLISON. *Journal of Agricultural Research*, 6 (June 26), 485-514.

**Legal Standards for Dairy Products.** ANONYMOUS. This is a revised summary issued May 1st, giving the legal standards for dairy products in force on July 1, 1915. The following products are listed for each state or major political division of the United States including insular possessions: Milk, skimmed milk, cream, butter, whole cream cheese, skimmed milk cheese, condensed milk, evaporated milk and ice cream.

**Farm Manures and Fertilizers.** Unnumbered leaflet of the States Relations Service which discusses the value, methods of handling, and proper application of farm manures and fertilizers. Summaries of the characteristic analyses, costs, and value of each typical fertilizer are of particular interest to the soil chemist.

#### COMMERCE REPORTS—JUNE, 1916

A number of plants yielding **dyes** are found in abundance in Ecuador. (P. 817.)

The manufacture of **aniline dyes** has been initiated at Amsterdam, Holland. (P. 833.)

The **beet sugar** industry of Canada shows a marked increase. (P. 865.)

A new **superphosphate** factory is to be erected in Holland. (P. 866.)

Exportation of **logwood** from Tabasco, Mexico, has greatly increased. (P. 890.)

A large assortment of **artificial dyes** is now being made in Japan. (P. 890.)

Considerable **tanning extract**, derived from mangrove bark and leaves is now being exported from Brazil. (P. 900.)

The important **vegetable oils** expressed in Marseilles are peanut, cocoanut, and palm kernel. (P. 922.)

Extensive deposits of **alunite**, containing about 5 per cent of potash, have been discovered on Vancouver Island, British Columbia. (P. 947.)

Data on the world's production of **fertilizers**, collected by the International Institute of Agriculture, include the figures for 1912 and 1913 for natural phosphates, basic slag, superphosphate, potash salts, sodium nitrate, calcium nitrate, ammonium sulfate, and calcium cyanamide. (P. 986.)

Among available sources of **alcohol** in the Philippines, are sugar beet, sugar cane, beet and cane molasses, cassava, potato cutts, sweet potatoes, maize, nipa sap and cocoa sap. Owing to the advance in the price of **gasoline** (to \$0.50 per gal.) the use of alcohol as motor fuel is increasing. (P. 988.)

The methods of manufacturing **sand-lime bricks** in Europe are described. (P. 996.)

**Phosphate** deposits containing about 20 per cent  $P_2O_5$  are found in Tonkin, Indo-China. (P. 1012.)

The **dyestuff** industry of Japan is developing rapidly, though

still hampered by lack of heavy chemicals and of a market for by-products. (P. 1016.)

The annual output of **zinc ores** from Japan has increased from 40,000 to 70,000 tons. A new glass factory, and an aluminum plant are nearing completion. (P. 1027.)

**Titanium salts** (oxalate or tartrate) in connection with tannic acid are being used extensively in England as mordants for yellow, orange, khaki color, etc., on cotton. (P. 1040.)

A new hydro-electric plant for both smelting and refining of **zinc** is being erected in Norway. (P. 1045.)

Efforts are being made by New Zealand to increase the market for **Kauri gum** in the United States. (P. 1073.)

The **rubber** industry of the Malay Peninsula is very prosperous. Much of the rubber is being sent directly to the United States instead of *via* England, as formerly. (P. 1091.)

Since Japan acquired Formosa in 1895, the annual **sugar** output of Formosa has increased from 75,000 to 350,000 tons. (P. 1121.)

**High-speed steel** is being made by a new process in England, without using any tungsten, molybdenum, cobalt, or vanadium. (P. 1127.)

The output of **copper** from the Rio Tinto mines shows a marked increase, much of the product, of copper, copper ore, and sulfur ore being shipped to the United States. (P. 1133.)

Considerable amounts of **zinc dust** are being exported from Japan to the United States. (P. 1149.)

The **bauxite** and **aluminum** industry of this country are very active, much of the metal being used in an explosive "ammonal" consisting of aluminum powder and ammonium nitrate. (P. 1151.)

A new **paper mill** is to be erected near Pernambuco, Brazil. (P. 1169.)

Considerable amounts of natural **dyes**, principally from India, South and Central America, are being used in Bradford, England. (P. 1176.)

The annual export of **chicle** from Venezuela to the United States is nearly \$1,000,000. (P. 1182.)

The **kelp** industry of British Columbia is being developed. (P. 1188.)

A Mond by-product plant, principally for the production of **ammonium sulfate** is being erected in South Africa. (P. 1191.)

Only one plant in France is now making **aniline dyes**, of which there is a great shortage. (Sup. 5d.)

#### SPECIAL SUPPLEMENTS ISSUED IN JULY, 1916

FRANCE, Havre, Grenoble, La	UNITED KINGDOM, Liverpool—19c
Rochelle, Nice, St. Etienne—5c	UNITED KINGDOM, Manchester—19f
FRANCE 5d	UNITED KINGDOM, Bradford—19g
NORWAY, Bergen, Stavanger—10a	CHILE—41a
SPAIN, Canary Islands—15a	PERSIA—57a

#### STATISTICS OF EXPORTS TO THE UNITED STATES

GRENOBLE, FRANCE— Sup. 5c	LIVERPOOL, ENGLAND —Sup. 19c	MANCHESTER, ENG— Land—Sup. 19f
Emery	Blood	Asbestos
Pterochrome	Bones	Dyestuffs
Ferrosilicon	Coal	Aniline
Ferromanganese	Copper	Carbolic acid
Ferrotungsten	Bone dust	Sodium cyanide
Monomethyl sulfate	Fibers	Naphthylamine
	Grease	Hides
LA ROCHELLE, FRANCE —Sup. 5c	Hides	Rubber
Cassia	Rubber	Indigo
Glue stock	Ferromanganese	Animal oils
Hides	Cocoanut oil	Vegetable oils
Sodium silicofluoride	Palm oil	Linoleum
	Soya oil	Paper
	Palm kernel oil	Paper stock
NICE, FRANCE—Sup. 5c	Whale oil	Zinc dust
Filter paper	Paper stock	BRADFORD, ENGLAND —Sup. 19g
Glassware		Aniline
BERGEN, NORWAY— Sup. 10a	CHILE—Sup. 41a	Antimony compounds
Aluminum	Argols	Dyes
Guanio	Beeswax	Potassium carbonate
Hides	Copper	Fibers
Cod liver oil	Glue	Grease and oils
Lubricating oil	Hides	Hides
Sugar	Potassium chloride	Paper
	Sodium nitrate	CANARY ISLANDS— Sup. 15a
PERSIA—Sup. 57a	Soap bark	Cochineal
Gum tragacanth	Rubber	Copper matte
Opium	Silver	Hides
	Zinc	Pumice
	Gold	



# BOOK REVIEWS

**A Student's Book on Soils and Manures.** By E. J. RUSSELL, D.Sc., Director of the Rothamsted Experiment Station, Harpenden. Cambridge Farm Institute Series, Cambridge: At the University Press, 1915. 190 pages of text; appendix on Soil Analysis; index; 34 illustrations. G. P. Putnam's Sons, New York City. Price, \$3.90.

The text of this book is written in an easy style, readily comprehended by a layman of quite scanty technical equipment. Experiments easily performed are suggested. The text is divided into three parts: An account of the soil, the control of the soil, and fertilizers. Anyone reading the book will undoubtedly acquire in easy fashion quite a comprehensive knowledge of the art of producing crops. Technical investigators will not always agree with Dr. Russell's statements of theory but cannot cavil at his manner of making them. Practical farmers and greenhouse men in America will probably dissent pretty strongly with some of the statements which are obviously made for English conditions and from English experience.

Quotations from American sources are fairly frequent and generous. Every one pretending to keep informed on scientific matters generally, as well as students of agriculture, should read the book. Dr. Russell's very unusual knowledge of the literature of agriculture is often in evidence and every chemist and agricultural investigator will probably find something new to himself in his reading of the book. The reviewer has done so times enough to make him feel he must read it again.

FRANK K. CAMERON

**Elementary Practical Metallurgy for Technical Students and Others.** By J. H. STANSBIE, B.Sc., F.I.C., Associate of Birmingham University, and Lecturer on Metallurgy in the Birmingham Municipal Technical School. 151 pages. J. and A. Churchill, London; P. Blakiston's Son & Company, Philadelphia. Price, \$1.40 net.

In the preface the author states that the book was prepared for the use of those who wish to obtain a practical knowledge of the common metals by means of a laboratory course. He first discusses furnaces and other apparatus, then takes up fuel, refractory materials, slags and fluxes, formation and reduction of oxides and of sulfides. This is followed by chapters on mechanical testing; non-ferrous metals and alloys; iron and steel; gold and silver.

The book is extremely elementary and "practical," and apparently written for work in a laboratory lacking modern equipment. A cut shows the wind furnace which is used for most of the work, even down to the manufacture of alloys of 50 g. To determine the calorific power of fuel the old Thompson calorimeter is used, and no other is mentioned.

For technical and night-school courses the book covers the ground in a very interesting way, and fills its purpose. The main criticism is in regard to the presentation of the subject of alloys. Their constitution ought either to have been omitted entirely, or else presented from the modern standpoint. As it is, solid solutions, eutectics, etc., are spoken of, but in such a way that the student cannot possibly obtain a correct idea of what an alloy is or the changes which take place during solidification and subsequent cooling. Such statements as "It is well known that the structure of copper-zinc alloys passes through a temperature range somewhat below a red heat. The metal becomes comparatively rotten and is readily broken up," or, "Some metals, though well mixed in the molten state, separate either partially or completely on solidification. This is due to the fact that one metal is soluble in the other in the

solid state only to a limited extent, or not at all; also to the absence of eutectics in the structure of the alloys" are misleading, to say the least.

There is still need for a book in practical metallurgy, apart from assaying, which is elementary, practical, and at the same time scientific.

WILLIAM CAMPBELL

**The Metallurgists' and Chemists' Handbook.** By DONALD M. LIDDELL, Consulting Metallurgical Engineer and sometime Managing Editor of *The Engineering and Mining Journal*. 603 pp. 1916. McGraw-Hill Book Co., Inc., New York and London. Price, \$4.00.

The scope of this handbook is indicated by the following table of contents:

SECTION	PAGES
I—Mathematics	1-52
II—Price and Production Statistics	53-74
III—Physical Constants	75-232
IV—Chemical Data	233-301
V—Sampling, Assaying and Analysis	302-338
VI—Ore Dressing	339-402
VII—Cyanidation	403-412
VIII—Fuels and Refractories	413-439
IX—Mechanical Engineering and Construction	440-474
X—General Metallurgy	475-582
XI—First Aid	483-488

The author has compiled tables of factors and constants that are indispensable to the practical worker and has arranged them as systematically as it is possible to arrange such a mass of heterogeneous material. To avoid clumsiness, many tables of more or less special character are of necessity omitted. For the most part the author has exercised considerable care and good judgment in the selection of his material. However, it is the reviewer's opinion that if the author had seen fit to include a table of organic compounds with their properties corresponding to the table of "The Properties of the Principal Inorganic Compounds," the usefulness of the book would have been increased, particularly at the present time when organic industrial chemistry is receiving so much attention.

Besides tables of factors and constants, much useful information of a general and varied character is given. For example, a list of seventeen flotation processes is given together with a brief description of each and the names of concerns using the same.

The volume is bound in a good flexible leather binding, the type is clear and legible, the paper of a good grade, though rather too transparent. The size is  $4 \times 7 \times \frac{3}{4}$  in. A complete workable index is given, thus making the material contained in the volume readily accessible. Altogether it is a very usable book either in the library or the plant.

As is almost invariably the case with first editions, errors are frequent. No attempt has been made to scan the book for errata, but those observed incidental to its use in the laboratory are here noted:

	Molecular Weight	Correction
P. 210—Ammonium Chromate, $(\text{NH}_4)_2\text{CrO}_4$	136.08	152.08
P. 221—Potassium Acetate, $\text{K}_2\text{C}_2\text{H}_3\text{O}_2$	137.22	$\text{KC}_2\text{H}_3\text{O}_2$ 98.13
P. 223—Sodium Acetate, $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$	175.27	136.08
P. 224—Sodium Sulfate, $\text{Na}_2\text{SO}_4$	119.07	142.06

P. 211—Ammonium phosphomolybdate. Formula given is  $(\text{NH}_4)_3\text{PO}_4 \cdot 10\text{MoO}_3 \cdot 3\text{H}_2\text{O}$ . The ratio of  $\text{P}_2\text{O}_5$  to  $\text{MoO}_3$  is 1 : 24 instead of 1 : 20.

The author has met a long-felt need among metallurgists and chemists for a handy reference book that is more than a collection of figures and tables.

A. A. BACKHAUS

# NEW PUBLICATIONS

By IRENE DeMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

**Alternating Current Phenomena.** C. P. STEINMETZ. 5th Ed. 8vo. Price, \$4.00. McGraw-Hill Book Co., New York.

**Canning of Fruits and Vegetables.** J. P. ZWALLA. 8vo. 226 pp. Price, \$2.50. John Wiley & Sons, Inc., New York.

**Chemistry in the Service of Man.** ALEXANDER FINDLAY. 8vo. 255 pp. Price, \$1.60. Longmans, Green & Co., New York.

**Chemists: Kelly's Directory of Chemists and Druggists, Including Manufacturing Chemists.** 843 pp. Price, 25 s. Kelly's Directories, Ltd., London.

**Coal Miners' Pocketbook.** 11th Ed. 16mo. 1200 pp. Price, \$4.00. McGraw-Hill Book Co., New York.

**Diesel or Slow-Combustion Oil Engine.** G. J. WELLS AND A. J. WALLIS-TAYLER. 8vo. 304 pp. Price, \$3.00. D. Appleton & Co., New York.

**Drainage: Textbook of Land Drainage.** J. A. JEFFREY. 12mo. 256 pp. Price, \$1.25. The Macmillan Co., New York.

**Engineering Applications of Higher Mathematics.** VLADIMIR KARAPETOFF. 8vo. Pt. 2, 3, 4, 5. Price, ea. \$0.75. John Wiley & Sons, Inc., New York.

**Engineering Training: The Principles of Apprentice Training with Special Reference to the Engineering Industry.** A. P. M. FLEMING AND J. G. PEARCE. 12mo. 202 pp. Price, \$1.20. Longmans, Green & Co., New York.

**Essences: Manual for the Essence Industry.** ERICH WALTER. 8vo. 427 pp. Price, \$4.00. John Wiley & Sons, Inc., New York.

**Explosives: Industrial Nitrogen Compounds and Explosives.** GEOFFREY MARTIN AND W. BARBOUR. 4to. 125 pp. Price, \$2.50. D. Appleton & Co., New York.

**Fertilizers: The Source, Character and Composition of Natural, Home-made, and Manufactured Fertilizers.** E. B. VOORHEES. Rev. Ed. 12mo. 365 pp. Price, \$1.50. The Macmillan Co., New York.

**Gas Engine Ignition.** E. B. NORRIS AND OTHERS. 8vo. 174 pp. Price, \$1.50. McGraw-Hill Book Co., New York.

**Heating and Ventilating Ducts: Practical Sheet Metal Duct Construction.** W. NEUBECKER. 8vo. 194 pp. Price, \$2.00. Sheet Metal Publishing Co., New York.

**Industrial Chemistry: Outlines of Industrial Chemistry.** F. H. THORP. 3rd Ed. 8vo. 660 pp. Price, \$3.75. The Macmillan Co., New York.

**Industrial Preparedness.** C. E. KNOEPEL. 12mo. 145 pp. Price, \$1.00. Engineering Magazine Co., New York.

**Inorganic Chemistry: Conférences de chimie minerale.** MARCEL GUICHARD. 2nd Ed. 8vo. 422 pp. Price, 15 fr. Gauthier Villars et Cie., Quai des Grands Augustins, 55, Paris.

**Limes and Cements.** E. A. DANCASTER. 12mo. 212 pp. Price, \$1.75. D. Appleton & Co., New York.

**Materials: Mechanical Handling and Storing of Materials.** G. F. ZIMMER. New Ed. 4to. 766 pp. Price, 42 s. Crosby Lockwood & Son, London.

**Mechanical Technology.** G. F. CHARNOCK. 8vo. 635 pp. Price, \$3.00, net. D. Van Nostrand Co., New York.

**Mineral Resources of Minas Geraes (Brazil).** 8vo. 100 pp. Price, \$2.00. Spon & Chamberlain, New York.

**Oil: Principles of Oil and Gas Production.** R. H. JOHNSON AND L. G. HUNTLEY. 8vo. 371 pp. Price, \$3.75. John Wiley & Sons, Inc., New York.

**Oil and Petroleum Manual for 1916.** W. R. SKINNER. 8vo. 257 pp. Price, 2 s., 6 d. W. R. Skinner, London.

**Organic Compounds: A Method for the Identification of Pure Organic Compounds. Vol. 2. Compounds of Order 2.** S. P. MULLIKEN. 8vo. 336 pp. Price, \$5.00. John Wiley & Sons, Inc., New York.

**Paper and Its Uses.** E. A. DAWE. 8vo. 162 pp. Price, \$1.50. D. Appleton & Co., New York.

**Power Transmission by Leather Belting.** R. T. KENT. 8vo. 114 pp. Price, \$1.25. John Wiley & Sons, Inc., New York.

**Sanitation: The Elements of Physiology and Sanitation.** L. J. RETTGER. 12mo. 389 pp. Price, \$0.80. A. S. Barnes Co., New York.

**Science: Laboratory Courses in General Science.** HERBERT BROWNELL. 12mo. 212 pp. Price, \$0.80. The Macmillan Co., New York.

**Steam Traction Engineering.** S. R. EICHINGER AND N. S. HUTTON. 8vo. 317 pp. Price, \$2.50. D. Appleton & Co., New York.

**Steels: British Standard Specifications for Wrought Steels.** 24 pp. Price, 7 s., 6 d. Crosby Lockwood & Son, London.

**Steel: The Metallurgy of Steel.** F. W. HARBORD AND J. W. HALL. 2 vols. 5th Ed. 568 pp. Price, 36 s. Chas. Griffin & Co., London.

**Tars: British Standard Nomenclature of Tars, Pitches, Bitumens and Asphalts.** 41 pp. Price, 5 s. Crosby Lockwood & Son, London.

**Water Power: The Modern Development of Water Power.** A. STEIGER. Price, 2 s. E. & F. N. Spon, London.

## RECENT JOURNAL ARTICLES

**Acetylene or Electricity.** A. G. RAKESTRAW. *Acetylene Journal*, Vol. 18 (1916), No. 1, pp. 21-22.

**Alcohol: Ethyl Alcohol from Wood.** F. W. KRESSMANN. *Metallurgical and Chemical Engineering*, Vol. 15 (1916), No. 2, pp. 78-82.

**Antimony: Determination of Antimony.** H. R. LAYNG. *Mining and Scientific Press*, Vol. 113 (1916), No. 2, pp. 57-58.

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**Blasting Practice in Chuquicamata, Chile.** H. W. MOORE. *Mining and Scientific Press*, Vol. 113 (1916), No. 2, pp. 60-61.

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**Turbines: Efficiency Tests of a 30,000 Kw. Cross Compound Steam Turbine.** H. G. STOTT AND W. S. FINLAY. *The Electric Journal*, Vol. 13 (1916), No. 7, pp. 335-339.

**Valves: New Valves for Regenerative Furnaces.** J. A. HERRICK. *Iron Trade Review*, Vol. 59 (1916), No. 2, p. 84.



# INORGANIC CHEMICALS

Acetate of Lime gray.....	100 Lbs.	7.00	@	7.05
Alum. lump ammonia.....	100 Lbs.	4.00	@	—
Aluminum Sulfate, high grade.....	Ton	65.00	@	70.00
Ammonium Carbonate, domestic.....	Lb.	9 1/2	@	10
Ammonium Chloride, gray.....	Lb.	10	@	15
Ammonium Phosphate, commercial, 98-100%.....	Lb.	—	@	—
Aqua Ammonium, 26°, drums.....	Lb.	5	@	5 1/2
Arsenic, white.....	Lb.	6 1/4	@	6 1/2
Barium Chloride.....	Ton	100.00	@	105.00
Barium Nitrate.....	Lb.	18	@	19 1/4
Barytes, prime white, foreign.....	Ton	—	@	—
Bleaching Powder, 35 per cent.....	100 Lbs.	4 1/2	@	4 3/4
Blue Vitriol.....	Lb.	8 3/4	@	9
Borax, crystals, in bags.....	Lb.	6 1/4	@	7
Boric Acid, powdered crystals.....	Lb.	11 1/4	@	12 1/2
Brimstone, crude, domestic.....	Long Ton	30.00	@	32.00
Bromine, technical, bulk.....	Lb.	2.40	@	2.50
Calcium Chloride, lump, 70 to 75% fused.....	Ton	26.00	@	28.00
Calcium Chloride, granulated.....	Ton	14.78	@	15.00
Caustic Soda, 74 per cent.....	Lb.	3 1/2	@	3 3/4
Chalk, light precipitated.....	Lb.	4 1/2	@	5 1/4
China Clay, imported.....	Ton	18.00	@	30.00
Feldspar.....	Ton	8.00	@	12.00
Fuller's Earth, foreign, powdered.....	100 Lbs.	80	@	1.05
Glauber's Salt, in bbls.....	100 Lbs.	65	@	70
Green Vitriol, bulk.....	100 Lbs.	1.25	@	1.50
Hydrochloric Acid, commercial, 18°.....	Lb.	2 1/2	@	2 3/4
Hydrochloric Acid, C. P., conc., 22°.....	100 Lbs.	2 3/4	@	3
Iodine, resublimed.....	Lb.	4.25	@	4.30
Lead Acetate, white crystals.....	Lb.	15 1/8	@	15 1/4
Lead Nitrate.....	Lb.	15 1/2	@	16
Litharge, American.....	Lb.	9 1/4	@	9 3/4
Lithium Carbonate.....	Lb.	97	@	98
Magnesium Carbonate.....	Lb.	19	@	22
Magnesite, "Calcedined".....	Ton	—	@	—
Nitric Acid, 36°.....	Lb.	7 1/4	@	7 1/2
Nitric Acid 42°.....	Lb.	8 1/4	@	—
Phosphoric Acid, sp. gr. 1.750.....	Lb.	30	@	31
Phosphorus.....	Lb.	—	@	—
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, casks.....	Lb.	37	@	38
Potassium Bromide (granular).....	100 Lbs.	2.90	@	3.00
Potassium Carbonate, calcined, 80 @ 85%.....	Lb.	80	@	85
Potassium Chlorate, crystals, spot.....	Lb.	45	@	47
Potassium Cyanide, bulk, 98-99 per cent.....	Lb.	—	@	—
Potassium Hydroxide.....	Lb.	83	@	90
Potassium Iodide, bulk.....	Lb.	3.90	@	—
Potassium Nitrate.....	Lb.	—	@	—
Potassium Permanganate, bulk.....	Lb.	1.60	@	1.70
Quicksilver, flask, 75 lbs.....	80.00	@	—	—
Red Lead, American, dry.....	Lb.	9 1/4	@	—
Salt Cake, glass makers'.....	Ton	9.00	@	10.00
Silver Nitrate.....	Oz.	39 3/8	@	—
Soapstone in bags.....	Ton	8.00	@	12.00
Soda Ash, 48 per cent.....	100 Lbs.	2 1/2	@	—
Sodium Acetate.....	Lb.	14	@	15
Sodium Bicarbonate, domestic.....	100 Lbs.	1.75	@	2.00
Sodium Bicarbonate, English.....	Lb.	3 1/2	@	3 3/4
Sodium Bichromate.....	Lb.	35	@	37
Sodium Chlorate.....	Lb.	30	@	32
Sodium Fluoride, commercial.....	Lb.	—	@	—
Sodium Hyposulfite.....	100 Lbs.	2.00	@	—
Sodium Nitrate, 95 per cent, spot.....	100 Lbs.	3.10	@	—
Sodium Silicate, liquid.....	100 Lbs.	1.25	@	1.75
Sodium Sulfide, 30%, crystals, in bbls.....	Lb.	2	@	2 1/2
Sodium Bisulfite, powdered.....	Lb.	6	@	7
Strontium Nitrate.....	Lb.	42	@	45
Sulfur, flowers, sublimed.....	100 Lbs.	2.30	@	2.70
Sulfur, roll.....	100 Lbs.	1.95	@	2.25
Sulfuric Acid, chamber, 60°.....	Ton	\$25.00	@	—
Sulfuric Acid, conc., sp. gr. 1.842.....	100 Lbs.	2.50	@	3.00
Sulfuric Acid, oleum (fuming).....	100 Lbs.	5	@	—
Talc, American white.....	Ton	9.00	@	12.00
Terra Alba, American, No. 1.....	100 Lbs.	75	@	80
Tin Bichloride, 50°.....	Lb.	15 1/4	@	16
Tin Oxide.....	Lb.	49	@	51
White Lead, American, dry.....	Lb.	8 3/4	@	—
Zinc Carbonate.....	Lb.	24	@	28
Zinc Chloride, commercial.....	Lb.	13	@	15
Zinc Oxide, American process.....	Lb.	8 3/8	@	8 1/4
Zinc Sulfate.....	Lb.	6 1/2	@	7 1/4

# ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.....	Lb.	65	@	65
Acetic Acid, 60 per cent, in bbls.....	Lb.	13	@	14
Acetic Acid, glacial, 99 1/2%, in carboys.....	Lb.	37	@	38
Acetone, drums.....	Lb.	40	@	42
Alcohol, denatured, 180 proof.....	Gal.	49	@	50

Alcohol, grain, 188 proof.....	Gal.	2.64	@	2.70
Alcohol, wood, 95 per cent, refined.....	Gal.	.65	@	.68
Amyl Acetate.....	Gal.	5.25	@	—
Aniline Oil.....	Lb.	.37	@	.40
Benzoic Acid, ex-toluol.....	Lb.	6.75	@	7.50
Benzol, 90 per cent.....	Gal.	.70	@	—
Camphor, refined in bulk, bbls.....	Lb.	.54	@	—
Carbolic Acid, U. S. P., crystals, drums.....	Lb.	.55	@	.60
Carbon Bisulfide.....	Lb.	8 1/2	@	—
Carbon Tetrachloride, drums, 100 gals.....	Lb.	.17	@	—
Chloroform.....	Lb.	.44	@	.50
Citric Acid, domestic, crystals.....	Lb.	.64	@	.67
Cresol, U. S. P.....	Gal.	.75	@	.80
Dextrine, corn (carloads, bags).....	100 Lbs.	3.30	@	3.40
Dextrine, imported potato.....	Lb.	.9	@	—
Ether, U. S. P., 1900.....	Lb.	.15	@	.20
Formaldehyde, 40 per cent.....	Lb.	12 1/2	@	.13
Glycerine, dynamite, drums included.....	Lb.	.40	@	.45
Oxalic Acid, in casks.....	Lb.	.58	@	.60
Pyrogallic Acid, resublimed bulk.....	Lb.	2.75	@	—
Salicylic Acid.....	Lb.	2.75	@	2.80
Starch, cassava.....	Lb.	3 3/4	@	4 1/4
Starch, corn (carloads, bags).....	100 Lbs.	2.25	@	—
Starch, potato.....	Lb.	—	@	—
Starch, rice.....	Lb.	.8	@	.10
Starch, sago.....	Lb.	3 1/2	@	.8
Starch, wheat.....	Lb.	.5	@	.6
Tannic Acid, commercial.....	Lb.	.60	@	.64
Tartaric Acid, crystals.....	Lb.	.70	@	.72

# OILS, WAXES, ETC.

Beeswax, pure, white.....	Lb.	47	@	55
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2	@	—
Castor Oil, No. 3.....	Lb.	16 3/4	@	.20
Ceresin, yellow.....	Lb.	.10	@	.14
Corn Oil, crude.....	100 Lbs.	8.40	@	—
Cottonseed Oil, crude, f. o. b. mill.....	Gal.	.69	@	.71
Cottonseed Oil, p. s. y.....	Lb.	10 3/4	@	—
Creosote, beechwood.....	Lb.	4.00	@	4.25
Cylinder Oil, light, filtered.....	Gal.	.21	@	—
Fusel Oil, crude.....	Lb.	4.50	@	—
Japan Wax.....	Lb.	15 3/4	@	.16
Lard Oil, prime winter.....	Gal.	1.04	@	1.08
Linseed Oil, raw (car lots).....	Gal.	.65	@	—
Menhaden Oil, crude (southern).....	Gal.	48 1/2	@	—
Naphtha, 68 @ 72°.....	Gal.	.33	@	—
Neat's-foot Oil, 20°.....	Gal.	1.10	@	1.20
Paraffine, crude, 118 & 120 m. p.....	Lb.	.5	@	—
Paraffine Oil, high viscosity.....	Gal.	29 1/2	@	—
Rosin, "F" Grade, 280 lbs.....	Bbl.	—	@	6.90
Rosin Oil, first run.....	Gal.	.30	@	.32
Shellac, T. N.....	Lb.	26	@	26 1/2
Spermaceti, cake.....	Lb.	.25	@	.26
Spermi Oil, bleached winter, 38°.....	Gal.	.80	@	.82
Spindle Oil, No. 200.....	Gal.	.24	@	.25
Stearic Acid, double-pressed.....	Lb.	12 1/2	@	13 1/2
Tallow, acidless.....	Gal.	.92	@	—
Tar Oil, distilled.....	Gal.	.30	@	.31
Turpentine, spirits of.....	Gal.	.44	@	—

# METALS

Aluminum, No. 1, ingots.....	Lb.	.58	@	.60
Antimony, ordinary.....	Lb.	.13	@	.14
Bismuth, N. Y.....	Lb.	3.15	@	3.25
Copper, electrolytic.....	Lb.	26 1/2	@	—
Copper, lake.....	Lb.	26 1/4	@	—
Lead, N. Y.....	100 Lbs.	6.30	@	—
Nickel, electrolytic.....	Lb.	—	@	—
Nickel, shot and ingots.....	Lb.	—	@	—
Platinum, refined.....	Oz.	60.00	@	65.00
Silver.....	Oz.	62 3/4	@	—
Tin.....	Lb.	31 7/8	@	—
Zinc, N. Y.....	Lb.	.10	@	—

# FERTILIZER MATERIALS

Ammonium Sulfate.....	100 Lbs.	3.40	@	—
Blood, dried.....	Unit	2.50	@	—
Bone, 4 1/2 and 50, ground, raw.....	Ton	—	@	—
Calcium Cyanamid.....	Unit of Ammonia	2.55	@	—
Calcium Nitrate, Norwegian.....	100 Lbs.	—	@	—
Castor Meal.....	Unit	—	@	—
Fish Scrap, domestic, dried, f. o. b. works.....	Unit	3.00	@	10
Phosphate, acid.....	Unit	.80	@	.85
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	2.75	@	3.00
Tennessee, 78-80 per cent.....	Ton	5.00	@	5.50
Potassium "muriate," basis 80 per cent.....	Ton	300.00	@	325.00
Pyrites, furnace size, imported.....	Unit	.15	@	.15 1/2
Tankage, high-grade; f. o. b. Chicago.....	Unit	2.65	@	10

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## EDITORIALS

### SOMETHING TO THINK ABOUT AT THE SEPTEMBER MEETING

During the week of September 25th the American Chemical Society meets at New York, and the time is ripe for a consideration of the industrial side of chemistry in the United States, its prospects, and the part the American Chemical Society may play in it.

It appears that there will be a large attendance, and this is good; for the occasion is important. There will be the Chemical Exhibition going on during the same week, and on the last three days the American Electrochemical Society meets also in New York, with the usual interchange of courtesies. A part of the social entertainment will be of a joint nature. This is also favorable. The American Chemical Society is big enough to encourage as many other scientific organizations to meet with it as possible. The subject of chemistry is very much bigger than all the societies and institutes put together. And now that we have physical chemistry on the mind, in the kidney, breaking out through the skin, interleaving textbooks and controlling the operation of filter-presses, it is well to bring chemists together with those engaged in physics from every angle of attack. The contribution of papers is promising. In the ordinary sense of the word, the prospects of the meeting are very favorable. The exhibition, which some feared would be merely an advertising hurrah, proved last year to be an occasion of industrial and engineering importance, and bids fair this year to be of much greater interest than before.

But there is more than the reading of papers and seeing sights and miscellaneous entertainment to be done at this meeting, because the Society will have to determine its policy. This will take place whether any resolutions as to policy are passed or not.

A glance at chemical industry in this country shows factories of one sort or another to have cropped out all over, like measles on a baby. The great works have met the situation in most cases, with their customary intelligence. Enormous fortunes have been made and active research has been prosecuted along many lines. But there are a vast number of works, busy at the moment, when selling is easy and buying is hard, that are totally uncorrelated, and that are no more prepared for ordinary times than is the genius at the end of the line who "hired one of these here experts to make pitric acid" for export. The laws of this country prohibit a great deal of coöperation that is needed and wholesome. Times in chemical industry have been so hilariously prosperous that it is among the few, rather than the many, that proper provision for times of easy buying and hard selling has been made. There is a great uncoördinated chemical industry started in this country and some day before long the question will have to be settled whether we shall continue to have it here or not. If many methods and ways of to-day are continued there is only one

answer possible: a good part of it will die out for good and sufficient reasons.

We have also some bad habits. There is, for instance, a tradition of secrecy that is as absurd as it is expensive. It comes down from the days of alchemy. It is a tradition of quackery and little more. Of course, nobody cares to tell his competitors everything he knows; but in all the muggy cloud of mystery around chemical works, how much that is kept secret is of actual value? We venture the guess that it is not a tithe. The rest is just tradition, and it goes through the whole establishment. The result is disastrous. Chemical industry walks with pussy-footed tread. Cryptic utterances are in the air. Men speak in parables. The poker eye is in evidence. Everybody raises and nobody calls. Nobody knows what anybody else is making—"to a certain extent," let us say, with a view to precision. Every maker of special products is at times at his wits' ends to know where to buy something that another is anxious and willing to sell. One of the most needed things to do is to effect a method of exchange for intermediates. This must be done soon.

Another thing of equal importance is a discriminating apparatus of some sort that will help to avoid mistakes. As soon as chemical industry goes beyond the mistake-limit, just so soon will a fat measure of industrial chemistry go out of the country—for keeps. When a man in business is up against a chemical problem he is more helpless than in almost any other predicament. We can blame him all we please for his ignorance, but that will not help matters. The man wants advice and he doesn't know where to get it. The means of telling him must be invented, or the scrap-heap of defunct chemical factories will grow so fast as to make the bankers shiver.

And right here is where the American Chemical Society comes in. It is the only available medium of exchange of chemical information. It can go ahead printing papers, maintaining a catalogue of members and meeting at intervals, just as it does now; and that is an eminently respectable career. Nobody can condemn it for doing evil. But it can miss its chance. It can watchfully wait until the apple cart is upset. Or it can get busy and meet the situation in every way possible. We have mentioned two functions that it may perform and we shall content ourselves with elaborating them.

A bureau of information may be established, the business of which is to tell who makes what, so long as the maker is willing to have the fact known. It need have nothing to do with prices, for trading is not the Society's business. But technical information is its business so long as it maintains an Industrial Journal and recognizes industrial chemistry as a part of its field.

Suppose a constant series of enquiries as to buyers

and sellers of rare chemicals and, in times like these, of standard goods, were to be circulated among members of the Society. They could maintain their wonted secrecy as long as they desired to. Xm might be in the market for oleum or glycol or phthalic anhydride or ethylene chloride and ask who had it for sale. Zippah might respond that he could furnish glycol. Then, when both parties are willing, the startling revelation is made to each who t'other is. Suppose they prove to be competitors, after each other tooth and nail. This would not occur often, but it might; the business end of chemistry is full of tricks. Well, Zippah could name a price that would take all the sport out of Xm's discovery. The futility of secrecy would soon show itself and manufacturers would come out into the open. Gorgonzola would tell his real name, while Xm and Zippah would prove to be honest men of business who would soon learn that all the world is not after them or their trade.

It would be gratuitous to dictate how such a bureau should be organized or operated; but if the Society wants to do it, it can.

Now we come to the second feature which is of a like nature. It is very easy to become a member of the Society and for the annual fee each receives his money's worth, if he is engaged in the active practice of chemistry. Membership does not give him a "character" or even the Society's backing as a man of science. Every member stands on the same footing, but every member is not to be recommended as a special authority in every branch of the science. The list of members does not tell anything of interest to the man who wants special information. And yet, just such information is available about many others than chemists. Every year there are published voluminous "Who's Who" books that tell what each man of supposed prominence has to say for himself. In like manner every member of the American Chemical Society could, and we venture to say substantially all those who are open to consultation would give a memorandum of his work, his achievements, the kind of work he is prepared to undertake and the places where an enquirer could find out about him. Unfaithful employees could be picked off like ripe cherries. The information about available men could be card-catalogued and this could be cross-indexed so that an industrial organization in need of advice could get a list of men who are informed, on short notice. Then a pharmaceutical manufacturer who wanted the synthesis of some drug extracted from bird's-eye maple cut in the dark of the moon, would not get a metallurgist to undertake the task.

A list of good men could be made out and such a list would grow. The knowledge that it existed would be a great encouragement to industry. Unexpected trades and lines of business would come around, and no establishment would be too big to listen to the enquiries that would have their origin in such a bureau.

Again we do not propose to give details as to how it should be organized or how it should be supported.

The need of it is great enough to make it sustain itself; and the details, while full of difficulties, could be worked out. The only question now is, whether the American Chemical Society wants to undertake it or not. It can be done.

#### EFFECTIVE COÖPERATION BETWEEN THE UNIVERSITY AND THE INDUSTRY

During the past year a lengthy discussion of the relations between the university and chemical industry brought out interesting and helpful suggestions, but, judging from the character of the report of the Committee appointed to consider the matter, produced nothing capable of being reduced to tangible action and of bringing forth practical results. At the end of the discussion the bystander was left with the impression of the incapacity of two parties, each interested in the other's welfare, to succeed in finding common ground for action and coöperation.

Fortunately, however, one of the men who took part in that discussion was of the rare type able to reduce words to action. Convinced, as everyone has been throughout, of the desirability of essential unity in effort on the part of the chemical departments of our universities and of the industries which they serve, he has set to work to develop an effective and practicable plan of coöperation, and has himself launched the first attempt to improve the product of our universities by coordinated effort on the part both of the University, which exists to furnish the training, and of the Industry, for whom the men are trained but without whose aid the training must necessarily remain inadequate. Not only the Massachusetts Institute of Technology, but chemical education throughout the United States, and indeed higher education as a whole, are deeply indebted to Mr. Arthur D. Little of the Corporation of the Institute for the development of the School of Chemical Engineering Practice, a description of which appeared in the previous issue of *THIS JOURNAL*.

The scheme of Mr. Little involves the utilization of the plants of a number of selected industries as laboratories of chemical engineering for the training of men who have already substantially completed a chemical engineering course of university rank. On the other hand, this practice school is restricted to men who possess the ability and character necessary to profit thereby, and is to be followed by a year of post-graduate work allowing specialization along some specific line in chemistry or engineering. The plant experience is to be under the direction of members of the Faculty of the Institute, and is to be designed for educational effectiveness in the development of the student. This, and the fact that the students are of exclusively post-graduate grade, are the essential points in which it differs from previous experiments, and are full of promise for the success of the school.

The Institute proposes to compensate the industries for the use of their plant equipment as an educational laboratory, by the establishment and maintenance



for each plant of a research laboratory for the solution of the problems of the specific industry. Such a laboratory will bring the chemical department of the Institute into most intimate touch with the problems of applied chemistry. That the return to the industries will be adequate is promised by the success not only of the research laboratories in many of our industries but of the Research Laboratory of Applied Chemistry at the Institute itself, the Director of which, Dr. Wm. H. Walker, is to be in charge of this new

school. More intimate contact of the University with Industry could not possibly be attained, and the advantages of the reflex action of this contact upon both may surely be anticipated.

The Institute and the country at large owe much to Mr. Arthur D. Little for this reduction to practice of the hitherto unworked theory of cooperation between the University and Industry.

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## ORIGINAL PAPERS

### LABORATORY INVESTIGATIONS CONCERNING THE REDUCTION OF BARIUM SULFATE TO BARIUM SULFIDE<sup>1</sup>

By ARTHUR E. WELLS  
Received July 3, 1916

The necessity of having more exact information than was available in the literature on the subject, concerning the reduction of barium sulfate to sulfide, arose in connection with a critical study of the Wet Thiogen Process<sup>2</sup> for the recovery of elemental sulfur from smelter gases. The study of this process was undertaken by the Bureau of Mines in cooperation with the Thiogen Company, forming a part of the general program of the work carried out in the Coöperative Metallurgical Exhibit Laboratory at the Panama-Pacific International Exposition,<sup>3</sup> which dealt with the general problem of elimination of waste in smelting operations. At the close of the Exposition this laboratory investigation was continued in the Bureau of Mines laboratory in the Hearst Mining Building, at the University of California, Berkeley.

\* Stated briefly, the Wet Thiogen Process involves the recovery of the sulfur dioxide from smelter gases by passing them up through absorption towers, in which a descending "mother liquor" solution absorbs the sulfur dioxide. Barium sulfide is added to the solution of sulfur dioxide and a precipitate, consisting of barium thiosulfate, barium sulfite and sulfur, is thrown out. This precipitate is filtered and the elemental sulfur, with one-half of the sulfur from the thiosulfate, is distilled, leaving a residue of barium sulfite and some sulfate. This residue is then reduced to sulfide and the barium sulfide used again for precipitation, the barium thus being kept in circulation through cycles.

In order that the barium shall be most efficient as a precipitant during these cycles, it is very necessary that the maximum reduction of the sulfite or sulfate to the water-soluble sulfide be attained in each cycle. Thus, it was very necessary to determine the conditions under which the barium sulfite or sulfate was reduced most completely to the sulfide, and considerable experimental work has been conducted on that problem. As barium sulfate must be used at the start

in the initial reduction, and was present to a large extent in all precipitates after distillation, and also, as this material could be obtained in quantities much more readily than the sulfite, the greater part of these investigations were concerned with the reduction of the sulfate. This is a problem that, aside from its applicability to the Thiogen Process, is of general interest, and especially to those who are engaged in the manufacture of barium salts.

While it is true that in these investigations most of the reduction tests were conducted with a much purer grade of barium sulfate than is generally used by the manufacturers of barium salts, yet it is felt that some of the data obtained in these tests are of such general application that a brief presentation of these data may be of possible value at this time when considerable attention is being devoted to the manufacture of barium salts.

In this paper only the data concerning the first reduction of barium sulfate will be discussed. In order to fully understand the data concerning the reduction of the products from cyclic operations, it would be necessary to go into a discussion of the action of the reduced barium compounds as a precipitant in the Thiogen Process cycles, and as such discussion is reserved for another paper, the data concerning the cyclic reductions are also reserved for that paper.

In answer to several inquiries concerning what was being accomplished at the present time in the reduction of barium sulfate at various plants where barium salts were being manufactured from barium sulfate, the information was gained that although 80 or 85 per cent of the barium was readily reduced to acid-soluble compounds, yet current practices rarely reduced more than 60 or 70 per cent of the barium to water-soluble barium sulfide.

The literature verified these statements.<sup>1</sup>

The barium compounds found in the reduced products are classified in this discussion as follows:

I	II	III
Readily Soluble in Hot Water	Difficultly Soluble in Hot Water but Soluble in Dilute HCl	Insoluble in Acid
BaS	BaO BaCO <sub>3</sub>	BaSO <sub>4</sub>
BaS <sub>x</sub>	BaS BaSiO <sub>3</sub>	
BaO	Traces of BaSO <sub>3</sub>	

<sup>1</sup> Published by permission of the Director of the Bureau of Mines and the Thiogen Company.

<sup>2</sup> "Metallurgical Smoke," by Charles H. Fulton, Bureau of Mines, Bull. **84**, 74-77.

<sup>3</sup> "The Coöperative Metallurgical Exhibit at the Panama-Pacific International Exposition," by G. H. Clevenger and A. E. Wells, *Met. & Chem. Eng.*, **13** (1915), 743.

<sup>1</sup> "Mineral Industry," Vol. 19. Schuyler-Frazier, "Calcining Plant for Barium Sulfate." A. H. Fay, "Roasting Barytes." Maximilian Toch, "The Barium Industry in the United States since the European War," *Met. & Chem. Eng.*, **14** (1916), 47.

## I—WATER-SOLUBLE BARIUM

The reduced product, ground to 100 mesh, was leached in a flask with 250 parts water, just below boiling, and filtered into a flask which was tightly stoppered while the solution was cooling. An aliquot part of the solution was then titrated with iodine, and in another aliquot part barium and sulfur were determined. As a check for the iodine value, *i. e.*, the barium sulfide content, the material was frequently treated directly in a flask with excess iodine for about 5 min., and then the excess iodine determined. In many cases there was barium oxide present in the water solution. In other products there was a slight excess of sulfur over that required for the barium to form sulfide, indicating a polysulfide. In several products of reductions at high temperatures (1050 to 1200° C.), where excess carbon was present, the presence of the carbide was indicated but was not determined quantitatively.

## II—BARIUM COMPOUNDS SPARINGLY SOLUBLE OR INSOLUBLE IN HOT WATER, BUT SOLUBLE IN DILUTE ACID

In many products from the first reduction, a large portion of the oxide present was very sparingly soluble in hot water, but was soluble in dilute hydrochloric acid.

In most products of the reductions which were effected in a direct fired furnace at high temperatures and where slight sintering had taken place, a small amount of the sulfide was found to be in the water-insoluble portion. In some products, from 4 to 6 per cent of the total sulfide was found to be sparingly soluble in water. The solubility of this material was increased somewhat by finer grinding. In a typical average product from the first reduction of barium sulfate, 97 per cent of the sulfide and 40 per cent of the oxide were readily soluble in hot water, the rest being found in the acid-soluble portion. In this water-insoluble, but acid-soluble, portion was also found the carbonate in varying amounts. The products from slow reductions, at low temperatures, contained more carbonate than did those from rapid reductions at high temperatures. Very few products contained more than a trace of the sulfite or thionates.

The reduction tests here discussed will be considered under five series.

## SERIES I—TESTS TO DETERMINE THE RELATIVE RATES OF REDUCTION OF BARIUM SULFATE BY HYDROGEN, CARBON MONOXIDE, AND A MIXTURE OF THESE GASES WITH OTHER HYDROCARBONS AT DIFFERENT TEMPERATURES

In these tests precipitated barium sulfate (99+ per cent  $\text{BaSO}_4$ ) was placed in a quartz tube of about 12 mm. (0.47 in.) diameter, and heated in an electrically heated tube furnace. The barium sulfate was placed between two asbestos plugs, filling the tube for a distance of about 30 mm. (1.18 in.), but was sufficiently loose to allow the passage of gases through the material. The gases were passed through the

tube at the rate of about 2 cc. per min. The data obtained probably did not represent the chemical equilibrium at any temperature. The comparative rate of reaction at different temperatures was obtained, however, as were data concerning the character of the gaseous products.

**REDUCTION WITH HYDROGEN**—When hydrogen was reduced as the reducing agent, there was practically no reaction at any temperature below 550° C. Around 600° C., the reaction was extremely slow, less than 5 per cent of the hydrogen passing through the plug, reacting. The gaseous product contained considerable hydrogen sulfide. At 650° C., about 15 per cent, and at 700° C., about 35 per cent of the hydrogen reacted. Between 600 and 700° C., the amount of hydrogen sulfide formed was a maximum. At 800° C., practically all the hydrogen had reacted and very little hydrogen sulfide was present in the gaseous product. In general, these data checked those of a previous investigation.<sup>1</sup> In the products from these reductions with hydrogen, the ratio of sulfur to barium was less than one atom of sulfur to one atom of barium.

If the reductions were effected slowly at lower temperatures (between 600° and 750° C.), the loss of sulfur was greater than if the reductions were effected more rapidly at higher temperatures (900 to 1000° C.). In one test lasting for an hour at 1000° C., 94.0 per cent of the sulfate was reduced to sulfide and 6.0 per cent to oxide. This was the maximum reduction obtained using hydrogen.

In some correlated tests, it was found that, between 700 and 900° C., water vapor reacts slowly with barium sulfide, forming sulfur dioxide, hydrogen sulfide and barium oxide. For example, through a reduced product of about 20 mesh size, containing 89 per cent of the barium as sulfide, 7 per cent as oxide and carbonate, and 4 per cent as sulfate, was passed, at 900° C., a mixture of about 16 per cent water vapor and 84 per cent nitrogen; about 1 per cent of the water vapor reacted, forming nearly two volumes of sulfur dioxide per volume of hydrogen sulfide. The reaction between water vapor and barium sulfide at other temperatures was not determined.

**REDUCTION WITH CARBON MONOXIDE**—With carbon monoxide the reduction was very slow below 650° C., and was fairly rapid at 750° C., about 70 per cent of the carbon monoxide reacting. With temperatures up to 900° C., however, there was present in the gaseous product some unconsumed carbon monoxide. Above that temperature the gaseous product was almost entirely carbon monoxide. In these reduced products the ratio of sulfur to barium was slightly less than 1 : 1, showing that some sulfur had been removed in the gaseous products. In this series as in tests with hydrogen as the reducing gas, the loss of sulfur was less in the cases where reduction was effected rapidly at higher temperatures (above 900° C.), than when effected slowly at lower temperatures. Thus, the products of reduction effected rapidly at

<sup>1</sup> "Reduction of Sulfate of Alkaline Earths with Various Gases," L. Marino, R. University of Pisa, *Gazz. chim. ital.* **43** [1], 416-22. *Chem. Abs.*, **7** (1913), 3202.



high temperatures contained the smaller percentages of water insoluble barium oxide.

**REDUCTIONS WITH CITY GAS** A series of 20 reductions was made, in which an excess of city gas of approximately the following composition was passed at the rate of 2 cc. per min. through the charge in the quartz tube:

CH <sub>4</sub>	CH <sub>2</sub>	H <sub>2</sub>	CO	CO <sub>2</sub>	N <sub>2</sub>	O <sub>2</sub>	TOTAL
6.4	30.4	41.4	13.4	4.0	4.2	0.2	100.0 per cent

The data obtained are given in Table I. The percentage of barium in the product present in water-insoluble, but acid-soluble, compounds was less when

TABLE I—REDUCTION OF PRECIPITATED BARIUM SULFATE BY CITY GAS IN QUARTZ TUBE, EXTERNALLY HEATED

Temperature ° C.	Time Min	PER CENT OF TOTAL BA IN PRODUCT PRESENT AS		
		Water-soluble BaS and BaO	Water-insoluble but Acid-soluble BaO and BaCO <sub>3</sub>	Acid-insoluble BaSO <sub>4</sub>
650-700	60	2.5	4.0	93.5
	240	58.0	15.8	26.2
	330	72.5	18.2	9.3
700-750	60	8.5	6.8	84.7
	240	75.0	13.8	11.2
	60	20.6	8.4	71.0
750-800	240	88.2	11.0	0.8
	60	50.8	7.8	41.4
	240	91.5	8.3	0.2
800-850	60	55.5	6.8	37.7
	240	91.8	8.0	0.2
850-900	60	65.2	6.2	28.6
	120	85.0	7.3	7.7
	240	92.5	7.5	0.0
900-950	60	74.7	4.8	20.5
	120	91.5	6.5	2.0
	240	93.2	6.8	0.0
950-1000	60	85.2	5.0	9.8
	120	92.0	6.5	1.5
	240	93.0	7.0	0.0

reductions were effected in a short period of time at temperatures above 900° C., than if effected over a longer period of time at lower temperatures; *e. g.*, compare the products obtained when the material was treated for 330 min. at 650 to 700° C., with those obtained in a reduction of 1000 to 1050° C., lasting only 60 min.

Any tendency for a reaction between the reducing gases and the reduced sulfide, resulting in the formation of water-insoluble barium compounds, is slight; *e. g.*, compare the proportion of these compounds in the products of reductions at 900 to 1050° C. for 60, 120 and 240 min.

#### SERIES 2—REDUCTION OF BARIUM SULFATE BY CARBON

In these tests, finely pulverized carbon, either coke or charcoal, was intimately mixed with the barium sulfate, and heated for varying periods of time at different temperatures, in crucibles or tubes placed in muffle furnaces. The theoretical amount of carbon required for the reduction is 10.3 per cent of the weight of BaSO<sub>4</sub>, if the carbon is completely oxidized to CO<sub>2</sub>, or 20.6 per cent if the carbon is oxidized only to CO. In these tests, the carbon added varied between 10 and 40 per cent of the BaSO<sub>4</sub>. The temperature range was between 700 and 1250° C. The time allowed for reduction varied between 15 and 360 min.

In all but a few of the tests where the time allowed for reduction was an hour or more, the mixtures, weighing from 50 to 100 g., were placed in 10- or 20-g. fire clay crucibles and heated in a muffle furnace. The muffle had been heated to the required temperature

before placing the crucibles in it, and thus the crucibles and charge were heated up quickly. When the time allowed for reduction was less than 1 hr., it was rather difficult to get satisfactorily concordant data with this size of charge and method of heating. In order to reduce the "heating up" period to a minimum, these reductions were made with much smaller charges (5 to 10 g.), in porcelain crucibles.

In Table II most of the temperatures recorded were measured near the crucibles during the period of reduction. Several, however, were measured in the charge itself, after it had come to the temperature of the muffle, but care was taken to have the heating of the muffle so regulated that the temperatures did not vary more than 15 or 20° C. either way from that desired; thus, a temperature of 700° C. means between 680 and 720° C., sufficiently close for the purposes of these investigations.

As, in these reductions, it was very important to keep the air from coming into contact with the material as far as possible, the crucibles were covered with a clay cover ground to fit. In some tests a charcoal cover about 2 mm. (0.04 in.) thick, was placed on the charge. Even with the tight covering, in some of the tests, there was a slight reversion of the sulfide to the sulfate, due possibly to a slight porosity of the crucible walls allowing air to pass through. Some of the data concerning this reversion will be given later.

In Table II are summarized the results of 76 tests made under conditions which were quite similar, so that the results are comparable. The barium sulfate used was the precipitated material. The carbon

TABLE II—REDUCTION OF BARIUM SULFATE BY CARBON  
PER CENT TOTAL BARIUM IN PRODUCT IN FORM OF:  
Water-soluble Barium Sulfide Soluble in Dilute HCl

Min.	15	30	60	90	120	240	360	15	30	60	90	120	240	360
700° C.	..	12	26	28	41	65	77	..	21	37	40	54	80	93
750	..	29	35	55	59	78	..	..	38	47	69	73	93	..
800	..	51	61	63	68	82	..	..	57	70	75	85	98	..
850	..	58	69	78	85	86	..	..	65	78	87	94	98	..
900	48	65	85	87	88	..	..	54	72	94	97	99	..	..
950	..	76	89	92	95	..	..	..	80	94	97	100	..	..
1000 to } 1100	75	84	96	..	..	..	..	80	89	100	..	..	..	..
1100 to } 1200	96	97	..	..	..	..	..	98	100	..	..	..	..	..

added was 20.6 per cent of the weight of the barium sulfate; it was pulverized to pass a 160-mesh screen and mixed with sulfate until the mixture looked homogeneous to the naked eye. The variables were the time allowed for reduction and the temperatures. Many of the figures given are the average of several determinations that in most cases gave concordant results.

In the products of reduction effected at the lower temperatures over a longer period of time, the difference between the acid-soluble barium compounds and the water-soluble barium sulfide is less in the reductions at higher temperatures for a short period of time, than in those at lower temperatures over longer periods. Most of the products contained excess carbon. Other series of tests were made to determine to what extent a decrease in the amount of carbon present in the charge affected the reduction.

When the tests were made in porcelain crucibles fitted with an ordinary porcelain cover, there was al-

ways sufficient air leaking into the crucible either to burn a small percentage of the carbon, or to reoxidize a small amount of the reduced sulfide back to the sulfate. As the data from these tests are, therefore, not quite accurate, they are not included in this paper.

Similar reductions were repeated in porcelain crucibles, when a light layer of carbon was placed on top of the charge and other precautions taken to keep the air from coming into contact with the charge during cooling, etc. Although the carbon cover did have some slight reducing action on the charge, it was decided that the data obtained were sufficiently accurate for recording in this paper, and they are given in Table III.

TABLE III—REDUCTION OF BARIUM SULFATE AT DIFFERENT TEMPERATURES IN PORCELAIN CRUCIBLES WITH VARIABLE AMOUNTS OF CARBON IN THE MIXTURES

Temp. ° C.	Time Min.	Per Cent Carbon to BaSO <sub>4</sub>	Per Cent of Total Barium in Product			Carbon Consumed	
			BaS	Acid-sol.	Insol.	Per cent of Total Carbon Consumed	Per cent of BaSO <sub>4</sub> Reduced to BaS
800	60	10.5	50	58	42	69	14.5
		21.0	51	56	44	49	20.2
		10.5	62	70	30	83	14.3
800	120	21.0	66	65	32	65	20.5
		10.5	66	70	30	86	13.2
		15.5	60	65	35	65	16.8
850	60	20.6	60	70	30	58	19.8
		10.3	78	85	15	97	12.9
		15.5	76	82	18	84	17.0
850	120	20.6	74	80	20	70	19.4
		10.3	80	85	15	100	12.9
		15.3	81	83	17	87	16.7
900	60	20.6	76	80	20	72	19.4
		10.3	80	86	14	100	12.9
		15.5	84	90	10	89	16.5
900	120	20.6	83	87	13	80	19.8
		10.3	80	83	17	100	12.5
		20.6	84	87	13	78	19.0
950	30	10.3	80	83	17	100	12.5
		20.6	84	87	13	78	19.0
950	60	40.0	78	79	21	59	
		10.3	94	97	3	100	12.8
		20.6	95	96	4	93	20.2
1050	30	30.0	82	82	18	61	23.4
		10.3	82	86	14	100	11.2(a)
		15.5	96	96	2	100	16.1
1150	20	20.6	95	96	4	89	18.7
		10.3	90	90	10	100	11.5
		15.5	99	99	1	100	15.6
		20.6	99	100	0	90	18.2

(a) This carbon consumption factor is probably slightly low due to a slight reduction action of the carbon cover.

Later reduction tests, effected in an atmosphere of nitrogen, *i. e.*, in an atmosphere neither oxidizing or reducing, gave results that checked the above-mentioned data fairly closely.

In another set of reduction tests the barium sulfate was mixed intimately with finely pulverized carbon and placed in a porcelain tube, in an electrically heated tube furnace. The tube was filled with nitrogen gas at the start, and the gases evolved were discharged through a water seal, or into caustic potash solutions. Thus, neither oxygen nor any reducing gases other than the carbon monoxide from the carbon came in contact with the BaSO<sub>4</sub>. From the data in Table IV it is to be noted that the carbon efficiency was greatest when the charge contained the smallest percentage of carbon, and the efficiency decreased with an increase in the amount of carbon present. In general, somewhat higher carbon efficiency was obtained in the reductions effected at the higher temperatures than at the lower. Although the highest carbon efficiency (about 12.0 to 12.5 per cent) was obtained when the carbon present was about 10 per cent of the barium

sulfate (the theoretical amount if the carbon oxidized completely to CO<sub>2</sub>), yet with this amount of carbon the maximum reduction of the barium sulfate at temperatures up to 1000° C. was only about 80 to 85 per cent. Between 900 and 1000° C., nearly complete reduction was obtained with a carbon consumption of about 14 to 15 per cent. When the carbon was present to the extent of 20 per cent of the BaSO<sub>4</sub>, the carbon efficiency was much lower, irrespective of whether the reduction was at high or low temperatures, but was slightly higher at the high temperatures than at the low.

With an excess of carbon, the reduction seemed to proceed slightly slower than with the lesser amount of carbon present. This is shown especially in the series at 850, 900 and 950° C. in Table III. However, it must be recognized that the degree of fineness to which the material is pulverized, the intimacy with which the sulfate and carbon are mixed, and the depth of material through which the carbon monoxide gas must pass before leaving the charge, are factors influencing these figures; *e. g.*, in several tests, straight barium sulfate was placed on top of the charge containing 20 per cent carbon. This barium sulfate cover was quite largely reduced by the carbon monoxide coming up from the charge proper, thus increasing the efficiency of the carbon when credited with the whole amount of barium reduced.

Summarized briefly, the data from Series 2 show that when the carbon and barium sulfate are finely pulverized and intimately mixed, and the reduction is effected in a muffle or crucible type of furnace in absence of outside air or products of combustion of fuel, and at temperatures between 850 and 1000° C., a high reduction (90 per cent or better) can be obtained when the carbon added is about 15 per cent of the barium sulfate. While the efficiency is greater with the addition of less carbon, the reduction is not so complete. With more than 15 per cent carbon, the carbon efficiency decreases, unless provision is made to utilize the carbon monoxide issuing from the charge, by passing it through another charge of barium sulfate.

TABLE IV—REDUCTION OF BARIUM SULFATE BY CARBON IN TUBE FURNACE, SURROUNDED BY ATMOSPHERE OF NITROGEN

Temp. ° C.	Per Cent Carbon to BaSO <sub>4</sub> in Charge	Per Cent of Total Carbon Consumed	Per Cent of BaSO <sub>4</sub> Reduced to BaS	Carbon Consumed Per Cent BaSO <sub>4</sub> Reduced
800	10	80	58	13.8
	10	100	70	14.3
	20	63	84	19.8
900	10	95	70	13.5
	10	100	74	13.5
	10	97	75	12.9
950	10	100	75	13.3
	15	90	82	16.4
	14	100	96	14.7
1000	10	100	90	16.7
	15	100	80	12.8
	15	100	90	15.6
	20	84	95	17.6

Different kinds of barium sulfate gave different results in reductions carried on under the same conditions, *e. g.*, the materials indicated in Table V, all finer than 200 mesh, were reduced at the same time under the same conditions (temperature 900° C., time 120 min.), with the results given in Table V.



TABLE 3. PER CENT OF TOTAL BARIUM IN PRODUCT FROM DIFFERENT COMPOUNDS

MATERIAL	Per Cent BaSO <sub>4</sub>	Water-soluble	Water-insol. Acid sol.	Acid-insol.
Pptd. BaSO <sub>4</sub>	99.6	88	10	2
Pulverized 1	98.0 (a)	8	13	9
Barytes - 1	92.8 (b)	72	18	10
Pptd. BaSO <sub>4</sub> + BaSO <sub>4</sub>		93	7	0

(a) The impurities were 1.4 per cent BaCO<sub>3</sub> and 0.6 per cent Fe<sub>2</sub>O<sub>3</sub>.

(b) About 3 per cent Fe and 3 per cent SiO<sub>2</sub> were present.

Some comparative tests were made to determine the effects of iron on the reduction of barium sulfate. Four charges were made up in which iron to the extent of about 6 per cent was mixed with the precipitated barium sulfate. The iron was added to different charges as ferric sulfate, ferrous ammonium sulfate, ferrous sulfate, and ferric oxide. Two charges of the pure precipitated barium sulfate were reduced under the same conditions (temp. 850° C., time 120 min.).

PER CENT OF TOTAL BARIUM PRESENT IN COMPOUNDS (AVERAGE OF 4 TESTS)

MATERIAL	Water-soluble	Water-insoluble Acid-soluble	Acid-insoluble
Pure BaSO <sub>4</sub>	80	10	10
BaSO <sub>4</sub> with 6 per cent Fe	68	17	15

#### REOXIDATION OF BARIUM SULFIDE TO SULFATE

It has been stated that barium sulfide, when at red heat, is readily reoxidized to the sulfate. The data from several of the crucible reduction tests were found to be of no value since adequate precautions had not been taken to prevent the oxygen from getting into the crucible. An example of the effect of small air leakages into the crucible is given below. These results were obtained when reducing pulverized barytes (98 per cent BaSO<sub>4</sub>) with 20 per cent willow charcoal at 1000° C.

PER CENT BARIUM IN PRODUCT PRESENT IN COMPOUNDS

TIME, Min.	Water-soluble (BaS)	Water-insoluble Acid sol. Comp.	Insoluble (BaSO <sub>4</sub> )	FIT OF COVER
60	94	6	0	Tight
	76	3	21	Loose
120	56	4	40	Tight
	35	3	62	Loose

That the reoxidation product is the sulfate and not the oxide, is shown in the above and also in some special tests made to determine the product of oxidation of barium sulfide. In these tests, material containing 95 per cent of the barium as BaS was heated in the air for varying periods of time at different temperatures. In most cases practically all the sulfide was reconverted to the sulfate, and only small amounts of oxide were formed. The maximum conversion to oxide was about 7 per cent and was obtained when the material was heated to 800° C. for 2 hrs.

#### SERIES 3. BARIUM SULFATE, MIXED WITH CARBON, MADE INTO BRIQUETTES AND REDUCED IN A SHAFT FURNACE HEATED BY OIL

Precipitated barium sulfate was mixed with lampblack carbon from the local oil gas works, and the mixture pressed into the form of cupels, 1 in. (2.5 cm.) in diameter, and 1 1/4 in. (3.2 cm.) high. These cupels were dried and then charged into a small shaft furnace, 12 in. (30.5 cm.) in diameter and 30 in. (76.2 cm.) high, which was heated to about 950–1100° C. by an oil flame, the products of combustion or excess gases passing through the shaft and maintaining strongly reducing conditions in the shaft. The furnace was

kept filled with briquettes during a test, more briquettes being added at the top as the reduced product was withdrawn below. The time the briquettes were in the furnace varied between 1 1/2 hrs. and 3 hrs. During an average run of 6 hrs., about 80 kg. of these briquettes were reduced. The best average product obtained from any of the days' runs contained 82.5 per cent of the barium as sulfide, 13.8 per cent as oxide and carbonate, and 3.7 per cent as insoluble sulfate. The best product from any charge during this run contained 87 per cent of the barium as sulfide; during this run the maximum furnace temperature was 1150° C.; the average carbon monoxide content of the gases in the shaft of the furnace was 4 per cent.

In this shaft furnace, several runs were also made with briquettes of pulverized commercial barytes (92.5 per cent BaSO<sub>4</sub>), and lampblack carbon. These briquettes were 2 1/2 in. (6.36 cm.) long, 2 1/2 in. (6.35 cm.) in diameter and weighed about 0.81 lb. (370 g.), each. With these briquettes, very unsatisfactory reductions were obtained, even though the temperature of the furnace was raised to 1100° C., and broken pieces of coke were charged with the briquettes. The best products contained only about 70 per cent of the barium as sulfide. Also, unless these large briquettes were broken up and chilled immediately on being removed from the furnace, they retained their heat for a long time, and the barium sulfide to a great extent oxidized back to the sulfate.

One charge of reduced briquettes weighing about 25 kg., and containing at the time of withdrawal from the furnace about 70 per cent of the barium as sulfide, was allowed to stand unbroken in an iron container for about 15 hrs. At the end of this time, the briquettes in the center of the container were still glowing. The outside cooled briquettes contained less than 15 per cent of the barium as sulfide, the rest having oxidized back to sulfate.

#### SERIES 4. REDUCTION OF BARIUM SULFATE IN THE MULTIPLE HEARTH ROASTING FURNACE

DESCRIPTION OF FURNACE—The multiple hearth furnace used for these reduction tests was one designed by Mr. Utley Wedge and loaned to us for these investigations (see Figs. I and II). The furnace was 24 in. inside diameter and 34 in. high, *i. e.*, between bottom of the cast-iron drying hearth to top of bottom hearth. Beneath the bottom hearth was a calcine pit, 12 in. deep. Above the drying hearth were placed the driving gears, roller bearings, etc. The total height over all was 6 ft. The walls of the furnace were of specially moulded fire brick, 8 in. thick, containing openings for gas burners, pyrometer tubes, gas sample tubes and mica windows, or peepholes. Outside the brick walls of the furnace was placed a covering of magnesia board 1 1/2 in. thick; this magnesia was covered with a layer of asbestos cement 1/8 in. thick, with a thin layer of Portland cement on the outside.

To a revolving center column inside the furnace were attached three cast-iron hearths 22 in. in diameter. Thus, there was an annular space 1 in. wide

between these hearths and the furnace walls. Between these movable hearths and below the lowest one were placed three stationary hearths resting on shelves provided on the brick walls. The opening at the center of these hearths was 6 in. in diameter, leaving an annular space 1 in. wide between the

brick plugs were provided in the walls of the furnace, which gave access to the interior for cleaning off the hearths. At times these movable plugs were found to be convenient, as some charges had a tendency to ball up in front of the rabblers.

The furnace was heated by oil fuel or by city gas. In most of the tests, the latter fuel was used. The gas was burned through Mcker burners, using 20 lbs. air pressure at the burners.

It is not considered that the fuel consumption in this furnace furnished data for calculating the fuel which would be required in a standard furnace of this type, if properly designed to prevent radiation losses, etc. The center revolving column was water-cooled. The cooling water removed from  $\frac{1}{5}$  to  $\frac{1}{3}$  of the total heat supplied to the furnace by the combustion of the gas. In most of the reduction tests, the furnace was operated only under a very slight draft, just enough to allow the products of combustion, etc., to be removed from the furnace.

#### SUMMARY OF REDUCTION TESTS IN MULTIPLE HEARTH FURNACE

In Table VI are summarized briefly 20 tests made in this furnace; the variables were:

##### (1) Length of time the material was in the furnace

This was controlled by the rate at which the charge was fed and by the speed of revolution of the center column. Rate of feeding was varied between  $2\frac{1}{2}$  and 9 kg. per hr. Length of time the material was in the furnace varied between 2 and  $3\frac{1}{2}$  hrs.

##### (2) Furnace temperatures

TEMPERATURE	1st Hearth	3rd Hearth	5th Hearth
Minimum.....	180° C.	560° C.	840° C.
Maximum.....	485	905	920
Average.....	360	800	850

##### (3) Reducing conditions—In all cases there was excess city gas used above that required for the com-

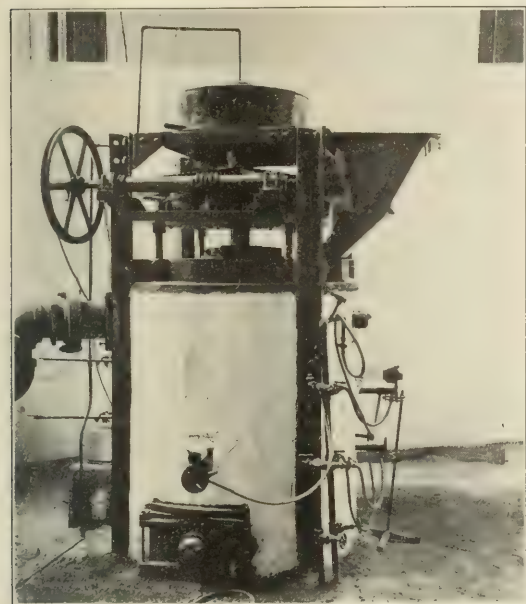


FIG. I MULTIPLE HEARTH ROASTING FURNACE  
Loaned by Mr. Utley Wedge

stationary hearths and the center columns. The total effective hearth area was 16.5 sq. ft.

Rabblers were attached to ribs cast on the under side of the hearths, these rabblers stirring and moving the ore across the hearths immediately below. The ore on the cast-iron drying floor was moved by rabblers revolving with the center column. From the drying floor the ore fell to the center of the top movable hearth, and was moved by the rabblers suspended from the stationary drying hearth, to the outside of this revolving hearth, falling on to the second hearth, a stationary hearth. It was then moved by rabblers attached to the first movable hearth, to the center of the stationary hearth, and fell on the third hearth, a moving hearth. The ore was thus moved through the furnace in a manner similar to that in a regular, large size, multiple, roasting furnace.

The cast-iron hearths lasted for many tests when the temperatures were not over 800° C., but when temperatures above 900° C. were maintained they warped and cracked and had to be replaced after eight or nine 12-hr. runs.

Bristol pyrometers were inserted through the walls of the furnace for measuring the temperature on the first, third and fifth hearths. Gas samples were also drawn from the furnace at these hearth levels. Peepholes were provided at several points for observing the charge in the furnace. Movable

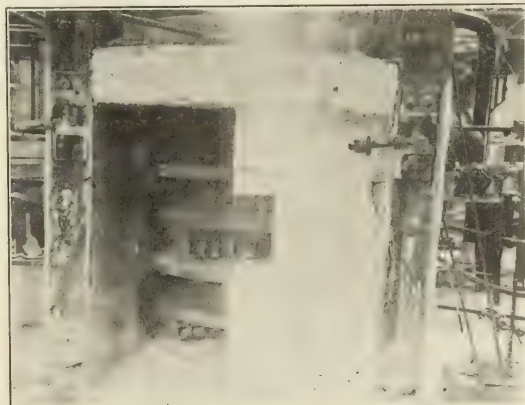


FIG. II MULTIPLE HEARTH ROASTING FURNACE, SHOWING HEARTHS AND RABBLERS

bustion, to maintain the proper temperatures. In the 20 tests here summarized, no free oxygen was allowed in the furnace. The carbon monoxide content of the gases taken from the furnace on the third and fifth hearth ranged between 0.5 and 5 per cent. The fuel gas consumption was between 3 and 6 cu. ft.



TABLE VI—REDUCTION OF BARIUM SULFATE (OR BARYTES) IN MULTIPLE HEARTH FURNACE BY EXCESS  $H_2$ ,  $CO$ , OR HYDROCARBONS ENTERING FURNACE THROUGH BURNERS

Barium Compound Used Character of Carbon Used Test No.	PRECIPITATED BARIUM SULFATE (99+ % BaSO <sub>4</sub> ) Intimately Mixed with Carbon Used										PRD. BARIUM SULFATE (99+ % BaSO <sub>4</sub> ) No Carbon Used							PULVERIZED COMMERCIAL BARYTES As used in Pallets by W. P. Fuller Co. Pulv. Coke L. B. P. C. No Carbon											
	LAMPBLACK					PULVERIZED COKE					B-3	B-4	B-5	B-6	B-7			C-1	C-2	C-3	C-4	D-1	D-2	D-3					
	1	2	3	4	5	6	7	8	9	10																			
Percent Carbon to BaSO <sub>4</sub> in Charge	20	16	20	25	25	17	18	18			0	0	0	0	0			20	20	20	20	0	0	0	0	0	0	0	0
Rate Charge to Furnace, Kg. per hr.	8.9	5.0	3.5	3.5	3.5	2.8	3.0	3.5			3.4	3.4	3.4	3	3			3.5	3.5	3.5	3.0	3	3	3	3	3	3	3	3
Rate Gas Consumption, Cu ft. per min.	5.2	5.0	5.0	3.7	4.6	3.5	3.5	4.5			4.8	5.1	4.8	5.0	4.5-5.0			3.8	4.5	5.0	4.2	5	5	5	5	5	5	5	5
Time of Material in Furnace, Hrs. (approx.)	2	2.30	2.45	3	3	3.30	3.15	3			3	3	3	2.30	2.30			2.45	2.45	3	3								
Duration of Test, Total hrs.	8	9	12	9	9	10	10	12			14	14	30	9	12			12	30	8	6	7	10	11	10				
AVERAGE TEMPERATURE (°C.)																													
Top hearth	180	270	300	270	420	370	370	460			470	300	510	475	470			370	410	380	410	480	410	420	410	420	410	420	410
3rd hearth	560	590	640	570	760	810	790	890			895	840	880	830	890			760	790	760	780	850	820	810	810	810	810	810	810
5th hearth	810	860	880	890	895	880	885	890			900	890	890	885	895			870	895	890	865	890	880	900	900	900	900	900	900
Maximum Temperature of 5th hearth	840	880	890	895	905	905	910	900			905	905	900	900	900			910	900	900	890	910	900	905	905	905	905	905	905
Average % CO in Furnace Gases (3rd hearth)	4.5	5.0	4.7	1.6	2.0	0.5	0.5	2.0			1.8	3.5	1.0	4.0	3.0			0.5	1.0	2.5	1.0	0.8	2.0	4.2	4.2	4.2	4.2	4.2	4.2
ANALYSES OF PRODUCT OF TEST																													
Per cent of Total Ba, Water-soluble	18	71	75	55	77	80	76	77			69	69	60	72	68			51	65	68	68	53	67	68	68	68	68	68	68
Acid-soluble	65	12	7	28	8	2	6	10			84	87	73	83	81			59	75	89	80	64	75	82	82	82	82	82	82
Insoluble (BaSO <sub>4</sub> )	35	88	93	78	92	98	94	90			76	13	27	17	19			41	25	20	30	36	25	18	18	18	18	18	18
Max % Ba, Water-soluble in Hourly Samples	43	73	79	67	78	82	80	77			...	...	...	...	...			60	68	70	...	70	72	...	...	...	...	...	...

(a) Note maximum reduction. (b) Products from all tests except 7, and 7 contained excess carbon.

(a) Note maximum reduction. (b) Products from all tests except 7, and 7 contained excess carbon.

per min. The main efforts in these tests were to obtain the maximum reduction rather than the highest efficiency of the reducing agent, carbon or gases.

It is to be noted from Table VI that with precipitated barium sulfate, the highest reductions were obtained when the material was mixed with carbon, either as pulverized charcoal or lampblack, and when the higher temperatures were maintained in the furnace. Under these conditions the percentage of excess-reducing gases present in the furnace could be reduced to a very low figure. The pulverized commercial barytes was more difficult to reduce than was the precipitated barium sulfate.

When the maximum temperature in the furnace was above  $850^{\circ}C$ , the material was slightly sintered into balls about  $\frac{1}{8}$  in. in diameter, like cement cinder. These slightly cindered balls formed in the first reductions were easily broken up, and the material was pulverized readily for subsequent use as a precipitant in the solutions.

It is to be regretted that reduction tests at higher temperatures, *i. e.*, above  $900^{\circ}C$ , could not have been made with this type of furnace. However, we were not equipped with refractory hearths to withstand higher temperatures over longer periods of time.

#### SERIES 5—REDUCTION OF BARIUM SULFATE IN CEMENT KILN

Through the courtesy of the Chemistry Department of the University of California, we were given the use of a small cement kiln in the chemistry building of that university, for further work at higher temperatures on the reduction of barium sulfate. The cement kiln was 12 ft. long, 19 in. outside diameter and 10 in. inside diameter. The number of revolutions was 1.15 per min., the pitch was 1:18 (see Fig. III).

In the tests at this furnace, city gas or oil fuel was used for heating. The lower end of the kiln was closed by a sheet-iron plate covered with asbestos. Through this plate a gas burner was inserted, the gas being blown in with air under low pressure. A small gate was provided in this sheet-iron plate to allow drawing out the reduced product intermittently.

The charge to the furnace was fed in by hand at

the back of the furnace. Provision was made for taking samples of gas at several points along the length of the kiln, and also for measuring the temperatures at these points by thermocouples.

The gaseous products of the kiln were discharged into a brick stack. The draft at the furnace was reduced to a minimum, so that the reducing conditions in the furnace could be controlled by the air and gas entering through the burner pipe. Even with the draft reduced to a minimum, there was considerable barium sulfate carried out of the furnace by the gases. In one test, when oil was used and was being discharged through the burner by a high air pressure directly along the center line of the kiln, the loss of barium sulfate was very high, about 30 per cent. When this oil and air mixture was discharged at right angles with this center line striking against the sides of the kiln, the loss was greatly reduced.

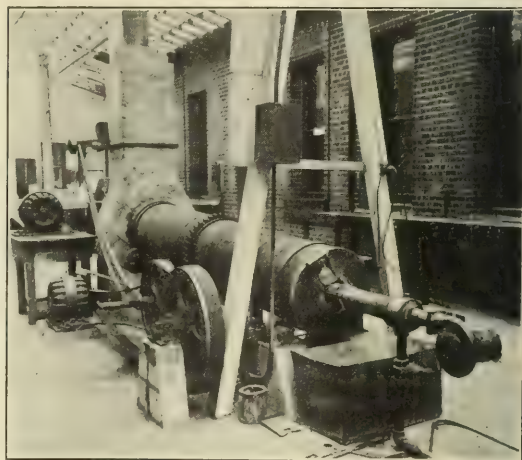


FIG. III—CEMENT KILN  
Chemistry Building, University of California

In these reduction tests, the temperature at the hottest part of the furnace was as high as  $1100^{\circ}C$ , and averaged  $1050^{\circ}C$ . For over half of the furnace the temperature was above  $850^{\circ}C$ . The average time the charge was in the furnace was  $2\frac{1}{2}$  hrs.

The average rate of feeding the charge to the furnace was 15 kg. per hr., ranging between 10 and 20 kg. per hr. The best reductions were obtained when the furnace was kept well filled with the charge.

The material used was finely pulverized barytes (98+ per cent  $\text{BaSO}_4$ ) (material used in paints by W. P. Fuller Co.), as large quantities of the precipitated barium sulfate could not be obtained. Six tests were made using city gas and one using oil for fuel. The main object in these tests was to obtain a high reduction of the barium to the water-soluble sulfide; high efficiency of the reducing agent was a secondary consideration. One test (5-7) below, however, was conducted for the purpose of obtaining a higher fuel efficiency than the others. This test showed that almost as high a reduction could be obtained with much less fuel consumption. None of these tests furnished conclusive data for calculating the fuel that would be required for effective reduction in a commercial sized kiln.

TABLE VII—REDUCTION OF COMMERCIAL PULVERIZED BARYTES IN CEMENT KILN

CHARACTER OF C USED	Pulverized Coke		Pulverized Charcoal		None	Pulv. Coke	
	5 1	5 2	5 3	5 4	5 5	5 6	5-7
TEST No. ....	1	2	3	4	5	6	5-7
Per cent C to $\text{BaSO}_4$ in charge.....	20	15	20	16	0	18	13
Rate Charge: Kg. per hr.....	10	10	15	15.2	12.5	16	18.7
Gas Consumption, Cu. ft. per min.....	5.4	5.6	6.1	6.3	6.2	oil(a)	3.8
Duration of Test, Total hrs.....	25	10	5	5	4	2	4
Av. Temp. ( $^{\circ}\text{C}$ ).....	450	460	420	400	510	...	370
Av. Temp. Middle of Kiln.....	850	880	880	860	900	...	840
Max. Temp. in Kiln (approx.).....	1050	1050	1100	1050	1100	1360	1050
Av. per cent CO in Furnace Gases (middle).....	3.8	4.2	3.1	4.2	6.2	...	1.5
ANALYSES OF PRODUCT OF TEST					(b)		
Per cent of Total Ba:							
Water-soluble.....	89	87	90	89	69	84	82
Acid-soluble.....	98	97	98	98	78	96	90
Insoluble ( $\text{BaSO}_4$ ).....	2	3	2	2	22	4	10

(a) Product of Test 5-5. Clinkered and unreduced  $\text{BaSO}_4$  left in interior of the clinker.

(b) Rate of oil consumption, 3 gals. per hr.

#### SUMMARY

I—The data obtained in the five series of reduction tests outlined above indicate that the maximum reduction of barium sulfate to sulfide was obtained at the higher temperature, *i. e.*, around  $1000^{\circ}\text{C}$ ., and when the reductions were effected in an indirect fired furnace, *e. g.*, in the muffle furnace, 15 or 16 per cent carbon gave the highest fuel efficiency consistent with completeness of reduction of the barium to the sulfide.

II—In reductions effected in a direct fired furnace (a cement kiln, multiple hearth roasting furnace, or a shaft furnace where hydrogen, hydrocarbons, or where the products of combustion of the fuel, water and carbon dioxide, were brought into contact with the sulfate or sulfide) there were formed a larger proportion of barium compounds insoluble in water, than were formed in a furnace indirectly fired. Thus, although the barium compounds in the best products from a direct fired furnace were 90 to 95 per cent soluble in acid, yet the barium present as the water-soluble sulfide was not more than 85 to 87 per cent of the total.

III—By effecting the reductions rapidly at high temperatures, *i. e.*, above  $1000^{\circ}\text{C}$ ., the proportion

of these water-insoluble barium oxides and carbonates was less than that formed in reductions at lower temperatures over a longer period of time.

IV—Below  $750^{\circ}\text{C}$ . the reduction by carbon or reducing gases was too slow to be considered commercial.

BUREAU OF MINES, WASHINGTON

#### THE THERMAL DECOMPOSITION OF THE ETHANE-PROPANE FRACTION FROM NATURAL GAS CONDENSATE

By J. E. ZANETTI AND E. H. LESLIE

Received August 3, 1916

In a previous paper<sup>1</sup> one of us presented the results obtained by the thermal decomposition of the propane-butane fraction from natural gas condensate. As a continuation of that work it seemed desirable to study the lower fraction, that containing chiefly ethane and propane, which fraction can likewise be found on the market and is used mainly for lighting and oxygen welding. This fraction comes in cylinders under 500 to 1000 lbs. pressure, and owing to the great difference in boiling points between ethane and butane,  $-93$  and  $+1^{\circ}$ , is little contaminated by butane. At 750 lbs. and the temperature of  $25^{\circ}$  the vapor pressure of butane as calculated from Burrell and Robertson's formula<sup>2</sup>

$\text{Log } P = -1633/T + 1.75 \log T - 0.01094 T + 7.590$  is 1545 mm., a little above 2 atmospheres. Since the pressure in the cylinder used was 750 lbs. above atmospheric, at  $25^{\circ}$  the amount of butane present in the issuing gas would be about 4 per cent. If we consider that the vapor pressure of the butane must be considerably diminished by the fact that it is dissolved in the liquid ethane and propane, the amount of impurity in the gas from this source becomes small. The very high pressure in some of these cylinders would indicate that there is also some dissolved methane in the liquid ethane. The critical temperature for ethane is  $+34^{\circ}$  and the critical pressure 50.2 atmospheres. As at  $25^{\circ}$  the pressures are often above the critical, the only other hydrocarbon present would be methane. This matter is dwelt on at present as it further bears out the observation made by one of us in connection with the propane-butane fraction that the aromatic hydrocarbons obtained from these fractions are built up from aliphatic compounds of lower carbon content than benzene. There is no possibility of aromatics having been obtained here by the splitting off of the benzene ring from phenyl paraffins as no such compound is known that would boil at the temperature of liquid ethane, under atmospheric pressure, or conversely under the pressure of liquid ethane at ordinary temperature. If such compound were present in this gas its vapor pressure would be so small in comparison with that of ethane and propane that it would constitute but a minimal fraction of the issuing gas and it could in no way account for the yield of tar obtained in these experiments—2.5 cc. of tar

<sup>1</sup> THIS JOURNAL, 8 (1916), 674.

<sup>2</sup> J. Am. Chem. Soc., 37, 2190.



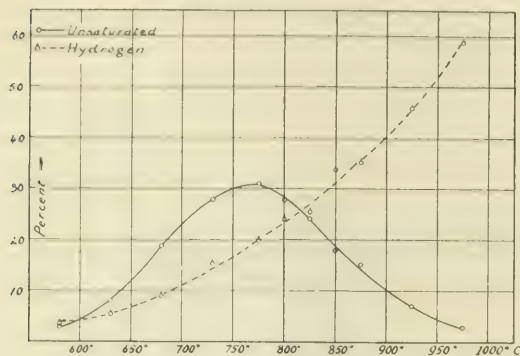


FIG. I—DECOMPOSITION OF ETHANE-PROPANE MIXTURE  
NO CATALYZER

(liquid) per cu. ft. of gas used. The cylinder of gas used showed a pressure of 750 at 25° which pressure remained constant, within the limits of accuracy of the gauge used, during these experiments. Analysis of the gas showed it to be composed chiefly of ethane and propane. No CO<sub>2</sub> was present and only less than 0.5 per cent "unsaturated."

The apparatus and method of procedure were exactly as described in the case of the propane-butane fraction. The gas was passed at a measured rate through a heating chamber, the tar "fog" formed precipitated electrically and samples of the gas analyzed for "unsaturated" and hydrogen. The results of these analyses are plotted in Fig. I. As in the case of the butane-propane fraction, the percentage of "unsaturated" increases gradually to a maximum in the neighborhood of 750°, decreasing again above that temperature to a minimum at about 950°. The content of hydrogen increases slowly at first, a marked increase in its rate taking place above 750°. The beginning of the decrease in "unsaturated" formation and of the increase in hydrogen formation are coincident, as noted in the case of the propane-butane fraction with the appearance of the tar "fog."

The "unsaturated," as shown by fractionation of the bromides, consisted chiefly of ethylene and propylene with small amounts of butene. The presence of butenes, which occurred in a very small amount, is doubtless due to the decomposition of the butanes, which, as pointed out above, must occur in the gas in small amounts.

The tar formation occurred at about 750°. The yield was very much smaller than in the case of the butane-propane fraction, amounting to only 2.5 cc. per cu. ft. of gas used. This might be expected from the fact that the average molar weight of the gas is much smaller than in the other fraction. How much of this aromatic formation is contributed by the ethane and how much by the propane is a question which we cannot discuss at the present moment. That the ethane does contribute to some extent can not be doubted since Bone and Coward<sup>1</sup> have found it to be the case, though only to a slight extent. The very small percentage of the lower boiling aromatics and

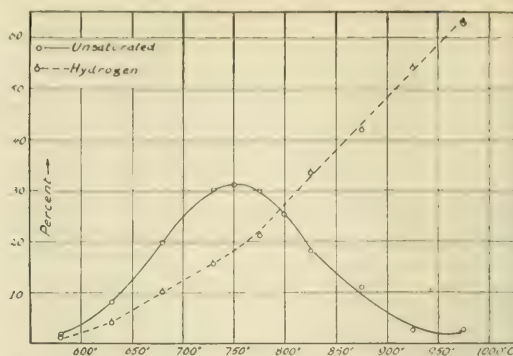


FIG. II—DECOMPOSITION OF ETHANE-PROPANE MIXTURE, USING COPPER  
AS CATALYZER

the unusually high one of naphthalene is worthy of notice. Only about 3 cc. out of 20 cc. of tar came over below 125° and about 1 cc. more below 200°. The rest was naphthalene and pitch. The naphthalene formed choked the condenser coil several times during a run and could be noticed in large flakes at the end of the quartz tube when cleaning out the apparatus between experiments.

The effect of copper as catalyzer was not marked in any way. The results when plotted (Fig. II) were, both for the "unsaturated" and for hydrogen, very similar to those obtained without a catalyzer. The aromatic formation proceeded in much the same way.

With iron as catalyzer (Fig. III) the same sharp drop in the unsaturated content at about 710° was noticed as with the propane-butane fraction, the hydrogen content increasing very rapidly as the "unsaturated" decrease. No aromatic formation was noticeable beyond the formation of a slight amount of "fog." Much carbon was deposited on the catalyzer necessitating its frequent renewal.

#### EXPERIMENTAL

**MATERIAL**—The material was a "liquid gas" from West Virginia in a steel cylinder under 750 lbs. pressure at 25°. The results of the explosion with oxygen are given in Table I. Analyses I and II were made at the beginning, III and IV at the end of the experiments presented. The gas had in addition 0.4 per cent "unsaturated" and about 0.5 per cent hydrogen. There was no CO<sub>2</sub>.

TABLE I—ANALYSIS OF GAS

ANALYSIS:	I	II	III	IV
Volume gas.....	12.3	12.3	11.7	12.2
Contraction.....	34.4	34.0	32.0	33.9
Volume CO <sub>2</sub> .....	29.9	29.6	30.9	31.7

**APPARATUS AND PROCEDURE**—The apparatus and procedure were the same in all respects as used for the propane-butane fraction and their description is unnecessary. The rate of gas flow through the chamber was the same, 0.45 cu. ft. per hr.

**GAS ANALYSIS**—The gas analysis was conducted over water. For the determination of the "unsaturated," bromine was used. The hydrogen was determined by combustion over copper oxide. The results are given in Table II.

<sup>1</sup> J. Chem. Soc., 93, 1197.

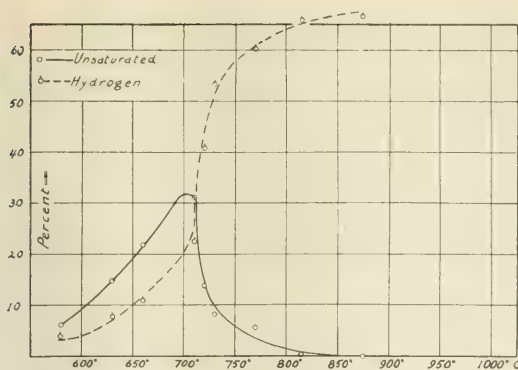


FIG. III—DECOMPOSITION OF ETHANE-PROPANE MIXTURE, USING IRON AS CATALYZER

THE "UNSATURATED"—The gases coming between 800° and 850° were passed into bromine till the latter became colorless. After drying, 25 cc. were distilled and the following fractions collected: 5 cc. below 127°; 9 cc., 127–132°; 5 cc., 132–142°; 5 cc. residue. On allowing the residue to stand a small amount of crystals separated out. Pressing from the mother liquor and crystallizing from alcohol they were obtained in the form of small, transparent, prismatic crystals melting at 116°.

AROMATICS—The tar obtained was quite fluid and after filtering showed a specific gravity of 1.075. Twenty cc. were distilled in a small flask. Three cc. came over below 125°, 1 cc. below 200°. Above that, naphthalene began to solidify in the condenser. The distillation was continued under reduced pressure, about 8 cc. coming over and solidifying to a yellowish

TABLE II—ANALYSIS OF GASEOUS PRODUCTS WITH AND WITHOUT CATALYZER

NO CATALYZER			COPPER AS CATALYZER			IRON AS CATALYZER		
Temp. ° C.	Unsat- urated Per cent	H Per cent	Temp. ° C.	Unsat- urated Per cent	H Per cent	Temp. ° C.	Unsat- urated Per cent	H Per cent
580	2.8	3.4	580	1.7	1.3	580	6.1	3.6
630	7.8	5.3	630	8.1	4.0	630	14.9	7.9
680	18.9	8.8	680	19.9	10.1	660	22.0	10.9
730	28.0	15.3	730	30.2	15.6	710	31.2	22.5
775	31.0	19.6	750	31.5	—	720	14.2	40.9
800	27.9	24.0	775	30.0	21.2	730	8.3	53.4
825	24.2	26.1	800	25.4	—	770	5.7	60.3
850	18.0	34.0	825	18.2	33.5	815	0.3	65.8
875	15.2	35.3	875	11.0	42.0	875	0.0	66.6
925	7.2	46.4	925	2.6	54.0			
975	3.0	58.8	975	2.8	62.7			

mass of crystals. On crystallizing from alcohol they gave a melting point of 79°. The residue solidified in the flask, forming a black pitch with a strong odor resembling anthracene. Nitrobenzole was obtained from the fraction boiling below 125°, but no nitrotoluols could be obtained from it.

#### SUMMARY

I—It has been shown that mixtures of ethane and propane decompose at high temperatures, giving ethylene, propylene and other "unsaturated," hydrogen and aromatics.

II—The percentage of "unsaturated" increases with increasing temperatures to a maximum in the neighborhood of 750°, then decreases with increasing temperatures. The aromatic formation begins at about 750° C. and is coincident with an increase in the rate of hydrogen formation.

III—The action of copper and iron as catalyzer has been studied. Iron prevents aromatic formation and favors the decomposition of the hydrocarbons into carbon and hydrogen.

Further work upon these topics is now in progress in this laboratory.

DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY  
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#### THE SOLUBILITY OF LEUCITE IN SULFUROUS ACID

By J. SCHROEDER

Received May 19, 1916

Leucite belongs to a class of potash-carrying silicates that has received considerable attention as a possible source of potash.<sup>1</sup> It is a metasilicate of aluminum and potassium having the formula  $KAl(SiO_3)_2$  or  $K_2O, Al_2O_3, 4SiO_2$ . On this basis its theoretical composition is: Silica, 55.0 per cent; alumina, 23.5 per cent; and potash, 21.5 per cent. From this it is evident that in potash content it is one of the richest minerals known.

Leucite occurs in the more recent volcanic rocks as embedded crystals, grains, or aggregates of grains. It is identified especially with the lavas of Mt. Vesuvius and other localities in Italy, though its occurrence is by no means restricted to these localities. In North America it is found in Lower California, New Jersey, Arkansas, British Columbia, and especially in several places outlying from the Rocky Mountains, notably the Leucite Hills of Wyoming. These hills are situated in southwestern Wyoming from 10 to 15 miles north of Bitter Creek, which is an eastern tributary of Green River and is followed by the Union Pacific Railroad.

The Leucite Hills consist of a number of conical peaks of lava protruded through the beds of rocks forming the plateau of the surrounding neighborhood. Each peak consists of a lava sheet, presenting an abrupt wall from 50 to 150 ft. high. These deposits are described in detail by Schultz and Cross.<sup>2</sup>

The leucite rocks of this neighborhood are of a yellowish gray color and often, if not always, of a pronounced cellular structure. The porosity, however, does not reach the pumice stage. The leucite inclusions are microscopic crystals 0.035 mm. in diameter. The chemical composition of the rocks as indicated by the analyses of the United States Geological Survey is about as follows: Silica, 53 per cent; alumina, 11 per cent; ferric oxide, 3 per cent; magnesia, 6.5 per cent; lime, 4.5 per cent; soda, 1.5 per cent; and potash, 11 per cent.<sup>2</sup>

To ascertain the possibility of recovering this potash by leaching, solubility tests were made with sulfurous acid. A sample of leucite rock from Batuku, Celebes, East Indies, containing 9 per cent potash, was obtained through the courtesy of Dr. J. P. Iddings of the United States National Museum. This was ground and separated, by sifting, into portions of different fineness and these portions shaken over night with a solution of sulfurous acid. The latter was prepared by passing sulfur dioxide through water to approximate satura-

<sup>1</sup> Cushman and Coggeshall, THIS JOURNAL, 4 (1912), 821.

<sup>2</sup> U. S. Geol. Survey, Bull. 512.



tion at room temperature. The total quantity of material dissolved was found by filtering the solution through a Gooch filter and weighing the residue, and the potash was determined by the chlorplatinic acid method. The quantity of sample used was 0.5000 g. and the volume of the solvent 200 cc. The determinations showed the following results:

FINENESS OF SAMPLE	PER CENT OF POTASH DISSOLVED		TOTAL MATTER DISSOLVED
	On basis of sample	On basis of K <sub>2</sub> O present	
0.5 to 0.25 mm.	3.7	41.7	16.4
0.25 to 0.10	5.1	57.0	18.8
0.10 to 0	6.7	75.2	25.8
0.10 to 0	6.8	76.4	26.2
0.5 to 0(a)	4.7	52.2	26.7

(a) This sample consisted of a mixture of the first three grades of fineness in the ratio of 5, 36 and 58 per cents.

From these results it is evident that potash may be dissolved from leucite rocks by means of sulfurous acid. This shows a possibility of an important industrial application since it indicates that smelter fumes, containing sulfurous acid gas, may be used directly for recovering potash from leucite. Of course it is known that sulfuric acid may be used for that purpose, but there is a demand among operators of smelters for a method of using sulfurous acid gas that does not involve the expensive installation required to convert it into sulfuric acid. It happens also that the leucite of the Leucite Hills occurs in a region accessible in a general way to the smelters of Utah, Colorado and Montana. It may be possible to devise methods whereby smelter fumes can be passed over or through the leucite rocks, in the presence of water, and the potash thus gradually leached out, perhaps with the minimum of installation and manipulation. It is recalled that the Wyoming leucite rocks are porous, somewhat resembling pumice. This fact may operate to facilitate the percolation of the material and the leaching of the potash. It is observed, furthermore, that the dissolution in sulfurous acid is selective. Thus, while other materials are dissolved from the rock, the potash is dissolved in the greatest relative proportion.

It has been shown that the quantity of potassic rocks in the Leucite Hills region is very great, the potash therein contained being estimated by Schultz and Cross at 197,349,617 tons. That large quantities of sulfurous acid gas are available at the western smelters is of course well known.

BUREAU OF SOILS  
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#### A NOTE ON THE CAUSE OF THE PINK COLOR OBSERVED IN CERTAIN HYPOCHLORITE BLEACHING SOLUTIONS

By H. G. ELLEDGE  
Received May 17, 1916

When sodium hypochlorite bleaching solutions are prepared for use in laundering, by treating a solution of calcium hypochlorite, or bleaching powder, with a solution of the so-called neutral washing powder,<sup>1</sup> after the calcium carbonate has settled out,

<sup>1</sup> These sodas are usually of about the following composition: normal sodium carbonate, 46.3 to 36.1 per cent; sodium bicarbonate, 37.7 to 50.0 per cent; and water, 16.0 to 13 per cent. See Faragher, *This Journal*, 6 (1914), 641. The observations of Faragher have been confirmed and extended by the writer.

a pink colored solution invariably appears. This coloration has been observed when various trade brands of bleaching powder were employed, some of which were of American manufacturers and others of English origin; in fact, it seems to result in every case where an excess of the HCO<sub>3</sub> ion is present in the solution. When bleaching solutions were made of the same bleaching powders, but, instead of the "washing sodas" mentioned, soda ash or sodium sulfate was used to precipitate the calcium, the color of the resulting solution was green. By agitating this green solution with sodium bicarbonate, the pink color was again obtained.

When certain laundries adopted soda ash as the wash-room alkali, the wash-room help thereof were concerned about the absence of the pink color which, through habit and also because of the influence of the sales agents of certain alkali companies, they had come to regard as an index to the bleaching qualities of the solution. Owing to this condition, the writer was requested by the Allegheny County Laundrymen's Exchange to explain the origin of the coloration and to ascertain definitely whether there was any difference in the bleaching properties of the green and pink solutions. As was to be expected, it was found that equal volumes of the solutions, when made up with identical weights of the same bleaching powder, gave the same values for available chlorine. Among others, bleaching tests on hemp strings indicated that one solution was as satisfactory as the other for laundry bleaching.

The writer was led to conclude that the color of the pink solution was attributable to the presence of traces of sodium permanganate, the manganese being derived from the bleaching powders used. This conclusion was reached after certain experimental work, of which the following is illustrative: There were made up two solutions of sodium hypochlorite of the same strength.<sup>1</sup> To one of them a small amount of manganous sulfate was added; this produced no change in color. Then to each of the solutions, 10 g. of sodium bicarbonate were added; after thoroughly shaking and settling, the solutions both assumed a pink color, but the one to which the manganous sulfate had been added possessed a much more intense color. By color comparisons, it was estimated that 0.02 per cent to 0.04 per cent of manganese in the bleaching powders would be sufficient to produce this color.

It was early suggested that the pink coloration might be caused by the presence of small amounts of sodium ferrate. Therefore, solutions were prepared as above, and to one of them, ferric chloride was added; then, to both solutions sodium bicarbonate was added, as above. After the precipitates had settled, no difference could be observed in the intensities of the pink color of the different solutions. These and other experiments led to the conclusion that the color was due to traces of manganese, which, by the catalytic action of the bicarbonate on the hypochlorite, was oxidized to

<sup>1</sup> The solutions were prepared by making a paste of 10 g. of bleaching powder and water, adding thereto 10 g. of soda ash, and, after thoroughly shaking in a flask, making the volume up to 250 cc. This is the strength usually adopted in the laundry for stock solutions.

the permanganate, and that, for laundry purposes, this coloration was of no consequence.

Subsequently, when the writer's report became available,<sup>1</sup> the contention was made by a representative of one of the prominent alkali manufacturers that the pink color was due not to the presence of permanganate, but of a ferrate; and in order to settle definitely the whole matter, the absorption spectrum of the pink bleaching solution was compared with that of a solution of potassium permanganate of the same color intensity. The solution used was made four times the concentration<sup>2</sup> usually employed and, after all the precipitate had settled, a saccharimeter tube was filled with the clear pink solution. A similar tube was filled with potassium permanganate solution of same color intensity and the absorption spectra were compared; they were found to be identical. To compare the two more carefully, the two absorption spectra were brought in view at one time, by means of the comparison mirror, and the positions of the lines were shown to be exactly the same.

No attempt is made here to account for the presence of the trace of manganese in the bleaching powder, but the writer feels that he has offered positive evidence that the color of the pink bleaching solutions is due to the presence of sodium permanganate, and not of sodium ferrate, as some have maintained.

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PITTSBURGH

#### ON THE USE OF CERTAIN YEAST NUTRIMENTS IN BREAD-MAKING<sup>3</sup>

By HENRY A. KOHMAN, CHARLES HOFFMAN, TRUMAN M. GODFREY  
LAUREN H. ASHE, AND ALFRED E. BLAKE

Received June 7, 1916

The work in bread-making at the Mellon Institute was begun in 1911 through the establishment of the Ward Fellowships and the results will now be published in a series of contributions.

One of the important problems studied in our bread investigations was the effect of certain mineral salts (such as are commonly found in natural waters) upon the fermentative activity of the yeast in bread-making. It was found necessary by the Ward Baking Company (who operate bakeries in several cities) to change the quantity of yeast as well as the fermentation period of their dough batches in the different cities, in order to produce a standard product, or nearly so, even though all the raw materials used were identical (being purchased through a central office). Upon investigation it was found that variations in the activity of the yeast were due to the differences in the mineral content of the waters used for making the bread in these cities. In the work reported in this paper the effect of mineral salts found in natural waters upon the fermentative power of the yeast, as well as the quantity of yeast necessary for leavening purposes, has been given particular attention and

<sup>1</sup> The conclusions were reported by bulletin to the Allegheny County Laundrymen's Exchange on April 17, 1916.

<sup>2</sup> The solution of sodium hypochlorite was prepared with 40 g. of commercial calcium hypochlorite, 40 g. of soda ash, and 40 g. of sodium bicarbonate, made up to a volume of 250 cc. with distilled water.

<sup>3</sup> A paper presented in abstract by Henry A. Kohman at the Urbana Meeting of the American Chemical Society, April 19, 1916.

close investigation. The mineral substances contained in flour, milk, yeast and other raw materials for bread were investigated in detail also, using a large variety of combinations and proportions.

Of the large number of substances investigated, those that have a really significant effect upon the fermentation in bread are surprisingly few. The salts of the mineral acids, such as the chlorides, nitrites, nitrates and sulfates, exert practically no influence except when combined with a cation which in itself has an effect. The carbonates are especially common in natural waters and as a class are objectionable in bread, since they neutralize the acids of the dough and thus interfere with the progress of the fermentation. More particularly, the carbonates of magnesium and the alkali metals should be considered as being detrimental to the fermentation of the yeast.

The salts of potassium, particularly the phosphates, were expected to exert a decided influence on the fermentation of bread, because these compounds constitute such a large proportion of the ash of yeast and are mentioned so frequently in connection with alcoholic fermentation. However, the potassium salts were found to influence the fermentation of bread only very slightly, while the phosphates had no noticeable effect. This is to be explained, no doubt, by the fact that the ash of flour is rich in these salts, consisting of about one-third potash ( $K_2O$ ) and one-half phosphoric acid ( $P_2O_5$ ), which abundantly supplies the yeast.

Because of their common occurrence in natural waters, the salts of the alkaline earth metals were studied in detail, with surprisingly interesting results. The calcium salts, especially, are of common occurrence in water and it is around these that the most interesting results presented in this paper center.

Besides the water problem, the utilization of stale bread was indicated as an important problem for research. One of the proposed methods for using stale bread comprised the cooking of the crumbs and then digesting with malt. The starches were thus transformed into sugars and the gluten remained in flakes which could be separated by filtration. From this gluten residue, by digesting with concentrated HCl in the ordinary way, glutamic acid hydrochloride was recovered in considerable quantities. The effect of the glutamic acid upon the parent substance, gluten, in bread was found to be a decidedly beneficial effect both upon the dough and upon the yeast.

#### AMMONIUM SALTS

Like many other acids, glutamic acid matures or ages the dough and, in addition, increases the gas production of the yeast. This accelerating effect upon the yeast was observed in bread and likewise in fermenting cane sugar, dextrose, and malt extract. In fermentation of this kind other acids failed to increase the fermentation as did glutamic acid hydrochloride, so we were led to believe that it was not a matter of acidity but that glutamic acid hydrochloride owes its accelerating effect to its nitrogen content. With this idea in mind, we conducted baking experi-



ments with other nitrogenous substances. Ordinary peptone, such as is used for culture media, as already known, accelerates alcoholic fermentation greatly but this substance is expensive and, accordingly, attention was directed toward cheaper materials which would accomplish a similar result. The salts of ammonium were found fully as efficient as peptone.

Before giving the experimental data, it should be said that during the course of this investigation, which extended over a period of several years, the conditions were changed from time to time; consequently, the results of any particular series of baking experiments can not be compared strictly with those of another. Every precaution was taken, however, to maintain the same conditions throughout each series, so that the individual loaves could be compared closely with the control and with each other. In each series of experiments the loaves were scaled, moulded, proofed and baked together. Therefore, when accelerators were added the loaves naturally had not all risen to the same height when they were placed in the oven, as they do in commercial baking practice. Consequently, the volumes given in the tables are an expression of the rate of fermentation rather than of the relative lightness or degree of expansion that may be obtained. For example, when there was, say, a 10 per cent increase in volume noted with the use of an accelerator, it does not mean that the expansion was increased but merely that the rate of fermentation was increased by that amount. If the two loaves had been brought to the same degree of maturity and proofed to the same height in the pans, as is customary in baking practice, both loaves would have conformed to the standard size. In many bread laboratories, also, it is customary to proof all the loaves to the same height, especially when the volumes are taken to represent the expansion, as is the case in testing flours. In the experiments of this paper, however, all the loaves of each series were baked simultaneously, so the volumes should be interpreted as indicating the rate of the fermentation rather than the expansion of the loaves.

The following series of experiments will serve to illustrate the effect of ammonium sulfate upon the yeast in bread-making. A kilogram of flour was used in each batch.

BREAD No.	Grams (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	LOAF Cc.	VOLUME % Increase	Cc. Gas in 7 1/2 hrs.	Per cent Gas Increase
646	0.0	1630	0.0	292	0.0
647	0.5	1790	0.8	311	6.5
648	1.5	1865	14.4	310	6.5
649	2.5	1870	14.7	329	12.6
650	3.5	1930	18.4	328	12.6
651	4.5	1900	16.5	338	15.7

Besides increasing the gas production and improving and securing a more uniform loaf volume, the ammonium sulfate improved the texture and the general uniformity and appearance of the bread. The gas production was estimated by taking a small portion (50 g.) from each dough and collecting the gas evolved over a saturated solution of calcium chloride in Bunsen gas holders.

In a cane-sugar medium, ammonium sulfate also greatly increased the fermentative power of yeast.

A series of seven fermentation experiments was made, using 68 g. of water, 1.2 g. of yeast and 6 g. of sugar, with varying amounts of ammonium sulfate. The results were as follows:

Experiment No.	1	2	3	4	5	6	7
Grams (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0.0	0.25	0.5	1.0	2.0	4.0	8.0
Gas, cc. in 6 1/2 hrs.	291	358	364	392	447	457	155
Per cent increase	0.0	24.0	25.1	34.8	53.7	57.2	46.8

While readings were taken every half hour, the total gas produced will serve to illustrate the accelerating action of ammonium sulfate. It will be noted that 8 g. has a marked retarding action.

Early in the research it was observed that the increased fermentation, due to ammonium sulfate, matured the doughs in a much shorter time. Bread fermented 3 1/2 hrs. with the use of ammonium sulfate was practically as mature as the control bread in 4 1/2 hrs. Obviously, then, this salt can be used for the production of bread in a shorter time. On first thought, one might infer that this action would be taken advantage of in increasing the output of a bakery; this, however, is not the case. The oven capacity, more than anything else, governs the productive power of a bakery. Although a short fermentation period is highly desirable in the bake shop, there is a limit beyond which it is not safe to go. Unforeseen delays are frequent in the daily operations, and since these often occur when the dough is already working, over-fermentation is the result. The shorter the fermentation period, the greater will be the over-fermentation when delay occurs. In our opinion, according to present practices, the fermentation period should not be less than 4 1/2 to 5 hrs. for hard wheat flours, excepting, of course, in special cases in which it is necessary to produce bread in a very short time to meet rush orders. In general, the increased fermentation due to the addition of ammonium sulfate can best be utilized by reducing the amount of yeast that is ordinarily required. The following series of baking experiments serves to illustrate the value of this salt in the diminution of yeast requirement:

BREAD No.	GRAMS YEAST	Fermented:	VOLUME OF LOAF (Cc.)		
			3 1/2 hrs.	4 1/2 hrs.	5 1/2 hrs.
193 (control)	12.0		1695	1735	1745
198	9.0 (25% less)		1805	1815	1875
194	8.4 (30% less)		1665	1755	1795
196	7.8 (35% less)		1655	1705	1805
197	7.2 (40% less)		1645	1695	1795

It is obvious that the amount of yeast that can be saved by the use of ammonium sulfate depends upon the length of time the dough is fermented. In a 4 1/2-hr. dough (4 1/2 hrs. is the time adopted in many bakeries for straight doughs), 30 per cent of the usual amount of yeast can be saved, while the saving in yeast in a 5 1/2-hr. dough is 40 per cent. Various processes are in use in different bakeries and the length of the fermentation period ranges from 3 1/2 hrs. to 6 or even 8 hrs. in straight doughs and from 5 to 10 or 12 hrs. in the sponge-dough process. The fact that the ammonium salt accelerates the activity of the yeast most toward the end of the fermentation period is considered significant. It is then that gas production is most essential, for it causes the loaves to "spring" or "kick," which is very desirable and

necessary for the production of a loaf with a fine close texture, good color and flavor. Especially is the "spring" desirable in the special types of loaves which are cut lengthwise, for it opens and ventilates them properly and gives to the top of the loaves a fine shredded appearance that is inviting and appealing to the sight and taste. In referring to good color here, it must be borne in mind that excessive fermentation will destroy such good color, as is reasonable to expect, dependent on the grade or quality of flour used, while proper fermentation will save or spare it.

Other ammonium salts than the sulfate may be used with equally good results. We have employed the chloride, phosphate, biphosphate, tartrate, oxalate, nitrate, acetate, formate, iodide, and sulfocyanate, and have observed no pronounced differences. However, for economic reasons, the sulfate and chloride are considered most suitable for commercial purposes. Because of its alkaline properties, ammonium carbonate can not be used successfully, as is shown by the following baking experiments:

Bread No.	1653	1654	1655	1656
Gram $(\text{NH}_4)_2\text{CO}_3$	0.0	0.24	0.5	1.0
Loaf volume, cc.	1505	1560	1530	1445
Per cent increase	0.0	+3.3	+1.6	-3.9

In small quantities, the volume remains practically unchanged, while it is diminished by 1 g. or more. Alkalies are very detrimental in bread and this, no doubt, explains the inefficiency of ammonium carbonate. Moreover, it was observed that ammonium carbonate imparted an objectionable odor to the bread. The carbonate may be used successfully only when sufficient acid is used to neutralize its alkalinity.

Ammonium fluoride accelerates the fermentation quite as much as other ammonium salts if used in small quantities; but in larger quantities it retards fermentation to a marked extent, as is evident from the following series of experiments:

Bread No.	847	848	849	850	851	852
Grams $\text{NH}_4\text{F}$	0.0	0.1	0.2	0.4	0.8	1.6
Loaf volume, cc.	1690	1850	1955	2080	1930	1400
Per cent increase	0.0	10.0	15.7	23.1	14.1	-17.1
Acidity	0.14	0.13	0.14	0.13	0.15	0.14

Evidently ammonium fluoride can not be used in as large quantities as ammonium sulfate, for, with the latter, the maximum acceleration was not exceeded even when 4.5 g. were used, while with the fluoride the maximum effect was obtained with less than 1 g.

In small quantities, however, the acceleration by ammonium fluoride is more pronounced, in equal weights, than that by ammonium sulfate, the explanation of which, no doubt, lies in the great difference in the molar weights. The inhibiting effect characteristic of ammonium fluoride in large quantities was also noted with hydrofluoric acid. Three doughs of the usual size were made with respectively 1, 2 and 4 cc. of hydrofluoric acid solution and none of them rose. Sodium fluoride is not so detrimental, as may be seen from the following results:

Bread No.	1338	1339	1340	1341	1342	1343
Grams $\text{NaF}$	0.0	0.1	0.2	0.4	0.8	1.6
Volume, cc.	1515	1555	1525	1485	1475	1505
Per cent increase	0.0	+2.6	+0.6	-1.9	-2.6	0.6

The diminution in volume observed in this series is not significant.

#### CALCIUM SALTS

The results of our experiments with calcium salts, which have already been mentioned in connection with their occurrence in natural waters, will now be taken up in detail. Their effect will be given both when used alone and in conjunction with other salts. The effect of calcium chloride is indicated in the following table:

Bread No.	609	610	611	612	613	614
Grams $\text{CaCl}_2$	0.0	0.5	1.5	2.5	3.5	4.5
Loaf volume, cc.	1830	1935	2040	2070	2090	2110
Per cent increase	0.0	5.7	11.4	13.1	14.2	15.3
Gas	348	361	380	393	391	385
Per cent increase	0.0	3.7	9.1	12.9	12.3	10.6

There was a decided increase in volume and gas production with the increase in the calcium chloride content of the doughs. The texture, flavor, and general appearance of the bread were improved, as well. The loaf volume was increased considerably more than the gas production, which would indicate that calcium chloride has an effect upon the gluten of the dough as well as upon the yeast. In the light of some experiments conducted by Hardy upon the effect of electrolytes on the strength of wheat flour, this seems highly probable.

The effect of calcium chloride upon the fermentation of cane sugar is shown in the table below. In each of the six experiments, 100 g. of water, 10 g. of sugar, and 2 g. of yeast were used.

Experiment No.	1 (control)	2	3	4	5	6
Grams $\text{CaCl}_2$	0.0	0.5	1.0	2.0	4.0	8.0
Gas in 6 1/2 hrs.	344	391	408	418	429	281
Per cent increase	0.0	+13.6	+18.6	+21.5	+24.7	-18.2

The accelerating effect of calcium chloride in bread, like that due to ammonium salts, can best be taken advantage of by reducing the amount of yeast ordinarily used. As with the use of ammonium salts, the amount of yeast that can be saved depends upon the length of the fermentation period. In a 4 1/2-hr. dough, about 25 per cent of the yeast can be saved.

The effect of other calcium salts is very similar to that of the chloride. The results given below with calcium bimalate indicate that it is equally effective.

Bread No.	573	574	575	576	577	578
Grams calcium bimalate	0.0	0.5	1.5	2.5	3.5	4.5
Loaf volume, cc.	1770	1850	1970	2005	2020	2110
Per cent increase	0.0	4.5	11.3	13.3	14.1	19.2

The increase in volume is even greater than with calcium chloride. However, as calcium bimalate is slightly acid, the two salts are not strictly comparable.

The sulfates of calcium in the following series of experiments, in which  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$  were compared in molar quantities, increased the volume rather less than the chloride, especially with the larger quantities.

BREAD No	Grams $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Grams $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$	LOAF VOLUME Cc	% Increase
3916 (control)	0.0	0.0	1670	0.0
3917	0.5	0.0	1710	2.4
3918	0.0	0.422	1723	3.2
3919	1.0	0.0	1726	3.4
3920	0.0	0.844	1796	7.6
3921	2.0	0.0	1863	11.5
3922	0.0	1.688	1826	9.4
3923	4.0	0.0	1830	9.6
3924	0.0	3.376	1853	11.0
3925 (control)	0.0	0.0	1676	0.4

In the following series of experiments the sulfate



and chloride were compared carefully, using small quantities:

BREAD No.	GRAMS SALTS	LOAF VOLUME	
		Cc	% Increase
1060	0 0	1830	0.0
1061	1 CaCl <sub>2</sub>	1915	4.6
1062	1 CaSO <sub>4</sub> · 1/2 H <sub>2</sub> O	1945	6.2
1063	2 CaCl <sub>2</sub>	2045	11.7
1064	2 CaSO <sub>4</sub> · 1/2 H <sub>2</sub> O	2065	12.6

In each case it will be noticed that the sulfate gives a slightly larger loaf volume. In small quantities, then—say, about 2 oz. per 60 lbs. of water, or approximately 160 lbs. of bread—the sulfate gives equally good, if not better results than the chloride. In practice there is used not more than 2 oz. per 160 lbs. of bread and as calcium chloride, owing to its extremely hygroscopic nature, can not be used satisfactorily, because it can not be conveniently shipped or kept in the dry state, the sulfate is preferable for commercial use.

The nitrate and phosphates of calcium have also been used successfully. Of the phosphates, Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> and CaHPO<sub>4</sub> are most suitable, as the normal salt is both alkaline and difficultly soluble.

Since both calcium and ammonium salts accelerate fermentation and improve bread, experiments were made with both salts in conjunction with bread-making. The results of one series of experiments were:

BREAD No.	Gram (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Grams CaCl <sub>2</sub>	LOAF VOLUME	
			Cc.	% Increase
548 (control)	0.0	0.0	1800	0.0
549	0.5	0.0	1800	0.0
550	0.5	0.5	1985	10.1
551	0.5	1.5	2050	13.9
552	0.5	2.5	2065	14.7
553	0.5	3.5	2115	17.5
554	0.5	4.5	2120	17.7

Thirty per cent less yeast was used with these salts. It will be seen that in conjunction with ammonium sulfate calcium chloride gives a further increase in the loaf volume. Since this was found to be true, a series of experiments was made to determine how much yeast could be saved by the use of both salts in bread. The results were as follows:

BREAD No.	Grams CaCl <sub>2</sub>	Gram NH <sub>4</sub> Cl	Yeast Used	LOAF VOLUME Fermented:			Mean Loaf Vol.	Per cent Increase in Vol.
				3 1/2 hrs.	4 1/2 hrs	5 1/2 hrs.		
555 (control)	0.0	0.0	Normal	1915	1820	1890	1875	0.0
556	0.0	0.5	30% less	2000	1920	2070	1995	6.4
557	2.0	0.5	30% less	2130	2270	2365	2255	20.2
558	2.0	0.5	40% less	2000	2165	2195	2120	13.1
559	2.0	0.5	50% less	1965	2060	2270	2095	11.7
560	2.0	0.5	60% less	1800	1880	2055	1910	1.8

With both salts, as with the use of an ammonium salt alone, the amount of yeast that can be saved depends upon the fermentation period employed. After 3 1/2 hrs. fermentation, only 50 per cent of the normal amount of yeast could be saved without a sacrifice in loaf volume, while after 4 1/2 hrs. 60 per cent could be saved. After 5 1/2 hrs. fermentation, the batch with 60 per cent less yeast produced a loaf volume that was decidedly larger than the control, indicating that still more yeast could have been saved.

The fact that the gas production is greatly increased toward the end of the fermentation period by the yeast nutrients, was observed also by collecting the gas from 60-g. portions of two doughs over a saturated solution of calcium chloride in Bunsen gas holders. The following data will serve to illustrate this point:

Time	GAS PRODUCED DURING VARIOUS PERIODS								TOTAL
	9 40	10 40	11 40	12 50	1 50	2 50	3 50		
Control	0	55	67	85	89	74	77		447 cc.
1643	0	28	43	62	73	75	80		361 cc.

It will be noticed that dough 1643 (with 50 per cent of the usual quantity of yeast, 1 g. of CaCl<sub>2</sub> and 0.5 g. of (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) evolves gas only about half as rapidly as the control in the initial fermentation, but that after 6 hrs. it exceeds the control in the rate of gas production. This is indeed significant, for it is at the end of the fermentation period when the dough has been moulded into loaves that active production of gas is required and most needed. If the yeast weakens when the dough is in the proof box or oven, the bread will not have the "spring" necessary to produce a well-risen loaf with a good shape and texture.

In this connection, it should be mentioned that others have experimented with ammonium salts in connection with research on flours. J. T. Willard and C. O. Swanson<sup>1</sup> found that ammonium chloride produced a beneficial effect on the baking qualities of flour, while the phosphate had no effect, and the tartrate and acetate had a detrimental effect upon the texture. The application of ammonium chloride or other ammonium salts to effect economies in yeast in connection with bread-making are not mentioned in the report of those investigators.

A. J. J. Vandervelde,<sup>2</sup> L. Bosmans, F. Le Perre, J. Mason and A. Revigu<sup>2</sup> state that ammonium chloride and nitrate have only a slight action and that calcium nitrate exerts a very unfavorable action. In our opinion, the quantities used were excessive, and, moreover, such discrepancies in the literature on bread are not uncommon and are to be explained, no doubt, by inaccuracy in experimentation and by the fact that so many factors, such as temperature, age of dough, strength of flour, stiffness of dough, etc., affect the results; consequently, they are often misinterpreted and important results are sometimes overlooked.

The fact that the initial fermentation with yeast nutrients with a reduction in the usual amount of yeast is much slower than that of a normal dough has an interesting economic significance. It is well known that during the normal fermentation of bread there is a considerable loss of dry material, due to the decomposition of the constituents of the dough into volatile products. These losses as determined by various investigators are: Voorhees,<sup>3</sup> 4.3 per cent; Heeren,<sup>3</sup> 1.57 per cent; Fehling,<sup>3</sup> 4.21 per cent; Croeger,<sup>3</sup> 2.14 per cent; Jago,<sup>4</sup> 2.50 per cent; and Snyder and Voorhees,<sup>5</sup> 2 to 6 per cent or even 11 per cent, in cases of prolonged fermentation.

One of us, in a previous paper,<sup>6</sup> demonstrated that the losses in bread-making depend to a large extent upon the amount of fermentation which the dough undergoes. In a normal fermentation the losses were found to be 5.15 per cent, while with the same flour

<sup>1</sup> Kansas Agr. Exper. Sta., Bull. 190, 248-251; Exp. Sta. Report March, 1912, 356.

<sup>2</sup> Rev. gén. chim., 16, 123, 136.

<sup>3</sup> U. S. Dept. Agr., Office of Experiment Stations, Bull. 35.

<sup>4</sup> Jago, "The Science and Art of Bread-Making," p. 361.

<sup>5</sup> U. S. Dept. Agr., Bull. 67, 11 and 28.

<sup>6</sup> Kohman, THIS JOURNAL, 4 (1912), 20-30 and 100-106.

the total losses were only 1.81 per cent, when the loaves were placed into pans at once upon mixing. The bread obtained in this way was decidedly poor, as is always the case when it is very much under-fermented, and it was made in this way merely to detect any difference in losses due to fermentation. In salt-rising bread the losses were found to be only 0.44 per cent. This difference in the losses in the two types of bread was explained as follows: (1) Yeast produces 1.04 parts of alcohol for every part of carbon dioxide, both of which are largely driven off during the process of baking, while in salt-rising bread there is no alcohol produced. (2) It is necessary to ferment yeast bread in the sponge and dough stages from 5 to 8 hrs., and, as it is allowed to rise in loaf form in the pans but one hour or less, only a small part of the total gas produced is actually used in aeration, while salt-rising bread is made into loaves and placed in the pans immediately upon mixing the dough and very little gas is lost. (3) The gases produced by yeast consist of carbon dioxide, while those produced by the salt-rising bacterium consist of about  $\frac{1}{3}$  carbon dioxide and  $\frac{2}{3}$  hydrogen, which is only  $\frac{1}{22}$  as heavy as the former.

The fact that the losses in ordinary bread are dependent upon the amount of fermentation led us to suspect that with the use of yeast stimulants the decomposition of sugar would be less than in a normal dough, because the initial fermentation is much slower and the total gas production is less. With this idea in mind, we made three normal doughs and three with a reduction of 50 per cent in the usual amount of yeast and with 0.5 g. ammonium sulfate and 1.2 g. calcium chloride in 1000 g. of flour. The gas evolved in the usual time from 50-g. portions of the doughs was collected in Bunsen gas holders, and from the total weight of gas produced the quantity of sugar decomposed was calculated, assuming that the carbon dioxide evolved represented 45 per cent of the loss in sugar. The results of these experiments are given below:

BREAD NO.	CC. GAS FORMED	PER CENT LOSS IN SUGAR Calculated on Flour
Controls { 1135	396	4.25
{ 1137	404	4.34
{ 1139	409	4.39
	Av. 403	Av. 4.33
NH <sub>4</sub> Cl { 1136	333	3.58
and { 1138	353	3.79
CaCl <sub>2</sub> { 1140	348	3.94
	Av. 345	Av. 3.70
		DIFFERENCE 0.63

It will be noticed that the consumption in sugar is considerably higher in the control dough than in the one with added salts. The difference represents the saving in sugar that is effected by the use of ammonium and calcium chlorides in bread.

#### USE OF POTASSIUM BROMATE

In connection with the use of these salts as yeast nutriment in bread-making, with special reference to the losses, mention will be made briefly of potassium bromate as used in conjunction with them. The functions of the latter salt will be more fully treated in a subsequent paper, inasmuch as it is not a yeast nutriment but acts upon the dough, imparting to it very desirable properties.

In the fermentation of bread, a twofold object is

accomplished; namely, the maturing, or aging, of the dough, and the aeration of the bread. The former is accomplished during the fermentation period, which takes from 4 to 6 hrs. in the best practice, and the latter during the proofing period, which requires from  $\frac{1}{2}$  to 1 hr. After the dough is sufficiently matured, or aged, it passes through the dividing and moulding machines, which press out practically all of the gas. Then it is put into pans and allowed to proof, and only the small fraction of the total gas which is produced while the bread is in the pans actually functions in aerating the bread. The effect of the potassium bromate upon the dough is essentially an aging, or maturing, effect and is characterized by the exceedingly small quantities required. The following series of experiments will serve to illustrate the changes in loaf volume with increasing quantities of potassium bromate:

Bread No.	4547	4548	4549	4550	4551
Gram potassium bromate.....	0.000	0.015	0.030	0.060	0.120
Loaf volume, cc.....	1735	1785	1755	1605	1375
Per cent increase.....	0.0	+218	+1.1	-7.4	-21.3

The maximum volume occurs with 0.015 g. per batch of 1000 g. of flour, and it will be noticed that with 0.06 and especially with 0.120 g. there is a marked diminution in volume. This influence upon the loaf volume is not due to any change in the rate of fermentation or gas production, but to the pronounced aging, or maturing, effect of the salt upon the dough itself. Similar changes in volume are effected by varying the amount of fermentation to which the dough is subjected. Up to a certain point, the gas-retaining power of dough and the loaf volume are increased by fermentation; then the dough becomes "rotten," *i. e.*, it no longer retains the gas well and, accordingly, the volume is greatly reduced.

A desirable quantity of potassium bromate—say 0.015 g. per batch of dough containing 600 g. of water—ages the dough so decidedly that 25 or 30 per cent of the usual amount of yeast can be saved without imparting to the bread any of the characteristics of under-fermentation, such as heaviness, dark color and coarseness in texture. In fact, the bromate in these quantities improves the bread with respect to texture even though the yeast is reduced by 25 per cent. This pronounced effect is attributed to the oxidizing power of this salt, for it has been found that by passing oxygen through the dough a similar maturing action is obtained, but to a lesser degree. This is probably due to the condition of the oxygen—in one case we have molecular oxygen and in the other we have nascent oxygen—the nascent oxygen being more powerful than the molecular, and, therefore, would have a greater maturing action on the dough. The effectiveness of the nascent oxygen is indeed surprising, for the quantity of the potassium bromate is so small that the total available oxygen is less than 1 cc. per loaf of bread.

When potassium bromate is used in addition to ammonium and calcium salts, it effects a saving in yeast of 25 to 30 per cent of the amount required without it. For instance, when 50 per cent of the usual



amount of yeast can be saved with the yeast stimulants, the saving may be increased to 65 per cent with the addition of potassium bromate.

The aging, or maturing, effect of potassium bromate upon the dough, without increasing the rate of fermentation or the sugar consumption by the yeast, results in a much greater saving in sugar than that due to the yeast stimulants alone.

To determine this saving, three normal doughs were made and three with 0.5 g. ammonium sulfate, 1.2 g. calcium chloride, and 0.015 g. of potassium bromate in 1000 g. of flour and 35 per cent of the usual quantity of yeast. The gas evolved from 50 g. portions of the doughs was used as the basis for calculating the losses in sugar due to fermentation. The results of these experiments may be thus summarized:

BREAD No.	Cc. GAS FORMED		PER CENT LOSS IN SUGAR Calculated on Flour	
Controls	2237 2238 2239	415 452 452	Av. 440	5.64 6.15 6.15
New Process	2240 2241 2242	225 244 267	Av. 266	3.62 3.62 3.62
			DIFFERENCE	2.36

The results of a similar series of experiments are tabulated below; these show the losses at the end of 5, 6 and 7 hrs., respectively.

BREAD No.	GAS IN Cc.			Cc. Gas between 6th & 7th hrs.	Loss in Sugar Per cent			Diff. in Loss between New & Old Process		
	5 hrs.	6 hrs.	7 hrs.		5 hrs.	6 hrs.	7 hrs.	5 hrs.	6 hrs.	7 hrs.
Controls	2251 2252 2253	309 310 312	373 375 379	435 440 442	62 65 63	5.26 5.26 5.30	6.34 6.38 6.42	7.44 7.50 7.50		
Average	310	375	439		64	5.27	6.38	7.48		
New Process	2254 2255 2256	184 177 178	250 239 240	322 302 309	72 63 69	3.12 3.00 3.02	4.25 4.07 4.07	5.44 5.10 5.25		
Average	180	243	311		68	3.04	4.13	5.26	2.23	2.25

Six hours' fermentation is the approximately normal period in the best baking practice, 5 hrs. in the dough state and 1 hr. after the bread is made up into loaves. The range between 5 and 7 hrs. fermentation will cover most variations in baking processes, due to the requirements of different flours and the type of bread desired. It is clear from the results cited above that the losses increase as the fermentation proceeds and that they are uniformly lower in the new process. The differences in the average losses between the two processes are 2.23, 2.25, and 2.22 per cent in 5, 6 and 7 hrs., respectively, which is practically a constant. This is to be explained by the fact that after 5 hrs. the rate of fermentation in the two processes is practically the same. The difference in decomposition of sugar occurs mostly in the initial stages of the fermentation before the nutriment greatly accelerate the activity of the yeast.

In another series of experiments, the losses were determined by direct weighing, as had previously been done by one of us,<sup>1</sup> and also by collecting the gas. Both batches were set with 1000 g. of flour, and, after mixing, were divided into two equal portions. One-half was used for the determination of the losses by weighing and from the other half three portions of 40 g. each were taken by collecting the gas. The

results given in the following table represent the mean of the three results obtained:

BREAD No.	MOISTURE-FREE MATERIAL PUT INTO BATCH	DRY BREAD	LOSS Grams	Per cent	PER CENT LOSS BY GAS COLLECTION
2340 (Control)	494.78 g.	458.7 g.	36.08	7.21	3:30 P.M. 6.12
2341 (New Process)	493.75 g.	469.7 g.	24.05	4.81	4:00 P.M. 6.59
					3.98 4.38

The losses<sup>1</sup> were calculated from the gas collected at 3:30 o'clock, when the bread was put into the oven, and again at 4:00 o'clock, when it was taken out. The fermentation was completely arrested between the two times, of course, and the results obtained by direct weighing can more strictly be compared with those calculated on the gas at 4:00. Rather lower results were obtained by collecting the gas than by direct weighing. The solution of gas in the liquid of the dough may in part account for this and it is also suggested that the losses may not be due entirely to the decomposition of sugar by the yeast. However, the agreement is fairly close, showing that most of the material lost is due to the destruction of sugar by the yeast.

Sugar analyses were made of breads prepared with and without added salts and the results afford additional confirmation of the destruction of sugar by the yeast. Three batches were made, one each by the two processes with the regular amount of sugar and one by the new process with 2.25 per cent less sugar (calculated on the flour), which represents the difference in sugar consumption by the two processes, as determined by collecting the gas. The results follow:

Hrs. Fermentation	PER CENT SUGAR IN BREAD CALCULATED ON FLOUR		
	CONTROL Normal Sugar (25 g.)	WITH ADDED SALTS Nor. Sug. (25 g.)	2.25% less Sugar
5	1.70	3.41	2.70
6	1.56	3.02	1.96
7	1.37	2.66	1.63

It will be noticed that with the normal amount of sugar and added salts the bread is much richer in this substance than the control, while if 2.25 per cent less sugar is used in the batch, the bread is slightly richer in sugar than the control bread.

To confirm the reduction in the destruction of fermentable material in bread by the use of the new process, gas-collection experiments were conducted in a large bakery where it is in operation. Three portions of 50 g. were taken from each of the two doughs (1600 lbs.) set by the new and old process, respectively. The losses, representing the mean of the three determinations, were as follows:

PER CENT LOSS SUGAR New Process	PER CENT SUGAR Old Process	PER CENT SUGAR SAVED	TIME Hours
0.24	0.39	0.15	1 1/2
0.43	0.69	0.26	2
0.55	0.97	0.42	2 1/2
0.69	1.27	0.58	3
0.82	1.58	0.76	3 1/2
1.10	1.96	0.86	4
1.38	2.36	0.98	4 1/2
1.64	2.68	1.04	5
1.84	3.13	1.29	5 1/2
2.25	3.48	1.23	6
2.49	3.85	1.36	6 1/2
2.81	4.18	1.37	7
3.03	4.35	1.32	7 1/2

The difference in the destruction of sugars in these

<sup>1</sup> It is assumed that the carbon dioxide represents 45 per cent of the sugar destroyed by the yeast.

<sup>1</sup> Kohman, *Loc. cit.*

experiments was 1.37 per cent at the time the bread was removed from the oven, which was considerably less than that obtained in the laboratory. This, we think, is due to the fact that less yeast in proportion to the dough batch is required in the bakery. It is common practice to use about twice as much yeast in laboratories as is required in bakeries to mature dough in the same time. This is to be explained in part, at least, by the fact that a batch of 1600 lbs. rises from 3 to 6° C. in temperature, due to the fermentation, while a small batch containing 1000 g. of flour remains practically constant in temperature. The authors have frequently observed a difference in temperature of 5 to 6° C. between the center and outside of a large dough batch. This is attributable, no doubt, to the evaporation of water on the surface of the dough, as the temperature of the room is the same as that of the dough at the time of its setting; naturally, then, the cooling effect will be much more pronounced in the case of a small dough. The small amounts of dough (50 g.) taken for collecting the gas from the large mass of 1600 lbs. in the bakery, would be especially subject to this cooling effect. Hence, we are inclined to regard the results obtained in the laboratory as nearer the truth than those obtained in the bakery, particularly when it is common knowledge that much higher proportions of yeast are required in laboratory batches.

The curves in Fig. I illustrate graphically the losses in bread-making due to the destruction of sugar. By means of the curves, the losses can be calculated at any desired time, which is impossible in determining the losses by direct weighing. In connection with the determination of the losses in bread-making, it should be mentioned here that the method involving the collection of the gas given off from an aliquot portion of the dough batch is novel.

An attempt was made to estimate the consumption of the sugars in bread by making sugar determinations upon the dough at intervals as the fermentation proceeded. Such determinations were made upon large-scale doughs set both by the old and new processes. Sugar determinations were also made upon sample loaves of bread that were taken from the batches at intervals and allowed to rise to the usual height in the pans and baked. The results are given in the following table:

PER CENT SUGAR CALCULATED ON FLOUR					
DOUGH—			BREAD—		
Time	Old Process	New Process	Time	Old Process	New Process
9: 50	5.21	4.72	12: 00	5.32	1: 10 4.82
11: 50	5.67	5.16	1: 10	5.14	2: 25 4.58
1: 55	5.22	5.44	3: 20	4.12	3: 50 4.35
3: 30	5.13	5.29	5: 00	3.47	4: 45 4.22
5: 05	4.27	4.88			

It is interesting to note that for several hours there is an increase in the sugar content of the dough, the old process reaching a maximum about 2 hrs. after the dough is set and the new one at about 4 hrs. In the light of this fact, it is evident that sugar analyses upon dough can not serve as an index to sugar consumption by the yeast. The results are of interest, however, in demonstrating the activity of diastatic enzymes. In the new process the sugar content is higher at the

end of the fermentation period than at the beginning, showing that the production of sugar is greater than the consumption; in the old process, this does not obtain, as there is nearly 1 per cent less sugar at the end. The difference in the sugar content between the two doughs at the beginning is due to the fact that less sugar is regularly used in the new process.

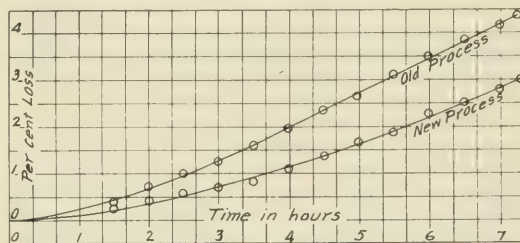


FIG. I.—LOSS IN BREAD-MAKING CALCULATED FROM CO<sub>2</sub> EVOLVED

The curves in Fig. II present graphically the changes in sugar content of the doughs during the fermentation period. As the curves cross, it is demonstrated clearly that although 1 per cent less sugar was used in the new process, the bread baked after the usual fermentation period was actually about 1 per cent richer in sugar than that made by the old process.

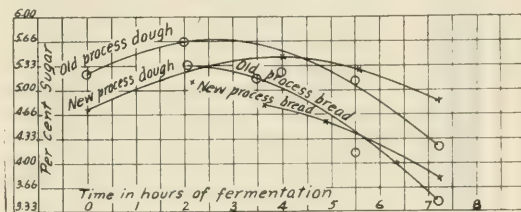


FIG. II.—CHANGES IN SUGAR CONTENT

The economic saving possible by the proper use of nutrient salts, in the advent of a rather general adoption, sums up to surprising figures. Take, for example, the saving in sugar on the average flour production of the State of Kansas—say 20 million barrels, or nearly 4 billion pounds. A saving of 2 per cent on this amount is 80 million pounds; and it is mainly sugar that is decomposed and thus lost in bread-making. The economies in the yeast are greater than those in the sugar. Even a moderate use of such a process means a considerable saving to the country and is a step towards conservation of resources. At the present time, this process is used commercially in the manufacture of more than a million loaves daily.

A further advantage incident to this process of bread-making was observed in the increased stability and stiffness of the dough. To one familiar with doughs this is easily discernible to the touch; it was also determined more accurately and with numerical data by means of the dough viscosimeter (see Fig. III).

The viscosimeter consists essentially of a cylinder having a graduated piston which forces the dough through an aperture at the bottom. The stiffer and more tenacious the dough, the slower is the descent



of the piston. The time that elapses while the piston descends the distance between two chosen marks is determined by means of a stop-watch. This reading in seconds represents comparative viscosities of the doughs. In the study of flours, the authors have found the viscosimeter very valuable.

Five doughs were made, four by the new process and a control. The water content of the four doughs was varied between 60 and 63 per cent, while the control was made with 60 per cent water. The viscosities, which represent the mean of five readings and the percentage of water used, are tabulated below:

	Control		New Process		
BREAD NO.....	2391	2393	2394	2395	2396
Per cent water.....	60	60	61	62	63
Viscosity.....	13	21	18	17	9

The control with 60 per cent of water is decidedly lower in viscosity than No. 2393, which has the same amount of water. It will be noticed, further, that to obtain a dough of normal stiffness and stability, from 2 to 3 per cent more water may be added, another evidence of the conservation of flour in the dough batch from the use of these yeast foods. The resistance to softening of flour during the progress of the fermentation is of great significance in the manufacture of bread, and the greater stiffness and stability obtained by the new process is a valuable feature.

During the fermentation of the dough, the gluten is softened and partially broken down by the yeast as well as gas and alcohol being formed from the sugar. The difference in sugars decomposed between the old process and the new process is about 2 per cent when figured on the flour used. By using the new process, we are thus able to decrease the quantity of flour used by 2 per cent and still have a dough of the same stiffness. This probably accounts for the fact that in the bakery we can use 1.5 per cent more



FIG. III

water or are able to decrease the amount of flour 2 per cent and still have a dough of the desired or usual stiffness.

The new process has been used for breads of various types, such as pan breads, Vienna and French breads; also, for rye, Graham and whole-wheat breads. Likewise, it has been used with spring, winter and Kansas flours, and the different grades of flour, and has been found to be universally applicable.

In connection with the different grades of flour, it should be said that the process can not be used to give bread the appearance of being made from a higher grade of flour than is actually employed. The improvement in color with the use of the new process is due to the improvement in texture and can not be regarded as a bleaching process. The grayish color of the lower grades of flour remains in the bread made

by the new process just as it does in the usual process. By any process, the color of the crumb is improved by fermentation up to a maximum and in the new process the same changes are noted; much less yeast, however, is required to accomplish the desired results.

The practical application of the new process has met with success and it is now in operation in a large number of bakeries. A number of these are under the direction of one superintendent, who claims that the process has been of material aid in standardizing the manufacture and maintaining uniformity of the bread in the different localities. As already stated, certain differences were noticed in the bread in a chain of bakeries, although all the raw materials were identical. These have been practically overcome by the new process, which virtually standardizes the water used for the baking purposes. This would be expected, because the required nutriment is supplied by means of these salts used as yeast food, and the addition of further mineral matter, either through the water or otherwise, has less and less effect as the quantities increase. It is a general rule that, in the addition of nutriments or activators in steps, the first portion added has a correspondingly greater effect than the succeeding portions.

For the sake of convenience and accuracy in the use of these salts, they are in practice mixed with flour and salt, so that it requires 8 oz. of the mixture for 60 lbs. of water, or approximately 160 lbs. of bread. An average bakery batch (1200 to 1500 loaves) contains about 480 lbs. of water, which requires 4 lbs. of the yeast food, a quantity that may be conveniently weighed with accuracy. The product has also been prepared as a liquid, in which case the salts are dissolved in water, so that 8 oz. of the solution for 60 lbs. of water deliver the required amount. For the dry product the sulfate of calcium is preferred, while in the solution the chloride is used. The use of either product introduces about 2 oz. of a calcium salt, a little less than 1 oz. of ammonium chloride and 0.02 oz. of potassium bromate into the batch for 60 lbs. of water used or for 160 lbs. of bread. In practice, the yeast food is first dissolved in the water used in the dough batch.

It is but natural to inquire: What becomes of the chemicals during the fermentation and baking of the bread? The purpose of the ammonium salt, as already stated, is to supply the nitrogen required by the yeast and it is of interest to know whether any of it remains in the bread.

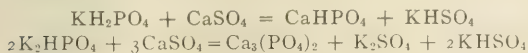
The following table, showing the analyses in public laboratories of five commercial breads of greater Boston, will answer this question.

RESULTS (PER CENT) OF ANALYSES OF VARIOUS BREADS					
BREAD NO.	Moisture	Ash	Lime (CaO)	SO <sub>2</sub>	Ammonia (NH <sub>3</sub> )
I.....	40.12	1.16	0.026	0.037	0.0053
II.....	40.19	1.04	0.029	0.016	0.0044
III.....	41.29	1.14	0.019	0.022	0.0037
IV.....	38.31	0.93	0.017	0.014	0.0011
V.....	41.06	1.05	0.015	0.019	0.0069

Bread No. I was made by the new process and it will be observed that it is not as high in ammonia as No. V, made without yeast nutriment. None of the breads has an ammonia content that is at all significant.

Additional analyses in our own laboratories confirm the above results.

It will be noticed, also, that No. II is higher in lime than No. I. The state of combination of the calcium in the bread is scarcely subject to question. It has been shown by Teller<sup>1</sup> that the phosphoric acid in flour exceeds by ten times the calcium and it may be safely said that, even by the use of the new process, the bread contains several times as much phosphoric acid as is required to combine with the calcium. Under these conditions, the potassium phosphate of the wheat undoubtedly interacts with the calcium sulfate, as it does in wort,<sup>2</sup> in accordance with the following equations:



It is known<sup>3</sup> that the calcium requirements of the body can be supplied by inorganic as well as by milk calcium. Abderhalden<sup>4</sup> has demonstrated that the complicated organic substances of our foods are replaceable by the simplest structural materials and that these are built up into various tissue substances. It should be mentioned in connection with the use of calcium salts in bread that Rudolph Emmerich and Oscar Loew<sup>5</sup> advocate the use of calcium salts in bread from a purely dietetic standpoint. In fact, the deficiency of calcium in our food is indicated clearly in *Experiment Station Record*, 20, 68. A detailed discussion of this subject, with special reference to white bread, was published recently by one of us.<sup>6</sup>

The increased lime content of bread by the use of the new process is a very happy coincidence, even though incidental. Unfortunately, in modern methods of milling, the greater part of the mineral constituents of wheat is lost to white flour. As indicated by Teller,<sup>7</sup> seven-eighths of the phosphoric acid and eleven-fourteenths of the potash and lime of wheat are found in the stock feed; consequently, a partial restoration of the lime in white bread must be considered highly desirable.

#### CONCLUSIONS

I—By the use of minute quantities of ammonium and calcium salts and potassium bromate in bread, from 50 to 65 per cent of the usual amount of yeast can be saved.

II—Incident to the economy in yeast thus effected, there is a saving of about 2 per cent of fermentable carbohydrates, calculated upon the total flour used, due to the greatly diminished consumption of these by the yeast.

III—The proper use of nutrient salts for the yeast gives greater control over the dough batches and aids in the production of better and more uniform bread, regardless of the locality.

IV—The added salts conserve the inherent qualities of the dough and consequently maintain its stability and strength to a far greater degree than by the old process.

V—The finished loaves are improved in quality, flavor, texture, bloom and uniformity.

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#### A STUDY OF THE SYRUP PRECIPITATE IN WHITE SUGAR MANUFACTURE

By CHARLES E. COATES AND L. C. SLATER

Received May 9, 1916

Although the manufacture of white sugar direct from the cane has been carried on to some extent in Louisiana for nearly a century, for certain reasons this industry has lately taken on a new lease of life and at the present time is of great importance. To such a degree is this true, that most of the larger Louisiana sugar houses are now equipped for the direct manufacture of white sugar without the intervention of the bone-black refinery and in many instances have installed apparatus which has proven valuable in the manufacture of beet sugar.

The experience of the last few years, however, would indicate that there are not only different chemical difficulties to overcome, but also certain mechanical differences in the manufacture of white granulated beet sugar and cane sugar, which make special detailed attention to the latter exceedingly necessary. For instance, leaving aside the important question of clarification, it has become evident that filtration of the clarified cane juice is imperative, but the method of filtration and the number of filtrations are points still somewhat in dispute.

Some sugar houses allow the clarified juice to settle and pass the decanted, clear juice through bag filters. Occasionally the filtered juice is filtered again before final evaporation, but ordinarily it passes direct to the effects, where it is evaporated to a Brix of from 50 to 55°. There is considerable difference of opinion as to the proper subsequent treatment of this syrup. Sometimes a little sulfur dioxide or phosphoric acid is added to restore the initial acidity, but usually the syrup is passed into tanks, where it is allowed to settle from 2 to 4 hrs., gradually falling in temperature during that time. When the syrup is finally drawn from the tanks, there is always to be found a precipitate, which is separated as well as possible by decantation. In certain houses the attempt has been made to filter the syrup through leaf presses. This gives a bright filtrate, but the process, being tedious and expensive, is ordinarily dispensed with, though something is always removed from the syrup. If what it removes does no harm in the subsequent manufacture of white sugar from the cane it is evident that syrup filtration could be safely omitted and the cost of manufacture lessened.

The syrup precipitate is probably not present in the solid form in the freshly evaporated syrup, inasmuch as it will form in the course of several hours in syrup which has been previously filtered, hot, through paper.

<sup>1</sup> Ark. Agr. Expt. Sta., Bull. 42, 70.

<sup>2</sup> Matthews' "Manual of Alcoholic Fermentation," pp. 194 and 195.

<sup>3</sup> Biochem. Z., 9, 185-207.

<sup>4</sup> Wien. med. Woch., 62, 177.

<sup>5</sup> Z. Hygiene, 77, 311-28.

<sup>6</sup> Kofman, Bakers' Review, 31 (1914), 61-62.

<sup>7</sup> Ark. Agr. Expt. Sta., Bull. 42.



It is not easy to get a satisfactory sample of the precipitate, which is gummy and difficult to obtain in a state of purity, but owing to the courtesy of two factories the writers succeeded in obtaining samples for preliminary investigations.

In Factory No. 1, the process of clarification was as follows: The juice was obtained by 9 rollers and a crusher, about 5 per cent maceration being employed. The extraction was relatively low, being 77 per cent on the weight of the cane. The purity of the juice was fairly high for Louisiana, being about 83. Sulfur dioxide was run into the raw juice until the acidity was raised to the equivalent of 4 cc. of  $N/10$  potassium hydroxide for every 10 cc. of juice, phenolphthalein being used as an indicator. Slaked lime was next added until the acidity was reduced to 1 cc. The juice was then heated, passed through a continuous settling apparatus and the clear juice filtered over sand. The filtrate was not particularly bright. The juice was next passed to the effects and concentrated to a Brix of about 53°. It was then run to the settling tanks, where, in the course of a few hours, a gelatinous precipitate settled. These settlings were removed, as far as possible, by decantation and it is this precipitate which is the subject of this study.

In Factory No. 2 there were also 9 rollers and a crusher, with a saturation of about 10 per cent and extraction of about 79. The juice had a purity of about 84.5. It was sulfured to an acidity of 9 cc., which was exceedingly high (in the writers' judgment, considerably too high), then limed back to an acidity of 1 cc. and passed through heaters to a continuous settling apparatus. The clear juice was passed through bag filters and thence to the feed tanks for the effects, where phosphoric acid was added until the acidity was raised to 1.4 cc. It was then passed to the triple effects where it was evaporated to a Brix of about 53°. The syrup was then heated to boiling with live steam and slowly passed through a battery of inclined, continuous separators, being about 4 hrs. in transit. During this time a precipitate settled at the bottom of the separators, which precipitate is the second one included in this study.

Both of these factories made white sugar. It will be noted that in the first factory no phosphoric acid was used in the clarification. In the second factory, phosphoric acid was added to the clear juice after it had passed through the bag filters. Ordinarily, when phosphoric acid or sodium phosphate is used it is added before the juice is filtered. This precipitate seems, however, to occur normally in the syrup at all sugar houses. It forms quite slowly, usually taking several hours before it can be noticed. In one instance a perfectly bright, bag-filtered syrup stood 5 hrs. in a test tube before the precipitate became evident, though it eventually deposited a fairly large quantity. As stated, in order to get rid of this precipitate, the syrup is sometimes filtered through some form of leaf filter press but after a time the filter cloths get hard and crack, thus necessitating a considerable expenditure for filter cloth. Moreover, the gelatinous nature

of the filtrate makes filtration slow, so that many factories prefer to omit syrup filtration entirely.

The sample of the settlings obtained from Factory No. 1 was filtered through paper and washed with cold water until the filtrate was practically without optical rotation. The precipitate was then removed, shaken several times with cold water and refiltered, the filtrate finally running clear. The same process was repeated with the settlings from Factory No. 2. The results are indicated in the following tables of analysis. For the sake of clearness, each set of analysis will be followed by the comments bearing on it specifically.

TABLE I

	Factory No. 1	Factory No. 2
Total amount of wet precipitate.....	71.5 g.	32 g.
Total amount of air dry.....	32 g.	13 per cent
Water.....	45 per cent	27.7 g.
Total amount of dry matter.....	39.3 g.	

It was impossible to estimate just how much of the original syrup this precipitate represented. In No. 2, however, we received a 50 l. carboy of the settlings from which we secured 27.7 g. dry precipitate. Taking the specific gravity of the syrup at 1.25, 50 l. equals 62,500 g. The precipitate therefore is about 0.04 per cent of the settlings and as these represent a much larger amount of juice, it is probable that the percentage of precipitate in the unfiltered syrup would be less than 0.01 per cent. The precipitate is so voluminous that the amount present seems much greater than it really is.

The dry precipitate was pulverized, extracted with ether and ignited, the loss in weight on ignition being taken as organic matter. The ether extract proved to be largely, if not entirely, cane wax.

TABLE II

	Factory No. 1	Factory No. 2
Ash in percentages.....	58	75.6
Organic matter in dry ppt.....	42	24.4
Ether extract.....		2.6

The excess of ash in No. 2 over No. 1 proved to be mainly calcium phosphate as shown in Table III, due to the use of phosphoric acid in clarification in one case and not in the other.

Part of the precipitate was ashed, boiled with concentrated hydrochloric acid, and evaporated to dryness. The silica was filtered off and the filtrate made alkaline with ammonia. The ammonia precipitate was filtered off and weighed. In each case considerable copper was found in the filtrate.

TABLE III

PERCENTAGES IN ASH	Factory No. 1	Factory No. 2
SiO <sub>2</sub> .....	75.3	53.7
Ammonia precipitate (P <sub>2</sub> O <sub>5</sub> .CaO.Fe <sub>2</sub> O <sub>3</sub> .Al <sub>2</sub> O <sub>3</sub> ).....	5.3	34.5
CaO in filtrate.....	8.0	4.1
Cu.....	11.3	1.2
Total P <sub>2</sub> O <sub>5</sub> .....	0.6	13.5
(SO <sub>3</sub> ).....	4.0	0.0

The large excess of silica in No. 1 may have been due to the use of sand filtration. It seems to have been present as colloidal silicic acid. The large amount of copper in No. 1 was doubtless due to an imperfect sulfur stove, which delivered the gas hot and probably with an excessive amount of SO<sub>3</sub>: the resulting sulfuric acid seems to have attacked the various copper coils in the subsequent flow of the juice and syrup. As a matter of fact the copper was found badly pitted

at the end of the campaign. Just how the copper was finally precipitated is not clear, especially since 50 g. of the mother liquor from the settlings gave no test for copper when ashed. In No. 2 where the sulfur stove was working well, the amount of copper in the precipitate was small, although there was an excessive amount of sulfur dioxide added in the sulfuring. This view is borne out by the fact that there was a fair amount of  $\text{SO}_4$  (probably as  $\text{CaSO}_4$ ) in No. 1, which was absent in No. 2.

In discussing the sulfitation process for white sugar making, the objection has been raised in Java that the sulfurous acid corrodes the coils. This has not been the Louisiana experience. When such corrosion does appear in excess it has been ascribed by some to sulfuric, rather than to sulfurous acid. This does not seem very probable, in our opinion. It might be noted here, however, that the coils used in sulfitation and the effect tubes as well are uniformly made of copper in Louisiana. In one instance brass tubes were substituted for copper tubes in a quadruple effect, evaporating juice of about 5 cc. initial acidity. These brass tubes corroded badly, though the writers understand brass has been successfully used in alkaline clarification in the beet sugar houses.

In Table III, the ammonia precipitate in Sample No. 1 proved, on analysis, to be mainly oxides of iron and aluminum together with what phosphoric acid was present. The excessive iron content was probably due to the poor sulfitation. In Sample No. 2 the precipitate contained little iron. Since in tricalcium phosphate the ratio of  $(\text{CaO})_3$  to the  $(\text{P}_2\text{O}_5)$  is 168 to 141, the precipitate is probably tricalcium phosphate with a little iron and aluminum phosphate and possibly some calcium silicate. As no sulfuric acid was present, it is evident that the excess calcium in the filtrate must have been originally present as insoluble salts of some organic acids.

After filtering off the first settlings through paper, the filtrate from No. 2 was corked and heated on a water bath in order to sterilize it. After an hour or so, a second precipitate separated out. This was filtered off, washed until the washing showed no optical activity, dried and analyzed with the following results:

TABLE IV			
Total Amount of Dry Precipitate 1.6 g.	Ash	Organic Matter	$\text{SiO}_2$ in Ash
	67.8 %	32.2 %	26.4 %

The filtrate from the  $\text{SiO}_2$  gave a heavy precipitate with ammonium hydroxide which proved to be tricalcium phosphate. The filtrate from this in turn contained a quantity of calcium. The determinations of calcium and phosphoric acid were accidentally lost, but it will be noticed that in addition to the calcium phosphate there was also an excess of calcium which must have been present as calcium silicate, or as calcium salts of organic acids. Why this precipitate formed at all is not clear. The syrup stood a couple of days before it was heated and was perfectly bright. The flocking of the precipitate took place as soon as the temperature of the water bath was reached. A possible inference from this might be that when

syrup is run into settling tanks and allowed to stand, the precipitate will form faster and more completely if the syrup is kept hot.

In order to get some clue as to the nature of the organic matter present in the precipitate, the following tests were made, the calculations being reduced to the basis of dry matter. The polariscope readings are in degrees Ventzke, for 10 g. of dry matter in 100 cc. reading in a 20 cc. tube. Reducing sugars were determined by weighing the reduced copper.

The moist precipitate was shaken thoroughly with cold water and filtered.

TABLE V		
	Factory No. 1	Factory No. 2
Direct reading.....	.....	-0.4°
Invert reading.....	.....	-0.3°
Reducing sugars.....	Trace	0.0 per cent

Some of the moist settlings were boiled 6 hrs. on the water bath with frequent shakings, cooled and filtered from the insoluble precipitate. The filtrate gave the following figures:

TABLE VI		
	Factory No. 1	Factory No. 2
Direct reading.....	-0.3°	-0.5°
Invert reading.....	-0.4°	-0.6°
Total solids in solution.....	1.7 per cent	3.9 per cent
Ash in same.....	0.4 per cent	2.0 per cent
Reducing sugars.....	Absent	0.03 per cent
Reducing sugars when hydrolyzed as for dextrin.....	.....	0.11 per cent

From the composition of the aqueous extracts in Tables V and VI, it may be inferred that the organic matter of the settlings contained little or no soluble sugar, gums or dextrans, but that a fairly constant quantity of a levo-rotatory substance was present, which was not a sugar. The residues from the water extracts were washed into a beaker with dilute hydrochloric acid, heated on the water bath for 3 hrs. and filtered from the insoluble residue. This filtrate was made neutral with sodium hydroxide and filtered from the resulting precipitate. The results were as follows:

TABLE VII—HYDROCHLORIC ACID DIGESTION		
	Factory No. 1	Factory No. 2
Polariscope reading.....	0.0°	0.0°
Reducing sugars.....	0.182 per cent	0.256 per cent

This digestion effected only a slight hydrolysis as indicated by the slight increase of reducing sugars, which may have come from fragments of fiber.

TABLE VIII—SODIUM HYDROXIDE PRECIPITATE		
PERCENTAGES	Factory No. 1	Factory No. 2
Ammonia precipitate.....	.....	19.0
CaO in filtrate.....	.....	2.4
Total CaO, in ammonia precipitate.....	.....	6.1
Total $\text{P}_2\text{O}_5$ , in ammonia precipitate.....	.....	4.0

This precipitate was redissolved in hydrochloric acid and aliquot portions analyzed.

The ratio of the  $\text{P}_2\text{O}_5$  and the total CaO to the total ammonia precipitate, makes it probable that more than half the calcium was present as a salt of some organic acid.

The residue insoluble in dilute hydrochloric acid was washed, dried at 110° C., extracted in ether, and ashed.

TABLE IX		
PERCENTAGES	Factory No. 1	Factory No. 2
Organic matter.....	Present	16.8
Ash.....	Present	83.2
Ether extract.....	Present	5.1
$\text{SiO}_2$ in ash.....	96.5	98.1



The ether extract was recrystallized from hot alcohol. It proved to be a saturated alcohol of high molecular weight, m. p.  $81^{\circ}\text{C}$ . It was clearly cane wax, probably present in a fine emulsion and carried down by the coagulated silicic acid. In ashing the residue there was an odor somewhat like that of burning feathers, but there was not enough material at hand to carry the investigation further.

As mentioned before, the filtrate from No. 2 settlings gave a second precipitate on being heated (see Table IV). Part of this precipitate was heated on the water bath for several hours with dilute hydrochloric acid and filtered from the insoluble residue which was almost entirely silica. The filtrate was made alkaline with sodium hydroxide which gave a precipitate as before. This was filtered off, redissolved in hydrochloric acid and analyzed. The filtrate from the sodium hydroxide precipitate showed neither optical activity nor the presence of reducing sugars, but showed 4.2 per cent  $\text{CaO}$ . The precipitate proved to be nearly pure tricalcium phosphate. A rough proximate analysis of Precipitate 2A would be as follows:

TABLE X

$\text{SiO}_2$ .....	25 per cent
Tricalcium phosphate.....	40 per cent
Calcium salts of organic acids.....	35 per cent
Gums and sugars.....	Absent

In every instance the filtrate from the sodium hydroxide precipitate in 2A was colored, the alkaline solution being strongly purple; in neutral solution, it was bright green, in acid, light reddish yellow. The color change was exceedingly sharp. It was thought at first that this coloring had been developed by hydrolysis, possibly of some member of the complex anthocyan group, which is known to be present in the rind of the cane. The coloring matter was very soluble in water, but when the solution was evaporated to dryness, it proved to be insoluble in chloroform, ether, alcohol-ether, alcohol or methyl alcohol and was, different in many ways from anthocyan. The residue was heated with concentrated hydrochloric acid and then with concentrated caustic soda in order to destroy any traces of carbohydrates which might have been present. What was left proved to be largely a copper salt, which seems to have been transformed by the sodium hydroxide into some soluble alk-oxide or protein compound. The original color was doubtless due to this copper compound together with possibly a small amount of an unknown natural indicator. There was not enough of the substances to permit of an extensive investigation, but the high coloring power may not be without significance in white sugar manufacture.

Comparatively little work has been done on the syrup precipitate. Prinsen-Geerligs<sup>1</sup> gives an analysis of it in his book on cane sugar. Geerligs concludes that the precipitate is practically identical in composition with the scale from different evaporating vessels and that it can not be removed by filtration owing to its gummy nature. On comparing the analy-

ses of the precipitates from Factories Nos. 1 and 2, it was noticed that they were quite different from each other and from that analyzed by Geerligs, who found but 27 per cent silica. Here the silica ran 75 per cent and 54 per cent. The character of the precipitate clearly differs as the method of clarification differs. With the sulfitation method as practiced in Louisiana it was found quite possible to filter the syrup on a large scale. If a little kieselguhr was thrown into the press first so as to coat the cloths, the precipitate could be washed from the cloths without much difficulty and a leaf press working with a head of about 6 ft. give a perfectly bright filtrate. But even when working under most advantageous conditions the process proved expensive and was frequently omitted when there was any pressure upon the filtering capacity of the house. Numerous experiments were made with a view to improving the filtering quality of the precipitate, mainly by the addition of phosphoric acid or a phosphate in order to precipitate the calcium salts. The factory practice showed no particular improvement under this procedure, which may be readily understood by noting the composition of precipitate (Table IV). Here the filtered syrup stood for several days at about  $12^{\circ}$  before it was heated on the water bath, but when heated there was a heavy precipitate of tricalcium phosphate and silicic acid. Clearly these substances, though insoluble in the ordinary sense, were held possibly in colloidal solution by the heavy syrup. This being the case, the addition of phosphates can not be expected to bring down the theoretical amount of calcium in the short time available in factory practice.

In Factory No. 1, using no phosphates, the precipitate was, essentially, 40 per cent organic matter, 30 per cent silica, the remainder being calcium phosphate, copper, iron and aluminum salts. In Factory No. 2, using phosphates, the precipitate was 25 per cent organic matter, 30 per cent silica, 25 per cent calcium phosphate, the remainder being copper, iron and aluminum salts. The copper seems to have been completely precipitated from the syrup.

The organic matter present in the precipitate does not yield reducing sugars by hydrolysis and is probably mainly a calcium salt of organic acids.

Taking into account the exceedingly small weight of the syrup precipitate in spite of its apparent volume, and considering also the fact that nothing in the precipitate would affect materially the finished product, the practice of filtering the syrup would hardly seem to do sufficient good to warrant the increased expense. The best procedure is to allow the hot syrup to settle for at least 4 hrs. and as the precipitate forms most completely and settles most quickly at high temperatures, it is well to have the settling tanks sheathed to prevent radiation as far as possible. The clear syrup can be decanted and the bottoms run back to the limed juice where the amount of the precipitate is not sufficient to interfere with the subsequent bag filtration.

<sup>1</sup> "Cane Sugar and Its Manufacture," 1909, p. 211.

# A CONTRIBUTION TO THE CHEMISTRY OF LAUNDRING

## I—THE RESULTS OF RELATIVE SURFACE TENSION MEASUREMENTS OF SOLUTIONS OF SOAP AND OF SOLUTIONS OF SOAP AND VARIOUS ALKALIES<sup>1</sup>

By H. G. ELLEDGE AND J. J. ISHERWOOD

Received May 3, 1916

During the course of an investigation of the various wash-room reagents which are employed in power laundries, the senior author was called upon to make a comparative study of various alkalies and alkaline mixtures marketed under trade names.

Among those examined were found sodium carbonate, mixtures of sodium carbonate and bicarbonate, mixtures of sodium carbonate and borax, trisodium phosphate, mixtures of disodium phosphate and borax, and a mixture of 3 per cent soap, 6.3 per cent caustic soda, 8.7 per cent soda ash, 36.3 per cent sodium silicate and sodium aluminate, and 45.7 per cent water. Under various trade names, these materials were sold to the power laundry trade, each with extravagant claims as to its excellence above all others. To the purchaser who desired to know the composition thereof, they were usually composed of a "sodium base" and mystery in equal proportions.

The mystery was really resolved by a *a priori* knowledge, to the satisfaction of the writers. Herbert Jackson<sup>2</sup> had shown that the values of the alkaline salts of weak acids—sodium carbonate, trisodium phosphate and borax—were equal when chemically equivalent weights were considered, and that sodium bicarbonate was either valueless or, within the limits of his observations, one-fiftieth of that of the others mentioned. It seemed desirable, however, to secure more evidence of a quantitative nature. Then, too, it was regarded as important to obtain quantitative data regarding the suitable proportions of alkali and soap to be used, and to demonstrate clearly to laundriers that because of the hydrolysis of soap in dilute solutions, the use of a certain quantity of alkali in excess of that required to precipitate the calcium and magnesium salts, is indicated by reasons of economy. These considerations induced the work reported in this communication.

The apparatus used was that described by H. W. Hillyer.<sup>3</sup> This apparatus consists of a 5 cc. capacity dropping pipette with capillary stem, which terminates with a perfectly plane surface, 10 mm. in diameter, upon which the drops form in a bath of kerosene. The reservoir containing the kerosene is equipped with an overflow in such a manner that the drops of the aqueous solution sink to the bottom and are discharged, leaving the kerosene undisturbed, throughout the experiment. A glass beaker was used for a water bath to control the temperature. Acknowledgment is hereby made for Dr. Hillyer's courteous advice on the construction of the apparatus and for his communication of certain precautions regarding

the necessary manipulation in counting the drops.

A 0.4 per cent solution of soap was made with distilled water and a good grade of commercial chipped soap, which, upon analysis, was found to be free from excess of alkali. A 0.5 per cent solution of sodium carbonate was made up from calcined sodium bicarbonate and distilled water. Solutions of trisodium phosphate, sodium hydroxide and sodium bicarbonate were made equivalent to a 0.5 per cent sodium carbonate solution, in order to facilitate the preparation of the solutions to be tested.

A field was plotted, with soap solutions as ordinates, in 0.05, 0.10, 0.15, 0.20 and 0.25 per cent, and the alkalies as abscissa in units of 0.10, 0.15, 0.20 and 0.25 per cent. Solutions of the percentages indicated by each intersection were then prepared and the drop number was read for the temperature of 100° C. The results obtained are indicated in Fig. I.

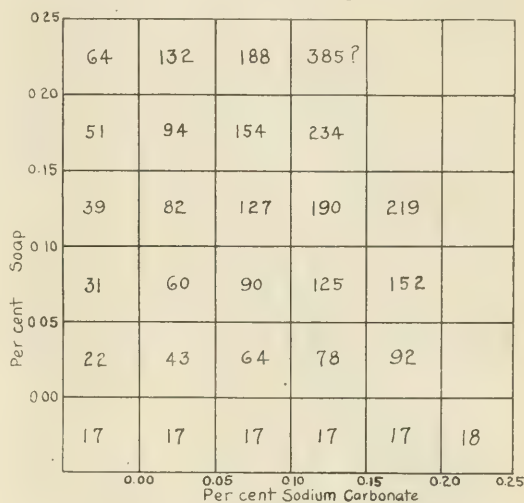


FIG. I—Drop Numbers for Soap and Sodium Carbonate Solutions.

Lampblack is a substance very comparable to street dirt. It is composed of finely divided particles of carbon, associated with various hydrocarbons which may be condensed on them. The same description is applicable to the smoke resulting from furnaces wherein bituminous coal is used. By placing weighed amounts of lampblack on filter papers of uniform texture, treating them with equal volumes of the various solutions of alkali and soap, and weighing the filter papers with the residue of lampblack that was not washed through, we were able to show more or less quantitatively, that solutions of the highest drop numbers would, under standard conditions, carry through a filter paper (S. & S. No. 589) the greatest amount of lampblack. Water and the solutions of alkalies used would not take any of the lampblack through. It was therefore concluded that solutions giving the highest drop number have the greatest detergent value with respect to unsaponifiable dirt.

This conclusion lends support to the contention of a number of investigations since the theory of

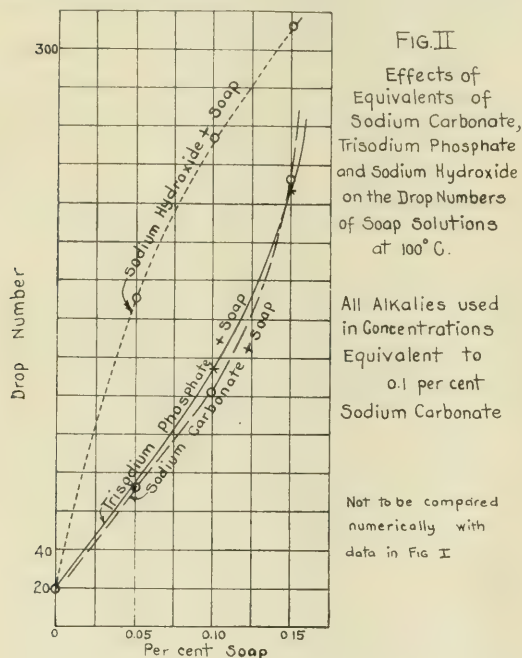
<sup>1</sup> Presented at the Urbana Meeting of the American Chemical Society, April 20, 1916.

<sup>2</sup> "Cantor Lectures," 1907.

<sup>3</sup> J. Am. Chem. Soc., 25 (1903), 511, 524, 1256.



Chevreul has been disproved, that alkaline solutions are in no sense detergents in the absence of free fatty acids or soap.<sup>1</sup> Water solutions of sodium hydroxide, sodium carbonate and trisodium phosphate, in the concentrations studied, showed very little changes in drop numbers with alterations in concentration. Within the limits of error of our observations, the changes in surface tension were about the same for chemical equivalents of the three solutions mentioned. The data for all are about as shown for sodium carbonate in the bottom row of Fig. I. Along with the facts mentioned, these results show that within the field examined the greater the quantity of alkali added to a soap solution, the better the detergent properties. This is limited in practice by the harmful effects on fabrics of large concentrations of the hydroxyl



ion; Faragher has shown that these effects are almost negligible in the case of sodium carbonate and cotton, up to a 1 per cent solution of sodium carbonate, provided careful rinsing is employed. This figure is from 5 to 10 times the amount usually employed in power laundries.

In Fig. II there are shown the effects of equivalents of sodium carbonate, trisodium phosphate and sodium hydroxide on the drop numbers of soap solutions at a temperature of 100° C. Because of a change in the dropping pipette, these data are not to be compared numerically with those presented in Fig. I, but they show that the values of equivalent weights of sodium carbonate and trisodium phosphate are equal, while that of sodium hydroxide is different within the field studied. The case of sodium hy-

droxide is of no practical interest, because it is, for obvious reasons, seldom used in power laundries. These facts indicate that, of the alkaline salts of weak acids, one is as efficient as the other as a wash-room reagent, excepting, of course, sodium bicarbonate, which, in cold solutions, does not affect the drop number of soap at all. This conclusion is in harmony with the findings of Jackson, cited above.

From the foregoing data, one is able to eliminate all of the mystery in the "trade name" washing sodas mentioned. This is a preliminary report on work being conducted in the Mellon Institute of Industrial Research for the Laundrymen's National Association of America, and it is the intention of the authors to study further the field outlined above as to the effect of these solutions on the breaking strength of cloth.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH  
PITTSBURGH

## NOTES ON SOME PHYSICAL CHARACTERISTICS OF PIGMENTS AND PAINTS

By HENRY A. GARDNER  
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### HIDING POWER OF PIGMENTS

The opacity or hiding power (covering ability) of a paint pigment depends upon its fineness, refractive index, and oil absorption. These physical properties are responsible for the fact that a coat of white lead in oil hides a dark surface better than a coat of silica in oil.

**FINENESS**—Paint pigments, if produced in sufficiently large size particles, would be more or less transparent like a lump of glass, since all such products allow the light to be transmitted in varying amounts. If any one of them, however, is broken down and powdered, the finely divided particles reflect the light in all directions and only a small amount of light is transmitted; the powdered substance thus appears opaque. Therefore, it may be stated that *the opacity of pigments increases with fineness of division*. With some pigments, however (produced by the fume process), there may be a point beyond which increasing fineness may result in a lowering of opacity.

**REFRACTION**—The refractive index of a pigment determines the amount of light that will be transmitted by it. The higher the refractive index, the greater the reflection and consequent hiding power. A layer of white lead will reflect more light than a layer of finely ground silica, since the refractive index of the lead is higher than the refractive index of silica. When either of these pigments are ground in water, the same phenomenon holds true, but both are less opaque than in dry form because water has a higher refractive index than air. *As the refractive index of the vehicle approaches that of the pigment, opacity diminishes*, an optical condition being produced by the film around the particles, that allows the passage of light, thus decreasing the reflection. When turpentine is used as a binding medium, the pigments show the same relative differences in hiding power, but both are less opaque than when in water, since turpentine is more highly refractive than water. When

<sup>1</sup> See Faragher, Rogers and Aubert's "Industrial Chemistry," 2nd Ed.; Hillyer. *Op. cit.*, and Jackson, *Op. cit.*

linseed oil is used as a medium, still less opacity is shown by the resulting paints, as linseed oil has a greater refractive index than turpentine. The resulting silica paint will now be practically transparent, since the refractive index of the medium is substantially the same as that of the pigment. The lead paint, however, will still be opaque, since white lead has a refractive index greater than that of the oil.

**OIL ABSORPTION**—*Opacity increases inversely with the amount of oil absorbed by the pigment.* This is shown by comparing the hiding power of lead and zinc whites. These pigments have substantially the same refractive index and theoretically should hide equally. As a matter of fact, however, a workable lead paint has greater hiding power, since it may be produced by grinding 70 parts of lead in 30 parts of oil, while a workable zinc paint will contain 50 parts of zinc and 50 parts of oil. More light will pass through a film of the zinc paint than through the lead paint, on account of the greater quantity of oil present in the former. This accounts for the difference in the hiding power of the two paints. The preponderance of oil in the zinc paint, however, accounts for the much greater durability of those paints which contain zinc oxide in combination with lead pigments, since abundance of oil is recognized as a necessity in exterior paints.

It is apparent from the above considerations that the hiding power of a white pigment is measurable by determining its physical characteristics. Various methods for determining fineness and oil absorption have been in use, but no method has apparently been adopted for determining the refractive index of pigments. It occurred to the writer that some application of the petrographic microscope might be made for this purpose. A series of pigments were therefore prepared and submitted to test, the readings being made by Dr. Frederick E. Wright, of the Carnegie Geophysical Laboratory of Washington. Small particles of the pigment under observation were rubbed up with media of known refractive indices, covered with glass, and submitted to examination. Some of the readings are shown below:

Quartz silica	1.55	Basic carbonate—white lead	2.0
Barium sulfate	1.6	Basic sulfate—white lead	2.0
Zinc oxide	1.9+	Zinc sulfide	2.2 to 2.37

#### OPAQUE ADSORPTION PIGMENTS

One of the most interesting pigments examined was lithopone. Difficulty was experienced in getting an exact reading, as it consists of a submicroscopic mixture of aggregated particles. It is possible that the average refractive index might be considered as being between 1.9 and 2.0. This pigment is prepared by the resulting interaction of chemically equivalent amounts of zinc sulfate and barium sulfide solutions. The precipitated pigment is calcined, quenched, washed and dried. It consists of approximately 70 per cent barium sulfate and 30 per cent zinc sulfide. When barium sulfate, which has a refractive index of 1.6, and zinc sulfide, which has a refractive index of 2.2 to 2.4, are *mixed* in the above named proportions, a pigment is produced which is deficient in hiding power. It is apparent, therefore, that the precipita-

tion process of preparing these pigments produces some physical change which is of great importance. It is the writer's opinion that the effect is due to adsorption of the zinc sulfide by the barium sulfate particles. Microscopical examination indicates that each particle of finely divided barium sulfate is coated over by adsorbed particles of opaque zinc sulfide. Experiments have been made with varying strengths of barium sulfate and zinc sulfide liquors in varying amounts, to determine whether it would be possible to produce even more opaque types of lithopone by increasing the amount of the zinc sulfide present. When lithopones are made containing as high as 50 per cent zinc sulfide, the hiding power has not been found substantially greater than that of lithopone which contains from 28 per cent to 38 per cent of zinc sulfide. Below 28 per cent of zinc sulfide, the hiding power of the pigment decreases. It is, therefore, between the limits of 28 per cent and 38 per cent zinc sulfide that the greatest hiding powers are obtained, and the increased hiding power of lithopone containing 38 per cent is hardly greater than that shown by those containing the theoretical equivalent of 30 per cent. Rapidity of precipitation, strength of solution, and temperature control are factors which also aid in the production of fine grained particles that give the pigment great opacity.

The phenomenon of surface adsorption shown by certain lake bases in the presence of organic coloring matters is also interesting, and explains why the highly colloidal pigments are often preferred for this purpose. A measure of the degree of dispersion of pigments might be based on their color adsorption values.

#### SUSPENSOID PIGMENTS

*The adhesive properties and cementing values of paint pigments apparently increase with approach to colloidal form.* That all paint pigments are to some extent colloidal, is the assumption of the writer as the result of some recent tests. These were first suggested by some previous experiments in which a number of white pigments were ground in clear linseed oil. After standing for a year, the oil upon the surface of the settled paints was examined and found to be much higher in ash than the original oil. This condition could easily be accounted for in the case of the lead and zinc paints by the presence of dissolved metallic linoleates formed by reaction between the pigments and the free fatty acid of the oil. No explanation, however, was offered as to the cause of the high ash in those paints made of silica, barium sulfate and other pigments which it was thought could exert no chemical effect upon the vehicle. A sample of the oil from one of the inert pigments (*blanc fixe*), after standing in a bottle for a further aging period, became viscous and thick, later on developing a peculiar cloudiness. Examination showed that the pigment had probably been held in colloidal suspension and previous to its precipitation had effected a change in the oil that had caused the gelatinous condition. As a result of these observations, the writer prepared a series of paints by grinding in a clear linseed oil



a number of standard white pigments, including basic carbonate- and basic sulfate-white lead, zinc oxide, lithopone, and china clay. After settling for a period of two weeks, the clear oil was removed from each paint. The oils were examined under the ultramicroscope by Dr. E. C. E. Lord, of the U. S. Office of Public Roads, and the writer. Particles were visible but apparently in a quiescent state. This condition was undoubtedly due to the viscosity of the oil media which exerted a cohesive force upon the particles, binding them together in aggregates and thus impeding their motion so that the Brownian movement was not observable. These liquids, however, after dilution with 4 volumes of redistilled 90° benzol (disperse free) were again examined. The viscosity of the media thus being reduced, great rapidity of motion of the particles was shown. This Brownian movement was observed in every liquid and indicated that all of the above pigments may contain particles that act as suspensoids in oil. A sample of the original oil used in making the paint was also examined and although Brownian movement was observed therein, the number of particles present was not comparable to those shown by the oils removed from the paints. The particles present in the original oil were probably due to the "foots" present, regarding which reference is made below.

For the sake of convenience, the writer has given the name of "Linolsols" to pigment suspensoids, since paint pigments are almost universally used in conjunction with linseed oil. When a condition is produced by these pigments, whereby the oil assumes the state of a gel, as in the case of the blanc fixé pigment mentioned above, the product of reaction might be called a "Linogel." The precipitation of the blanc fixé which was first visible as a cloudiness in the oil might possibly have been caused by absorption of oxygen by the oil, and would then be comparable to the precipitation of silica when carbon dioxide is absorbed by a sol of hydrated silicic acid. The term "Linoxyl" might, therefore, be more acceptable for such a product.

Experiments were then made with the same series of pigments ground in various oils, including a heavy bodied linseed oil of very high viscosity. In the latter, separation of the pigment from the oil, even after standing for two months, was only partial. After the paints were diluted with 4 volumes of benzol, only the coarser particles subsided, the liquid above remaining cloudy and suggestive of a true colloidal condition—the subdivided particles no longer showing any tendency to settle. Even after standing five weeks, the same cloudy condition was observed. It was apparently impossible to clarify the turbid liquid by sedimentation, even with the aid of a high-speed centrifuge. Attempts were then made to precipitate the Linolsols. It was found that by mixing two of the cloudy paints (zinc oxide and silica), a fairly clear liquid could be produced. The explanation of this phenomenon might be that the pigments being oppositely charged had neutralized each other and thus disturbed the disperse phase, resulting in precipitation.

#### COLLOIDAL COLOR PIGMENTS

In order to study the condition of finely divided colored pigments, several were selected, including Prussian Blue, Chrome Green, Chrome Yellow, Ultramarine Blue, Lampblack, and Paranitriline Red. These were ground in the same type of oil that was used with the white pigments, and treated in the same fashion. The clear liquid shown after settling was diluted with 4 volumes of benzol (disperse free) and examined. It is of interest to record the fact that the oil obtained from the settled Para Red pigment was only slightly colored, but when benzol was added, it became a bright, clear red. It is probable that part of the pigment present as a suspensoid was brought into actual solution by the solvent power of the benzol upon the organic coloring matter present in the pigment, thus accounting for the increase in color. When the liquids were examined under the ultramicroscope, Brownian movement was exhibited by each, the green and blue being most active and apparently containing many times the number of particles present in the others. Comparing the blue roughly with a counted solution of colloidal asphalt, it is probable that 1 cc. of the liquid contained over a hundred million particles.

Many of the particles or aggregates in the oil from the Chrome Green were colored crimson, orange, green, and blue. The colors were apparently permanent and did not change as would be the case if due to refraction. Since it is supposed that ultramicroscopic particles simply reflect light and therefore do not show colors, the above result is interesting and should warrant some extended work on the subject.

#### PREFERENTIAL ADSORPTION EFFECTS

The effect shown by carbon black is worthy of study. This pigment is supposed to be one of the most inert to linseed oil. It is probable, however, that it is really one of the most active in some ways. The great surface which its particles present, on account of their extreme fineness of division, probably gives to it very high adsorptive properties. The purest pigment obtainable by burning oil may be free of other solids and yet, according to F. P. Ingalls,<sup>1</sup> contain only from 80 to 90 per cent of carbon, the balance consisting of carbon monoxide, carbon dioxide, hydrocarbon compounds, nitrogen, oxygen, and water, all of which have been adsorbed by the carbon particles during the process of manufacture. That these substances are firmly locked to the particles is apparent, since vacuum treatment of the pigment fails to remove them. When ground in oil, however, the writer believes that the gas is removed from the pigment and the oil is adsorbed in place thereof by a preferential adsorption action of the pigment. Clifford Richardson has shown, for instance, that asphalt particles have the power of adsorbing some of the heavier constituents of a liquid by preferential adsorption. The present writer has similarly noticed that some finely divided pigments may adsorb the heavier constituents of an oil medium. This may be shown by dissolving a very heavy bodied linseed oil in benzine and grind-

<sup>1</sup> Private communication.

ing it with lithopone. After a period of time, a reaction will be effected, whereby the oil is adsorbed by the settled pigment, leaving a clear, oil-free benzine floating on top. Very strongly oxidized and bodied oils may even show precipitation upon standing after being mixed simply with benzine. It is a question, therefore, whether any true solution of the oil has originally taken place. It is very likely that the apparent miscibility of the benzine is due in this instance to a sponge-like process of imbibition which might be compared to the absorption of benzol by rubber, or the swelling of gelatin in water (these effects, however, are illustrative of emulsoids). The preference shown by pigment particles for various liquids is aptly illustrated in the manufacture of pulp lead. The white lead, which contains a large amount of moisture, if agitated with linseed oil will immediately unite with the oil, and the water will be thrown out, floating on the surface of the paste paint. Other pigments and liquids may show a similar reaction. When zinc oxide or lithopone, for instance, are ground in alcohol and subsequently agitated with linseed oil, the oil will immediately unite with the pigments and the alcohol will be found floating on the surface of the paste. It is probable that these reactions have been made possible by a lowering of surface tension by the introduction of the oil.

#### SUSPENSIDS IN OIL AND VARNISH

The "foots" present in linseed oil offers another example of what might be termed a "Linol." When freshly crushed from the flaxseed, the oil will be apparently clear. If heated to 100° C., it will become cloudy and a large precipitate will form. This is referred to as "foots" and consists of mineral matter—lime, silica, phosphoric acid, etc.—admixed with albuminous matter. The mineral matter is present in the raw oil as a suspensoid<sup>1</sup> and is agglomerated and precipitated when the albumen is coagulated by the heat. The aging of oil may accomplish a somewhat similar effect, but sufficient tankage space is not always available to the crusher, and, therefore the raw oil is often marketed immediately after it has been produced. In the writer's opinion, such oil is not fit for use in high-grade paints, and the grinder should demand a better product. If the crusher should heat the raw oil to 100° C. and then centrifuge it, this method might take the place of tanking and would, at the same time, accomplish the destruction of fat-splitting enzymes<sup>2</sup> which might be present in the oil.

Varnish constitutes another organic product that may contain mineral suspensoids. Tanking of clear, newly made varnish always results in a slow precipitation of "foots." Centrifugal force will bring about the result more rapidly. It is gratifying to note that the centrifuge has become a part of the equipment of every modern varnish plant, and its use in this industry is bound to be more extended in the future. E. E. Ayres<sup>3</sup>

<sup>1</sup> "Refining Vegetable and Animal Oils," Chas. Baskerville, *J. Franklin Inst.*, June, 1916.

<sup>2</sup> "Changes Occurring in Oils and Paste Paints, Due to Autohydrolysis of the Glycerides," H. A. Gardner, *J. Franklin Inst.*, May, 1914.

<sup>3</sup> "The Application of Centrifugal Force to Suspensions and Emulsions," E. E. Ayres, *J. Soc. Chem. Ind.*, June, 1916, p. 676.

has recently commented upon the clarification of pyroxylin varnishes by centrifugal action, and has mentioned the remarkable effect of a precipitant such as tricalcium phosphate. Similarly it is probable that the addition of certain mineral matter to freshly made varnishes, just previous to centrifuging, may effect more rapid and permanent clarification.

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#### COUMARONE RESIN AND ITS USES

By CARLETON ELLIS AND LOUIS RABINOVITZ

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Resinous bodies obtained by the polymerizing action of sulfuric acid on indene ( $C_9H_8$ ) and coumarone ( $C_8H_6O$ ) occurring in the fraction of coal-tar naphtha boiling between 160 and 180° C., are found in the market under the name of coumarone resin. Various attempts have been made, with some measure of success, to substitute these polymerization products for certain of the natural resins. This paper aims to give a brief review of the subject and a résumé of some experimental work carried out by us on coumarone resin.

Coumarone (or cumarone) resin was obtained by Kraemer and Spilker, during their investigation on indene and coumarone in coal-tar naphtha,<sup>1</sup> by the action of strong acids, particularly sulfuric, on coumarone; they called the product *para coumarone*. Somewhat later<sup>2</sup> they subjected this resin to a more thorough investigation and found that when pure coumarone which has been diluted with benzol is treated with a moderate amount of sulfuric acid, the greater part of the coumarone is converted into a resin soluble in benzol, while a lesser portion is transformed into a body insoluble in benzol and is carried down by the sulfuric acid, from which it may be removed by treatment with water.

The investigations of these chemists show that polymerization begins with an acid strength of 80 per cent (monohydrate). With this strength of acid the soluble resin is obtained almost exclusively. As the concentration of the acid is increased more and more of the insoluble resin forms. Increase in the proportion of the acid acts in a similar manner. With acid of 95 per cent strength applied in sufficient amount to a 2 per cent solution of coumarone in benzol the insoluble resin is formed almost quantitatively. When using 50 per cent of acid, calculated on the coumarone taken, about 25 per cent of soluble resin is formed while with four times the amount of acid no insoluble resin is formed.

Indene behaved very much like coumarone, only in that case the resinification was accompanied by a rise in temperature. The coumarone resin was found to melt between 107 and 108° C.

By the treatment of coumarone with a relatively large proportion of sulfuric acid,<sup>3</sup> at first a soft pasty mass was obtained which soon hardened to a brittle and infusible body, insoluble in all solvents. Kraemer

<sup>1</sup> *Ber.*, **23** (1890), 78, 3276.

<sup>2</sup> *Ibid.*, **33** (1900), 2257.

<sup>3</sup> *Ibid.*, **23** (1890), 81.



and Spilker were unable to state whether this body corresponded in composition to that of coumarone. It had a specific gravity of 1.25 at 10° C. Its molecular weight was four times that of coumarone and on heating the resin decomposed between 300 and 350° C.

Indene was found to give a resin similar to that obtained in the case of coumarone and the product was obtained by them in various modifications, of differing melting points and molecular weights. From pure indene they obtained a resin which melted at 210° C. By treating the purified fractions that came over at 155–158° C. with sulfuric acid and steam distilling the solvents, they obtained a crude indene resin which was in many respects very similar to the coumarone resin.<sup>1</sup>

Later Kraemer and Spilker analyzed the insoluble and infusible modification of coumarone resin and found that sulfur which they previously had noted and had regarded as a mere impurity was in fact chemically combined.<sup>2</sup>

In 1890 Kraemer and Spilker<sup>3</sup> called attention to the industrial possibilities of "para coumarone" or "coumarone resin." They noted that it formed a coating for wood and metal surfaces which on account of its resistance to acids and alkalies possessed certain advantages over the ordinary resin solutions and varnish coatings employed for this purpose.

Wendriner, who has done a considerable amount of work on coumarone resin, describes a process for the manufacture of a light-colored resin, as well as a white solvent naphtha, from coal-tar naphtha distilling at 160–180° C., by removing first the acidic and basic constituents of the oil with 3 to 5 per cent by volume of 60° Bé. sulfuric acid under constant agitation and then treating the naphtha with 0.25 to 0.4 per cent by volume of concentrated sulfuric acid in a thin stream until the temperature rises to 110–120° C. After this treatment the acid is removed from the oil and the latter containing the dissolved resin is neutralized, dried and distilled from the resin with superheated steam. A less pure coumarone resin is prepared by treating solvent naphtha in the presence of its acidic and basic impurities with 0.5 per cent instead of 0.25 by volume of concentrated sulfuric acid.<sup>4</sup> Wendriner modified the process by omitting the use of 60° Bé. acid and carrying out the polymerization under cooling and under slow introduction of concentrated acid. He mentions that care should be taken to use an amount of concentrated acid equal to 0.25 to 0.4 per cent by volume of the naphtha treated and that the temperature should not rise above 40–50° C. The advantages of this process are: A saving of 3 to 5 per cent of 60° Bé. sulfuric acid; avoidance of the danger caused by heating of the volatile naphtha; a product in appearance somewhat resembling a light Congo resin melting between 80–100° and having a color varying from yellow to amber, depending on the care exer-

cised in carrying out the reaction. According to Wendriner it is important to avoid sulfonation which has an influence on the color and boiling point of the naphtha yielded by the operation.

Knüppel<sup>5</sup> states that a hard brittle resin is obtained by blowing air through para coumarone and para indene for 3 to 5 hrs. at a more or less high temperature. According to Knüppel, the product is not tacky, dries with a high lustre and increases the drying power of the varnish prepared from it.

Fehringer<sup>2</sup> prepares a bronzing liquid or bronze powder varnish by dissolving coumarone resin in benzene, gasoline, benzol, chlorethylene or a mixture of these solvents.

Varnishes are prepared from cellulose esters by dissolving them in methyl alcohol, acetone oils, ketones or the like, with the addition of polymerization products of coumarone or indene, dissolved in benzol, alcohol or like solvents.<sup>3</sup> The resulting varnish is stated to be oily, lustrous, to dry uniformly, forming a very elastic coating which is stable in air and light. For instance, 1 part by weight of coumarone resin is dissolved in 5 parts benzol and added to a liquid consisting of a solution of 3 parts of collodion and 0.5 part of acetone oil, 10 parts each of alcohol and ketones: the resulting composition is diluted with 30 parts alcohol, 30 parts benzene and 10 parts methyl alcohol. Or, 1 part of coumarone resin is dissolved in a mixture of 2.5 parts each of fusel oil and tetrachlorethane; this solution is added to a mixture of 60 parts acetone and 30 parts methyl alcohol; 40 parts of acetyl cellulose are dissolved in this liquid. (See also U. S. Patent 1,185,514, May 30, 1916, to Lehmann and Stocker.)

Eichler<sup>4</sup> describes the simple preparation from the polymerization products of coumarone of a primer and varnish which is impervious to water vapors, caustic alkalies, ammonia and efflorescence. For example, para coumarone is melted and compounded with a solvent while heat is applied, whereupon the varnish is formed. The consistency of the varnish of course depends upon the quantity of solvent employed. Usually equal parts by weight of the resin and solvent are used. The primer and varnish may also be added to ordinary varnish to render the latter more impervious to water and more resistant to alkali. Benzene, gasoline, benzol or turpentine are good solvents for the resin. Eichler<sup>5</sup> also refers to the application of coumarone resin in linseed-oil varnishes in lieu of ordinary varnish resins.

Lender and Koch<sup>6</sup> note that coumarone resin may be used in a varnish base for the manufacture of varnishes, enamels and paints and as a binder in the manufacture of linoleum, linocrust and oil cloth. They state that all objections encountered in the preparation of paints or varnishes by incorporating Chinese wood oil with ordinary resins are overcome, if in place of these the

<sup>1</sup> Ber., **33** (1900), 2257.

<sup>2</sup> Ibid., **34** (1901), 1888.

<sup>3</sup> Ibid., **23** (1890), 81.

<sup>4</sup> German Patents 270,993 and 281,432; *J. Soc. Chem. Ind.*, **1914**, 474, *Chem. Abs.*, **1914**, 2248; **1915**, 2001; *Z. angew. Chem.*, **27**, 2582.

<sup>5</sup> German Pat. 253,437, 1912; *Z. angew. Chem.*, **25** (1912), 2506.

<sup>6</sup> *Chem. Abs.*, **1915**, 3369, U. S. Patent 1,157,768, Oct. 26, 1915.

<sup>7</sup> Ibid., **1915**, 1850; German Patent 281,265, 1913.

<sup>8</sup> U. S. Patent 1,133,432, March 30, 1915.

<sup>9</sup> U. S. Patent 1,133,433, March 30, 1915.

<sup>10</sup> U. S. Patent 1,019,666, March 5, 1912.

polymerization products of coumarone and indene, namely, para coumarone and para indene, are employed. A varnish of this type is prepared as follows: 10 kg. of Chinese wood oil are heated to 220–240° C. and a quantity of the polymerization products of coumarone and indene to suit the conditions of use, generally an equal weight, is added; the product is a homogeneous mass which is hard when cold. This material is the base from which varnish, lac, enamel or similar coating material are made. This base is then heated and mixed with a suitable solvent such as liquid hydrocarbons, *e. g.* benzine, benzol, ligroin, turpentine, etc., and also chlorinated hydrocarbons. The amount of solvent used is dependent upon the consistency of the product desired and the use to be made of it. It may be thinned at will. To the mixture of the base and solvent may be added any desired coloring matter and the varnish or paint is stated to dry rapidly to a brilliant elastic coating impervious to liquids and unattacked by gases. It is unusually resistant to water, acids, heat and cold. A varnish paint or other similar product of this character is claimed to have a wider range of use than any other similar product or any product consisting of Chinese wood oil and ordinary resins, especially as it does not become tacky and does not set or liver by the addition of such pigments as lead or zinc compounds.

Lender<sup>1</sup> states that a varnish can be prepared from indene or coumarone, or both, with or without the addition of vegetable or animal oil, by heating with sulfur or sulfur chloride under pressure or at ordinary pressure, and dissolving the product in a volatile solvent.

#### PROPERTIES OF COUMARONE RESIN

Bottler,<sup>2</sup> who has investigated the properties of commercial coumarone resin, states that the resin of commerce varies widely in character. Some varieties which he examined were solid and more or less brittle, others were soft and pasty. A rough and ready method for the determination of the hardness of a resin according to Bottler is to scratch the surface of the resin with a needle. On soft resins the needle traces a smooth and even line. On hard resins the line is rugged and rough.

Some of the coumarone resins, Bottler notes, were of a dark brown color, sometimes even black while others varied from a yellow-brown to a brown color. They occurred in lustrous non-transparent lumps having a shiny fracture. Some of the samples gave a light yellow, others a dark brown powder. They possessed a tar-like odor. The yellow and brown resins in powder form attracted moisture from the air on standing over night. In some cases it was found necessary to use a spatula to remove the powdered material from the mortar. Their melting point varied over a considerable range. Some of the yellow-brown and brown varieties melted at 55, 60 and 65° C. The darker varieties generally melted higher, softening at about 85° C. and melting completely at 98, 100 and 108° C. They fused more easily than various

natural resins. The fused material usually solidified very quickly to a resin of the original color.

A sample of brown coumarone resin, made in this country, was examined in this laboratory and found to melt completely at 65° C.

#### ACTION OF ALKALIES

A 5 per cent sodium carbonate solution, a 1 and a 5 per cent solution of sodium hydroxide and 10 per cent ammonia water did not affect coumarone resin. Only on prolonged warming with 5 per cent caustic was the resin somewhat acted upon, and the solution shows signs of frothing. At any rate no saponification took place.

#### SOLUBILITIES OF COUMARONE RESINS, ETC.

SOLVENT	HARD COUMARONE RESIN (BOTTLER)	COLOR OF SOLUTION
Alcohol.....	Slightly soluble	Light yellow
Absolute alcohol.....	Easily soluble	Yellow
Carbon tetrachloride.....	Completely soluble	Yellow to brown
Trichlorethylene.....	Completely soluble	Yellow
Benzine.....	Completely soluble	Yellow to red-brown
Turpentine.....	Soluble (slight residue)	Yellow
Linseed oil.....	Slightly soluble	
SOFT COUMARONE RESIN (BOTTLER)		
Ether.....	Soluble	Yellow
Carbon tetrachloride.....	Completely soluble	Brownish yellow
Trichlorethylene.....	Completely soluble	Brown color
Benzine.....	Easily soluble	Brownish color
Turpentine.....	Almost completely sol.	Yellowish brown color
Ether and 90% alcohol.	The resin is precipitated	
COLOR OF FILM ON TIN PLATE (BOTTLER)		
Ether.....		Lustrous and yellow
Carbon tetrachloride and trichlorethylene.....		Light yellow or yellow
Benzine.....		Brownish red
Turpentine.....		Yellow and lustrous
Ether and trichlorethylene.....		Yellow

Kraemer and Spilker state that para coumarone is easily soluble in ether, benzol and chloroform but difficultly soluble in benzol.<sup>1</sup> The films obtained from different varieties of resin in either carbon tetrachloride, trichlorethylene, benzine and turpentine possessed a certain degree of elasticity. It is stated that the resin possesses drying properties when exposed to air in thin layers.<sup>2</sup>

#### PREPARATION OF PURE INDENE

Kraemer and Spilker<sup>3</sup> describe a process for the purification of indene by means of picric acid. According to this method the fractions of crude naphtha boiling between 176–182° C. are treated with as much picric acid as is necessary to combine with all the unsaturated bodies present. The crystalline precipitate formed contained the picrates of coumarone and naphthalene as well as that of indene. On steam distillation the indene picrate is decomposed and indene distills over. Ten kg. of crude naphtha boiling between 176–182° gave 3 kg. of crude indene. The process is not without danger as these picrates are highly explosive.

Weisberger<sup>4</sup> describes several methods of a more practical nature, for the preparation of pure indene. Sodium amide is treated with the crude indene fraction boiling between 175–185° C. Ammonia is evolved and amide is converted into a dark heavy oil. The mixture is heated for 2 hrs. under agitation at 110–175° C. It is then distilled at 20–30 mm. pressure

<sup>1</sup> *Ber.*, **23** (1890), 81.

<sup>2</sup> *Seifen-Ztg.*, **1913**, 289, 344, 694.

<sup>3</sup> *Ber.*, **23** (1890), 3276.

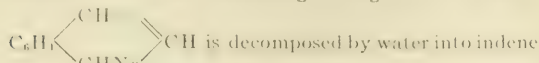
<sup>4</sup> *Ibid.*, **42** (1909), 569, and German Patent 205,465 (1908), and 209,694 (1909).

<sup>1</sup> German Patent 277,605; *Z. angew. Chem.*, **27**, II (1914), 583.

<sup>2</sup> *Kunststoffe*, **1915**, 277.



to remove the unchanged hydrocarbons which come over at 110–130° C. The solid amorphous mass left behind and to which Weisberger assigned the formula



and sodium hydroxide. The indene is recovered by steam distillation. A rough fractionation of this product yields pure indene.

A still purer product may be prepared by treating the crude indene with the theoretical quantity of metallic sodium and passing a slow stream of ammonia into the mixture at 120–130° C. for 5 or 6 hrs. The indene sodium compound obtained by this process resembles rosin in appearance, is very sensitive to the action of air and is easily decomposed by water yielding a very pure indene.

By heating the indene and sodium above 130° C. in the presence of small amounts (2 per cent) of basic bodies such as aniline, toluidine or pyridine, pure indene may be obtained without the use of ammonia gas. Weisberger states that by this method the yields of indene obtained from the fraction of heavy benzol boiling between 175–185° C. amounted to 35 per cent.

The methods for preparing pure coumarone are more involved and are of scientific rather than of practical interest.

#### THE PROPERTIES OF INDENE AND COUMARONE

Spilker and Dombrowsky<sup>1</sup> describe indene prepared from the sodium compound as melting at 92° C., and boiling at 182° C., having a specific gravity of 1.0002. Pure indene absorbs oxygen and becomes acid. The oxidized indene is insoluble in alcohol and cannot be distilled by steam.<sup>2</sup> It combines with mercuric sulfate, giving an indene mercuric oxide compound.<sup>3</sup>

Bizzarri<sup>4</sup> describes coumarone as a colorless liquid boiling at 169° C. and very resistive towards chemical agents or heat. Aniline or alcoholic ammonia has no action on it. Aluminum chloride was found by Heuser<sup>5</sup> to act violently on coumarone and indene with the production of a resin soluble in hydrocarbons. He states that it is impossible by a single treatment with sulfuric acid to remove completely the indene and coumarone from coal-tar naphtha, but that by the action of aluminum chloride these two bodies may be completely resinified. Two and one-half per cent of aluminum chloride is sufficient for this purpose. The indene and coumarone resins remain dissolved in the naphtha.

#### EXPERIMENTAL WORK

In some experimental work carried out by us, the fraction of varnish makers' solvent naphtha which boiled between 160–180° C. was treated with 1 per cent of 66° Bé. sulfuric acid and was stirred for several hours at room temperature. The temperature of the mixture did not rise above 35° C. The product

was then washed free from acid and steam-distilled with superheated steam. There was left in the vessel a pasty material which gave on drying on the steam bath a transparent brown substance of the consistency of molasses. Six hours of steam distillation with superheated steam did not materially affect the hardness of this product. Some of this soft resin was heated for 15 to 20 min. to 220° C. with about 10 per cent of sulfuric acid (66° Bé.). The resin darkened considerably and carbonized without undergoing any change in hardness. Another portion was subjected to the action of anhydrous zinc chloride and also to stannic chloride at 200° C. without undergoing any change. Chlorine combined readily with the coumarone resin giving a fairly hard, dark product. Darkening was the only visible effect that a powerful ultraviolet light had on coumarone resin after a 3-hr. exposure.

The effect of other polymerizing agents on solvent naphtha containing coumarone and indene was investigated in this laboratory. In one case, the naphtha was heated to boiling with reflux condenser for one hour with silver oxide. A part of the silver oxide was reduced to metallic silver with the formation of a bright mirror on the walls of the vessel. The liquid was filtered and steam-distilled. A dark brown material was left in the vessel which was considerably harder than the resin obtained with sulfuric acid. Phosphorus trichloride, phosphoric acid, chromic acid, hydrochloric acid, ammonium dichromate, formaldehyde and potassium hydroxide did not polymerize coumarone or indene in solvent naphtha, under the conditions tried. Zinc chloride at the boiling point of solvent naphtha gave rise to a small amount of resin. The action of anhydrous stannic chloride was similar to that of zinc chloride, while iodine was without effect.

Soft coumarone resin was distilled at 29 in. vacuum. When the temperature rose to 160° C. the distillation was stopped. The resin left in the flask was rather dark and melted completely at 60–65° C. It softened in the hands to a flexible mass which was not tacky.

Twenty grams of the soft coumarone resin were distilled at 29 in. vacuum.

Weight of Distillate	Weight of Residue	Temperature
9.0 g.	10.5 g.	to 168° C.
2.5 g.	8.5 g.	168–180° C.

From this data it can be seen that 57.5 per cent of the soft resin went over into the distillate. The hardness and melting point of the residue of resin increased with the amount of material distilled. The distillate was a highly viscous liquid which was somewhat brown in color. This coloration was due to the small amounts of resin that were carried over mechanically during the distillation. The distillate is probably an intermediate polymerization product. Its iodine number was found to be 28.5.

The resin obtained in this way became plastic at 38° C. and melted completely at 71° C. Its saponification number did not exceed 0.2. The iodine number of the hard resin was 38 to 43.5, which, it will be noted, is higher than the iodine number of the distillate.

<sup>1</sup> *Ber.*, **42** (1909), 573.

<sup>2</sup> Weger and Billmann, *Ibid.*, **36** (1903), 640.

<sup>3</sup> *Pharm.-Ztg.*, **1915**, 46.

<sup>4</sup> *J. Chem. Soc. [Abs.]*, **1891**, 566.

<sup>5</sup> *Z. angew. Chem.*, **1896**, 319.

In another case a sample of crude solvent naphtha, 25 per cent of which boiled above  $160^{\circ}\text{C}.$ , was treated with 1 per cent of sulfuric acid of 98 per cent strength and the mixture was agitated for 2 hrs. It was then freed from acid and distilled under ordinary atmospheric pressure at  $190^{\circ}\text{C}.$  The residue from this distillation was distilled to  $165^{\circ}\text{C}.$  under a vacuum of 29 in. and the residue from this second distillation was a thick, very viscous substance, dark in color and possessing a strong unpleasant odor which was quite different from the harder resin obtained from the solvent naphtha fraction (b. p.  $160\text{--}180^{\circ}\text{C}.$ ) used above. The yield of this viscous material amounted to 1.9 per cent of the solvent naphtha taken.

An interesting observation on the unsaponifiable nature of the coumarone resin was made with one of the harder samples obtained in this investigation. Solutions of the resin in benzol, etc., were applied to glass to form a thin film of the resin and when dry the plates were immersed in a liquid made by agitating Portland cement with water during the setting period. A thin paste of the cement and water was obtained in this way which was alkaline in reaction. The effect of this alkaline extract on the coumarone resin film was compared with the results obtained by similar treatment of films of drying oils and acid resins. In the case of the saponifiable bodies, the destructive effect of the alkali was quickly observed, but with the films of coumarone resin no disintegrating action was noticed even after exposure to the alkaline liquid for a period of several days. The films clouded and in some cases turned white, but the hardness and integrity of the coating did not appear to be affected. This property of the resin is of interest in connection with the production of a coating for concrete and stucco which is entirely resistant to the action of concrete alkali.<sup>1</sup>

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#### ON CALAMARY OIL

By MITSUMARU TSUJIMOTO

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This oil (Japanese: "Ika-abura") is obtained from the internal organs, especially the livers, of various species of cuttle-fish, among others the calamaries (the genera *Ommastrephus* and *Loligo*), and is a by-product of the manufacture of the so-called "dried cuttle-fish" (Japanese: "Surumé"). Although the annual production of the latter in Japan amounts to about 9,375,000 kg., the oil has been brought into market rather lately. According to a report of the Yokohama Fish Oil Company, the production of the oil in Hokkaido and other districts of Japan has annually increased, and it is stated that the Iwaté district (the northeastern coast of Honshiu) alone produced about 50,000 kg. of the oil in 1913. If all the fish used for the drying purpose were utilized, the production of the oil would be increased very considerably.

The oil is prepared by boiling the organs of the fish with water. The process appears to be rather primitive

and rough, judging from the quality of the commercial oil. The oil-content is recorded as about 2 to 3 per cent of the wet raw material.

J. Lewkowitsch, in his well-known work on oils, fats and waxes, has described the livers of decapods to be very rich in oil, but hitherto any further information on such oils seems to have been lacking.

The sample of calamary oil examined by the author was obtained from the Yokohama Fish Oil Company; it was produced in Miyako-chô in the Iwaté prefecture. The oil is a brownish red liquid of a very unpleasant odor; when spread on skin, a fishy smell peculiar to fish oils was observed. The taste is also very disagreeable. Cooled by ice, it solidified in a few hours. With concentrated sulfuric acid, a dark brown coloration with a slight purple tinge was formed. The chief properties of the oil were determined with the following results:

Specific gravity ( $15^{\circ}/4^{\circ}\text{C}.$ )	0.9316	Unsaponifiable matter..	1.14%
Acid value.....	3.88	Glycerine (extraction method).....	10.24%
Saponification value.....	189.64	Oxidized acids.....	0.69%
Iodine value (Wijs).....	177.02	Melting point of the mixed fatty acids.....	$35\text{--}36^{\circ}\text{C}.$
Refractive index ( $20^{\circ}\text{C}.$ ).....	1.4806	Polybromide of the mixed fatty acids..	57.45%
Butyrorefractometer ( $20^{\circ}\text{C}.$ )	84.0		

The polybromide was obtained by dissolving the mixed fatty acids in ether, and dropping bromine into the ice-cooled solution. It is a white powder, turning brown at  $200^{\circ}\text{C}.$  and decomposing at  $240\text{--}250^{\circ}\text{C}.$  without previous melting. Its bromine content was determined to be 70.91 per cent by the Carius method.

Calamary oil dries in the air when exposed in a thin layer, the drying property nearly corresponding to that of sardine oil.

The oil is not refined by Kambara earth with good results. It is best refined by alkali in the following way:

To 100 g. of the oil, 5 cc. of 20 per cent aqueous solution of caustic soda is added and stirred well. On gentle warming to about  $60\text{--}70^{\circ}\text{C}.$  the brown emulsion "breaks," with the separation of a dark viscous precipitate of coloring matters and impurities (the brown coloration is probably due to the soaps of oxidized acids). A little further heating suffices, and the oil is then filtered from the precipitate. The refined calamary oil is pale yellow; its smell somewhat recalls that of cod liver oil, the unpleasant odor being nearly removed.

The Yokohama Fish Oil Company values the calamary oil as about equal to herring oil. The refined calamary oil may be used as a substitute for cod liver oil, although its medicinal effects require some investigation. The oil may also be used for tanning, burning and soap-making purposes.

The oil, especially the refined, is easily hydrogenated by nickel catalyzer, giving, according to the author's experiment, a white tallow-like fat of m. p.  $43\text{--}44^{\circ}\text{C}.$  and iodine value 49.25.

The chief use of the oil will, therefore, probably be as a raw material for hardened oils, as its price is below that of other fish oils.

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<sup>1</sup> See U. S. Patents to Ellis, Nos. 999,439, 999,708 and 1,005,818.



## ON HARDENED CHRYSALIS OIL

By MITSUMARU TSUJIMOTO

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Raw chrysalis oil is unsuitable for the purpose of hydrogenation, as its nitrogenous and other impurities largely affect the activity of the catalyzer, even if we neglect the dark color and bad odor of the oil. However, the refining of chrysalis oil is by no means an easy one; but the process proposed by the author, which essentially consists in heating the oil with 5 to 10 per cent by vol. of dilute sulfuric acid (sp. gr. 1.39) and then treating it with Kambara earth, gives an excellent result.<sup>1</sup> The refined oil hardened by nickel catalyzer is a white fat which may be used as a useful raw material for soap-making.

The composition of chrysalis oil has been as yet little investigated. The results of experiments published by the author some years ago appear to be the only report on this subject.<sup>2</sup> According to this report, the fatty acids of chrysalis oil consist of about 25 per cent saturated and 75 per cent unsaturated acids (iodine value 178.73). Among the saturated acids, palmitic acid was identified; stearic acid is probably not present. The unsaturated acids consist of oleic, linolenic and isolinolenic acids; besides them, some isomers of linolic acid are present in a somewhat large quantity.

If the conclusion of the above-mentioned investigation be really the case, the final product of the hydrogenation of these unsaturated acids must be stearic acid. A study of the product is important from the point of view of utilizing the hardened chrysalis oil for technical purposes. The author made a few experiments which are described below.

## I—HYDROGENATION OF THE UNSATURATED (LIQUID) FATTY ACIDS OF CHRYSALIS OIL

Fifty grams of chrysalis oil<sup>3</sup> were saponified in a flask with 38 cc. of 50 per cent aqueous solution of KOH and 113 cc. of 96 per cent alcohol, by warming on a water bath; the excess of alkali was neutralized with acetic acid and 500 cc. of 7 per cent aqueous lead acetate solution was stirred into. The resulting lead soap was twice washed with 500 cc. of hot water and treated with 500 cc. of ether at 10° C. and then filtered (Tortelli and Ruggeri's method). The filtrate was then treated with dilute HCl, in order to decompose the lead soap, and was well washed with water: 250 cc. of the ethereal solution of the free unsaturated acids thus obtained, which contains about 20 g. of the acids of iodine value 176.17, were transferred into a strong glass bottle; 0.5 g. of Loew's platinum black was added.

The bottle was then connected to a hydrogen holder.<sup>4</sup> On expelling the air from the bottle by hydrogen, it was strongly shaken by means of a

mechanical contrivance. After 3½ hrs. shaking, a loss of about 2900 cc. of hydrogen was observed on the holder. Here the hydrogenation was stopped for a time. On evaporating off the ether, a residue amounting to 17.52 g. was obtained. It was a brown-yellow crystalline mass which when melted formed a brown-red liquid; it melted at 56.2° C., having the neutralization value 188.92 and iodine value 45.91. The hydrogenation was apparently incomplete; but before continuing the operation, it was found better to remove the unsaponifiable and coloring matters from the product.

Eleven grams of the above product were saponified with 50 cc. of 8 per cent alcoholic solution of NaOH; then 5 g. of NaHCO<sub>3</sub> and about 50 g. of pure sand were thoroughly mixed with it. The mass was dried, powdered and exhausted in a Soxhlet extractor with petroleum ether.

The crude unsaponifiable matter thus extracted was 2.22 per cent. The soap in the extractor was dissolved in hot water and decomposed with dilute HCl and then taken up with ether. The ethereal solution of the fatty acids which appeared brownish yellow, was decolorized with animal charcoal, and made up to 250 cc. by adding ether; then adding 0.3 g. of the platinum black, it was hydrogenized for 2 hrs. in the same way as before (the reading of the volume of hydrogen was omitted).

On evaporating off the ether, 8.3 g. of the hydrogenated acids were obtained. The white crystalline mass had a melting point of 68 to 68.5° C., neutralization value 195.19 and iodine value 0. This product is therefore a saturated compound, which in its m. p. and neutralization value nearly coincides with stearic acid (m. p. 69.3° C., neutralization value 197.5, molecular wt. 284). A mixture of the product with about an equal quantity of pure stearic acid melted at 68 to 68.3° C.

In order to perform the fractional crystallization of the acids, 5 g. of the hydrogenated product were dissolved in 100 cc. of 90 per cent alcohol and separated into three portions successively as follows:

- (1) 4.27 g.; white laminae with pearly luster; m. p. 69.5 to 70° C.; neutralization value 197.82; mean mol. wt. 283.59. A mixture with pure stearic acid melted at 69.5 to 69.7° C.
- (2) 0.21 g.; m. p. 68° C.; neutralization value 197.20.
- (3) Residue left on evaporating the mother liquor, 0.41 g.; a little colored solid; m. p. 50° C.; neutralization value 177.42.

The low m. p. and neutralization value are probably due to the accumulation of the impurities in this part and also to the esterification of the acids on evaporating off alcohol.

The result of the elementary analysis of (1) was as follows:

0.1245 gave 0.3487 CO<sub>2</sub> and 0.1439 H<sub>2</sub>O; C = 76.39; H = 12.84.  
C<sub>18</sub>H<sub>36</sub>O<sub>2</sub> requires C = 76.06; H = 12.68.

Therefore, the substance was confirmed to be stearic acid.

From the above experiment, it was concluded that the hydrogenated product of the unsaturated fatty acids of chrysalis oil consists mainly of stearic acid.

<sup>1</sup> *J. Chem. Ind., Tokyo*, 17, No. 191; *Chem. Rev.*, 1914, 58.

<sup>2</sup> *J. Coll. Eng., Tokyo*, 4 (1908), No. 3; *J. Soc. Chem. Ind.*, 1908, 455.

<sup>3</sup> This sample of the oil was procured from an oil factory in Ibaraki prefecture. It had the following properties: acid value 104.84, saponification value 187.03, and iodine value (Wijs) 140.33.

<sup>4</sup> Hydrogen was prepared by pure zinc and dilute H<sub>2</sub>SO<sub>4</sub>, and passed through the wash bottles containing concentrated potassium permanganate solution and concentrated H<sub>2</sub>SO<sub>4</sub>.

## II—ON THE SATURATED (SOLID) FATTY ACIDS OF CHRYSALIS OIL

Although the saturated acids have no direct relation to hydrogenation, an experiment supplementary to the former investigation<sup>1</sup> was performed as follows: The impure lead soap of the solid fatty acids obtained in the previous experiment on the liquid acids, was carefully detached from the filter paper and heated in a beaker with dilute HCl. The acids were then dissolved in ether and decolorized with animal charcoal. The crude solid acid which was left on evaporating off the ether, formed a yellow colored crystalline mass. The yield amounted to 11.5 g.

By dissolving in 100 cc. of 96 per cent alcohol, it was fractionally crystallized into five parts.

- (1) 3.78 g.; granular crystals; on melting, solidifies to a grayish white mass; m. p. 55–55.5° C.; neutralization value 205.09.
- (2) 1.40 g.; m. p. 55.5–56° C.; neutralization value 209.30.
- (3) 0.77 g.; somewhat granular crystals, faintly yellow; m. p. 56.5° C.; neutralization value 210.70.
- (4) 0.21 g.; pale yellow laminae; m. p. 57° C.
- (5) 3.61 g.; residue from the mother liquor; an orange-yellow soft mass.

A mixture of 3 g. consisting of 2.2 g. of (1) and 0.8 g. of (2) was dissolved in 100 cc. of 96 per cent alcohol and fractionally precipitated with magnesium acetate into the following fractions:

- (1) 0.9895 g.; m. p. 55.5° C.; neutralization value 203.22; mean mol. wt. 276.05.
- (2) 0.4920 g.; m. p. 56° C.; neutralization value 205.43; mean mol. wt. 273.09.
- (3) 0.4305 g.; m. p. 59° C.; neutralization value 207.98; mean mol. wt. 269.74.
- (4) 0.4785 g.; m. p. 60.5–61° C.; neutralization value 215.25; mean mol. wt. 260.16.
- (5) No precipitate was obtained by adding an excess of the precipitant. Therefore, it was abandoned. (The acid contained in this part corresponds to 0.6095 g.)

The result is not decisive, but it is certain that an acid or acids higher than palmitic are present. The mean molecular weight of about 270 seems to point to the presence of daturic acid,  $C_{17}H_{34}O_2$ . But as by repeated precipitations, the m. p. and neutralization values are regularly changed a little, it is more probable that the substance under examination consists of an eutectic mixture of stearic and palmitic acids.

## III—DETECTION OF HIGHER SATURATED FATTY ACIDS IN HARDENED CHRYSALIS OIL

To decide whether the hardened chrysalis oil contains saturated acids higher than stearic, the author applied the method proposed by H. Kreis and E. Roth<sup>2</sup> which had been modified and applied to the analysis of the hardened oil by W. Normann and E. Hugel.<sup>3</sup>

Ten grams of the mixed fatty acid obtained from a hardened chrysalis oil<sup>4</sup> (an oil from Nagano prefecture hardened by means of nickel catalyzer) were dissolved in 100 cc. of 96 per cent alcohol in a flask. By heating it on a water bath, 0.75 g. of lead acetate dissolved in 50 cc. of alcohol was added. On cooling the solution to the room temperature (20° C.), it was soon

filtered through a filter paper; the precipitated lead salt was washed well with alcohol and decomposed by dilute hydrochloric acid. The free acid was taken up with ether, and washed free from the mineral acid; the ether was then evaporated and a white solid acid was left.

It was dissolved in 25 cc. of 90 per cent alcohol and cooled to room temperature for 30 min. The mother liquor was filtered off; the deposited crystals were dried by pressing between dry filter papers. It was then twice dissolved in 12.5 cc. and 6 cc., respectively, of 90 per cent alcohol by repeating the same treatment as above.

The final deposit weighed 0.35 g. and consisted of nacreous laminae; m. p. 69.5–70° C.; neutralization value 194.76. This substance was, therefore, identified as stearic acid. No saturated acid higher than stearic was found in the hardened chrysalis oil. This result is in a good accordance with that obtained in the previous experiment.

## IV—INNER IODINE VALUE OF HARDENED CHRYSALIS OIL

It has been shown by J. Marcusson and G. Meyerheim,<sup>1</sup> that the inner iodine values of hardened fish oils are higher than 100, whereas lower values are found in the cases of hardened terrestrial animal oils. With a sample of "Talgol" which is of fish oil origin, they found a value of 107.

While belonging to a class of terrestrial animal oils, as chrysalis oil has a high iodine value, it appears not unlikely that the inner value of the hardened product still exceeds 100, and so in this respect it may resemble fish oils. To determine this, the author used the following two oils for examination:

(A) The same sample used in the previous experiment III.

(B) A hardened oil having the following properties: m. p. 56–56.5° C.; acid value 57.46; saponification value 191.08; iodine value 45.53. [The *original* chrysalis oil was the same as (A), the time of hydrogenation only being different.]

Three grams of the sample were treated in a manner equivalent to Tortelli and Ruggeri's method. After keeping at 6 to 10° C. for 2½ hrs., the ether solution of the lead soap was filtered off and decomposed with hydrochloric acid.

The iodine values were determined by Wijs' method. The inner iodine value of Sample A<sup>2</sup> was 87.60; of Sample B, 103.22, nearly approaching that of "Talgol."

In spite of the low iodine value (45.53) of Sample B, the inner value was comparatively very high. So, for a sample of the hardened chrysalis oil which has an iodine value near to that of "Talgol" (iodine value 65 to 70), a still higher inner value may be expected.

Of course, the process of hydrogenation, *i. e.*, the catalyzer, temperature, time, and method of stirring, etc., will essentially influence the inner iodine value

<sup>1</sup> Loc. cit.

<sup>2</sup> Chem.-Ztg., 1913, 58.

<sup>3</sup> Ibid., 1913, 815.

<sup>4</sup> Chem. Rev., 1914, 58. This sample is the No. B hardened oil. Its properties are as follows: m. p. 56° C.; acid value 57.16; saponification value 190.71; iodine value 35.81.

<sup>1</sup> Z. angew. Chem., 1914, 201.

<sup>2</sup> The liquid fatty acids of this sample obtained as above, solidified at the room temperature. It seems, therefore, to have contained more or less solid fatty acids.



of the product. That hydrogenation takes place by degree according to the unsaturation of the fatty acids, will not always be anticipated. It will be, therefore, unsafe to attach too much importance to the inner iodine value of a hardened oil without taking into account the iodine value of the oil itself. For hardened chrysalis oil of an iodine value above 50, an inner iodine value exceeding 100 may probably be expected.

#### V—SUMMARY

The results of the present investigations may be summarized as follows:

I—The hydrogenated product of the unsaturated fatty acids of chrysalis oil consists mainly of stearic acid.

II—Besides palmitic acid, some higher saturated acid or acids are present in chrysalis oil. This substance is probably an eutectic mixture of stearic and palmitic acids.

III—By the Kreis and Roth method, no saturated acid higher than stearic was found in the hardened chrysalis oil.

IV—An inner iodine value exceeding 100 may probably be expected in the case of a hardened chrysalis oil having the iodine value above 50.

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### THE USE OF DIPHENYL GLYOXIME AS AN INDICATOR IN THE VOLUMETRIC DETERMINATION OF NICKEL BY FREVERT'S METHOD

By C. L. KELLEY AND J. B. CONANT

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A volumetric method for determining nickel in iron and steel as devised by H. L. Frevert was published in Blair's "Chemical Analysis of Iron," 7th edition, 1912. Since that time the method has been constantly in use in this laboratory, but inasmuch as some small changes have been made from time to time it seems best to republish the method with these modifications. Accordingly we give below Frevert's method as originally proposed, except for the modifications mentioned above, and follow it with a discussion of the use of diphenyl glyoxime as an indicator.

#### FREVERT'S METHOD FOR THE DETERMINATION OF NICKEL IN STEEL

(A) SOLUTION OF THE SAMPLE—For ordinary nickel steels, a 1-g. sample is taken, but with less than 0.10 or more than 5 per cent of nickel, larger or smaller samples may be taken. In the absence of more than small amounts of chromium, solution is most rapid in 50 cc. of hot dilute nitric acid (sp. gr. 1.13), but with chromium present in amounts greater than 0.5 per cent, or under circumstances where chromium carbides are present, more satisfactory results are obtained by dissolving the sample in 60 cc. of dilute hydrochloric acid (1 : 1) with the aid of heat. When solution is complete, the iron and the carbides are oxidized by adding nitric acid, drop by drop, until effervescence ceases. Boiling removes the products resulting from the decomposition of the nitric acid after which the solution is cooled. The quantities

of acid given here are those which are convenient for use with samples of 1 g. or less.

#### (B) PRECIPITATION OF NICKEL DIMETHYL GLYOXIME

The solution obtained, as described above, is rapidly cooled by the addition of a lump of ice, after which are added in succession, 12 g. of citric acid or equivalent solution, 20 cc. ammonia water (sp. gr. 0.90), sufficient solution of dimethyl glyoxime to precipitate all nickel present and enough more ammonia to make the solution distinctly ammoniacal. The mixture is thoroughly stirred after each of these additions. The solution of dimethyl glyoxime is prepared by dissolving 20 g. of the reagent in 1300 cc. of ammonia water (sp. gr. 0.90), after which enough water is added to bring the volume up to 2000 cc. Ten cc. of this solution allow sufficient excess to completely precipitate 1.5 per cent of nickel in a 1-g. sample, *i. e.*, about 0.0150 g. of nickel.

(C) TREATMENT OF NICKEL DIMETHYL GLYOXIME PRECIPITATE—When the amount of nickel is small (0.10 per cent or less), time must be allowed for complete precipitation—an hour is usually ample. With amounts larger than this, no danger of low results attends immediate filtration. For this purpose an asbestos mat on a 2-in. perforated porcelain plate or a Buchner funnel may be used. The solution containing the suspended precipitate will usually have a volume of 200 to 250 cc. It should be stirred thoroughly and poured on to the asbestos mat in such a way that the funnel always remains partly filled with liquid. Strong suction should be avoided. Quantities of precipitate corresponding to less than 5 per cent of nickel in a 1-g. sample rarely cause trouble in filtering, but the difficulty rapidly increases with larger amounts. When all of the precipitate has been transferred to the asbestos, it is thoroughly washed with water. Both wash water and filtrate are discarded, although the latter may be tested with dimethyl glyoxime if it is believed that all of the nickel may not have been precipitated.

(D) SOLUTION AND DECOMPOSITION OF THE PRECIPITATE—The receiving flask and tip of the funnel are next well rinsed with water. With the mat still in place, but with suction off, enough nitric acid is added to cover the asbestos to a depth of  $\frac{1}{8}$  in. After a minute, suction is applied, the acid drawn through the filter and about as much more added, taking care to cover the entire surface. At this point there should remain no visible trace of the red precipitate. The mat is now to be thoroughly washed with water, the washings being collected in the flask with the acid. The solution so obtained is then transferred to a 400 cc. beaker in which it is heated to boiling. Here the solution is allowed to cool slightly to facilitate the addition of 1 g. of either potassium chlorate or ammonium persulfate. The solution is boiled until clear; this usually involves a considerable reduction in bulk, often as much as 50 per cent. Insufficient boiling may cause trouble (1) through failure to decompose the dimethyl glyoxime, which would reprecipitate when the solution is subsequently made ammoniacal, or (2) because if the solution is not freed from oxidizing products

of the chlorate or persulfate decomposition the indicator which is used to determine the presence of an excess of ammonia may be destroyed.

A cheaper and somewhat simpler device for dissolving and decomposing the dimethyl precipitate consists in treating it with 50 cc. of a mixture made up of 40 cc. of hydrochloric acid and 10 cc. of nitric acid. This acid filtrate and the wash waters when evaporated to a bulk of 50 cc. will be found to be free from dimethyl glyoxime and ready for the next step, the neutralization with ammonia.

(E) THE NEUTRALIZATION OF THE ACID NICKEL SOLUTION WITH AMMONIA—The cooling of the acid solution may be hastened by adding ice. Neutralization need not be made with great care, but it is well not to have the excess of ammonia indefinitely large: 5 cc. of strong ammonia water in excess of that necessary to neutralize 300 cc. of solution causes no harm, but quantities larger than this interfere. Out of several indicators tried, rosolic acid showed more stability in this solution than any other. Strong ammonia is usually added rapidly in excess. Dilute nitric acid and dilute ammonia are then used to complete neutralization, leaving a slight excess of ammonia. The red color of the indicator seems to have a beneficial effect upon the subsequent titration of the nickel. The volume should be 250 cc.

(F) TITRATION OF THE AMMONIACAL NICKEL SOLUTION—Titration is made with potassium cyanide, using silver iodide as indicator. In this connection solutions containing 8.0 g. potassium iodide, 0.5 g. silver nitrate, and 4.6 g. potassium cyanide per liter are used. The strength of the potassium cyanide solution is so adjusted that 1 cc. of the solution is equal to 0.0010 g. of nickel. This is accomplished by comparison with a nickel solution of known nickel content, or with a standard steel.

To make the titration, exactly 10 cc. each of the potassium iodide and silver nitrate solutions are added (with stirring), followed by the potassium cyanide. The first additions of potassium cyanide increase the turbidity of the solution, and up to this point the addition of the cyanide may be rapid. From then on, it is added in rapid drops (with stirring) until the turbidity is about the same as before adding any cyanide. The last 15 to 20 drops are added slowly, the end-point being taken as the disappearance of the last trace of turbidity. The cyanide added of course titrates the silver iodide as well as the nickel, and the result therefore must be corrected by the subtraction of a blank. To determine the blank, add 10 cc. each of the potassium iodide and silver nitrate solutions to a nickel solution which has been titrated and which has the volume at which titrations are usually made, and titrate with KCN. By repeating this several times with the same solution an average blank will be obtained which may be regularly used where these conditions apply. In this laboratory the blank has been found as 1.00 cc. of potassium cyanide solution, and this blank is accordingly subtracted from all titrations before calculating the result. The formula for calculating percentage of nickel in the sample is

Number of cc. of KCN — blank = per cent of nickel.  
Number of grams in sample  $\times 10$

#### (G) SOME DETERMINATIONS OF NICKEL IN STEEL

Sample A is a sample of steel prepared as a private standard which has been analyzed in this laboratory by a number of methods and found to have 3.03 per cent nickel. This sample is analyzed by this method twice daily as a check on the determination. The last fifty determinations made average 3.03(06) with the highest value 3.08 and the lowest 3.01.

Samples 32 and 33 are samples prepared at the Bureau of Standards. Our analyses with the official figures are given below:

Bureau of Standards No.	Sample NAME	OFFICIAL VALUE	PER CENT NI FOUND Four determinations			
32	Chrome Nickel Steel	1.62% Ni	1.63	1.64	1.62	1.64
33	Nickel Steel	3.33% Ni	3.34	3.32	3.34	3.32

#### THE USE OF DIPHENYL GLYOXIME<sup>1</sup> AS AN INDICATOR

In outline, the method consists in adding a measured excess amount of standard potassium cyanide solution to an ammoniacal solution of the nickel salt. A quantity of the indicator is then added and the excess of potassium cyanide titrated with standard nickel sulfate solution. In the early work on the method, the more widely used dimethyl glyoxime was employed as an indicator. This was suggested by Lundell<sup>2</sup> in an article in which he uses this method in the analysis of cyanide solutions. Our experience with this reagent demonstrated that it was unsuited to use as an indicator in the determination of nickel because the results were found to vary with the concentration of the indicator in the solution and with the excess of cyanide used. Theoretically diphenyl glyoxime is open to the same objections as the above reagent except in one respect, *viz.*, that owing to the lower solubility of its nickel complex it is not necessary to use the indicator in as high concentrations as was found to be necessary with dimethyl glyoxime.

A solution of the diphenyl glyoxime was obtained by dissolving 1 g. in a solution of 5 g. NaOH in 100 cc. of water. This was diluted to 1000 cc. Wetting the diphenyl glyoxime with alcohol before treating it with the sodium hydroxide often helps in obtaining more rapid solution. A solution of nickel sulfate was prepared which contained about 0.001 g. of nickel per cc. This was a convenient strength, for in working with a 1 g. sample of steel 0.1 cc. corresponded to 0.01 per cent of nickel. It was standardized by titration against potassium cyanide solution of known strength, using silver iodide as indicator. The titration by the method described here was made by making the nickel solution alkaline with ammonia, adding a measured excess of potassium cyanide solution, followed by a quantity of the indicator, and titrating with standard nickel sulfate solution. All titrations were carried on in a volume of 250 cc., and with every change in the amount of indicator solution used a new blank was determined, using the same volume of water and 5 cc. of ammonia (sp. gr. 0.90).

FACTORS UNFAVORABLE TO THE METHOD—Early in

<sup>1</sup> This reagent was recommended as a quantitative precipitant for Ni by Atack, *J. Chem. Soc.*, **103**, 1317.

<sup>2</sup> *Trans. Am. Electrochem. Soc.*, **25** (1914), 369.



the work on this method it was noted that it is unfavorably affected by (1) the presence of salts of strong acids or bases in more than small amounts (2 to 4 per cent), (2) by strong bases, (3) by weak bases to a less extent, and, of course, (4) by acids. Salts such as the chlorides, nitrates and sulfates of sodium, potassium or ammonium, in quantities of more than 4 per cent in the solution to be titrated, caused precipitation of the indicator and prevented its reaction with the nickel salt when this was present in excess. Strong alkalies, such as sodium hydroxide, in amounts greater than traces, entirely prevented the reaction between the nickel salt and the indicator. Quantities of ammonia corresponding to a concentration greater than two parts of strong ammonia in 100 parts of solution, made the end-point unsatisfactory. The fact that the titration depended upon the formation of the double cyanide of course made the absence of free acid necessary.

**THE CONCENTRATION OF THE INDICATOR**—In the results showing the variation in values obtained upon the nickel sulfate solution itself with a constant concentration of ammonia and differing concentration of indicator and nickel, the cyanide solution was of such strength that each cc. was equivalent to 0.001 g. of nickel; the nickel sulfate solutions contained 0.00106 g. of nickel per cc.; all titrations were made at room temperature in a volume of 250 cc. The results clearly indicated that 1 cc. of the indicator was too little to use. As we increased the concentrations of the indicator a point was reached where the end-point tended to appear too soon by larger and larger amounts. Titrating in a volume of 250 cc. with nickel solution of the concentration used here, 5 cc. of the indicator solution appeared to us to be the best amount. It is probable, however, that in titrating in smaller volume or with more concentrated nickel solution, it would be desirable to use less indicator; and on the other hand a larger amount of indicator would probably prove convenient if the titration were carried on in larger volume, or if a more dilute nickel solution were employed. The conditions which determine the amount of indicator and the concentration of nickel solution are that the amount of indicator shall be such as to give a definite color indication, yet avoid such concentrations in either nickel solution or indicator as will cause the precipitation of the nickel diphenyl glyoxime complex as a consequence of the momentary appearance of a local excess of nickel during the titration.

**THE CONCENTRATION OF AMMONIA**—Below are given results showing the effect of moderately high concentrations of ammonia upon the titration. In these experiments the indicated quantities of ammonia (sp. gr. 0.90) were added to 10 cc. portions of a solution of nickel salt which had previously been made barely alkaline with ammonia. The volume at titration was 250 cc., containing 5 cc. of indicator, 11 cc. of KCN solution and 0.106 g. nickel.

Ammonia used.....	5 cc.	5 cc.	10 cc.	10 cc.	15 cc.	15 cc.
Nickel found (g.)....	0.0107	0.0108	0.0092	0.0104	0.0100	0.0089

It is evident from these results that there is a maxi-

mum above which the concentration of ammonia should not go. A large number of determinations not shown here lead the authors to believe that equally good results may be obtained from any concentration from the minimum necessary to maintain the alkalinity of the solution during the addition of the nickel solution, up to 5 cc. of ammonium hydroxide (sp. gr. 0.90) in 250 cc. of solution. This wide margin makes neutralization comparatively easy, for in working with dilute ammonia several cc. in excess may be added without harm and the sense of smell is a sufficiently good indicator.

**THE PREPARATION OF THE NICKEL SOLUTION FOR TITRATION**—The nickel in the samples is separated from the iron and other constituents of the steel as described above under Frevert's method, Sections A, B and C. The solution of the precipitate is different from that given under Section D, however, with the object of avoiding a high concentration of salts in the resulting solution. Concentrated hydrochloric acid containing 10 per cent nitric acid is poured over the precipitate to dissolve it. Solution proceeds less rapidly than when nitric acid is used, but if the suction is not strong, no difficulty will be encountered in dissolving the precipitate in about 50 cc. of acid. Care must be taken that every visible trace of the red precipitate has disappeared before proceeding to the next step which consists in washing the asbestos with about 100 cc. of water. The total filtrate, having a volume of 150 cc., is now evaporated to small bulk. The combination of nitric acid and hydrochloric acid serves to oxidize the dimethyl glyoxime which would otherwise precipitate as the nickel complex upon subsequent addition of ammonia. The evaporation is carried almost to dryness in order to keep the concentration of ammonium salt, which will be formed when ammonia is added, down to the lowest possible value. If some separation of salt has occurred, a drop of either nitric or hydrochloric acid may be added, along with water enough to take it up. The volume of the solution is raised to 150 to 200 cc. by the addition of water and about 5 cc. of dilute hydroxide solution (1 to 3) added. (If this amount of ammonia water is not enough to render the solution alkaline, evaporation has not been carried far enough and trouble may be met later through precipitation of the indicator.) The solution is now ready to titrate and accordingly standard potassium cyanide solution is added with stirring until the opalescence (or bluish tinge) disappears, after which a further quantity of about 15 cc. is added. The next addition is of 5 cc. of the indicator solution which is followed by titration with standard nickel solution.

**THE ANALYSIS OF SAMPLES OF STEEL**—In Table I are given results obtained in the analysis of steels with and without added nickel solution.

TABLE I—ANALYSIS OF STEELS

Sample	Gram Nickel Added	Per cent Ni Found Duplicates	Per cent Ni Theoretical
A.....	None	3.03	3.03
A.....	0.0053	3.58	3.57
A.....	0.0106	4.08	4.07
A.....	0.0212	5.18	5.18
B. of S. No. 32.....	None	1.63	1.64
B. of S. No. 33.....	None	3.30	3.31
			3.33

## SUMMARY

I—In the foregoing paper, Frevert's excellent method for the determination of nickel has been restated in amplified form and methods for avoiding all of the ordinary difficulties have been indicated.

II—A new indicator has been suggested for use in the titration which may find favor with some who prefer the appearance of a color as an end-point to the disappearance of an opalescence.

III—Both methods are more accurate than any volumetric method for determining nickel in steel which does not involve the separation of the iron, and more rapid and less laborious than those which do. By Frevert's method a single determination of the nickel in a sample of steel may be made in 25 min. even in the presence of chromium. A trained operator can make 50 or more determinations in a day of 8 hrs. The method employing diphenyl glyoxime as indicator requires 35 to 40 min.

IV—While the methods are perhaps slightly less accurate than the method which involves weighing the precipitate of Ni-dimethyl glyoxime, the greater speed which is possible in routine determinations more than compensates for so small a loss in accuracy.

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### THE DETERMINATION OF SMALL AMOUNTS OF ALCOHOL AND WATER IN ETHER FOR ANAESTHESIA

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A recent study of the methods for the detection of the common impurities in ethyl ether by one of the writers made it seem desirable, on the grounds of completeness, to have a method for determining quantitatively the amounts of alcohol and water in anaesthetic ether. No claims for originality are made for the method given in the following pages since it is a development of one already used. Pure ether dissolves only about 1 per cent of water. Anaesthetic ethers in this country never contain more than 3 or 4 per cent of alcohol. Obviously, therefore, we are dealing with small quantities and extreme accuracy cannot be claimed. The results obtained by applying the method to five well-known brands of anaesthetic ether are given.

Of the numerous methods proposed for the detection of water in ether, only the colorimetric procedure with rosaniline acetate,<sup>1</sup> the bluing of anhydrous copper sulfate when brought into contact with moist ether,<sup>2</sup> the evolution of gas by amalgamated aluminum,<sup>3</sup> and the determination of the density before and after dehydration by potassium carbonate,<sup>4</sup> appeared to be applicable to the quantitative estimation of water in fairly pure ethers.<sup>5</sup>

A set of standard ethers containing respectively 0.1, 0.25, 0.5, 0.75 and 1.0 per cent water by weight was prepared. Five milligrams of dried rosaniline acetate were placed in a dry test tube and 10 cc. of ether added. The colors varied but the differences were not sufficiently marked to allow placing some seven ethers containing varying amounts of alcohol and water in between known members of the series using the eye to judge the tints.

Anhydrous ether containing 0.1 per cent of absolute alcohol gives a wine-yellow color different from the above colors. It would require considerable study to perfect the method even if the tint produced by alcohol could be shown not to interfere.

Ten milligrams of copper sulfate finely powdered and well dried at 220° C. were shaken with 10 cc. of each of the above standard ethers. After 15 min. the copper sulfate showed no change from its original light gray color in ether containing 0.1 per cent water, but in ether containing 0.5 per cent water, the salt became bluish and the difference between the ethers containing 0.5 per cent, 0.75 per cent and 1 per cent could be detected. After about half an hour the sample containing 0.25 per cent could be placed in its proper position below the 0.5 per cent sample. The seven unknown ethers could be placed in this series more satisfactorily than in the previous method, but the procedure is at best only an approximation.

Contrary to the experience of Baskerville,<sup>1</sup> we had no success with amalgamated aluminum although considerable effort was spent upon this reagent because it is stated to have the advantage of being uninfluenced by alcohol. We have observed the evolution or disengagement of small bubbles even when the amalgam is placed in pure ether rendered anhydrous by metallic sodium and ether containing 0.1 per cent of water showed no evident increase in the amount of gas liberated. It is not easy, therefore, to distinguish what degree of bubbling indicates the presence of water. Bein,<sup>2</sup> working with a dilatometer filled with pure ether at 25°, experienced great difficulty due to the disengagement of small gas bubbles from the slightest jarring of the instrument. The amalgam offering many sharp points might be expected to have a greater effect.

In passing, mention may be made of the fact that the test for the detection of water in ether by shaking with carbon bisulfide is valueless, for, where alcohol is present, little or no turbidity is produced.<sup>3</sup>

We also tried subjecting ether to a temperature of about -70° C. produced by carbon-dioxide-snow and acetone, in order to freeze out the water as a hydrate of ether.<sup>4</sup> The presence of about 0.1 per cent of added water may be detected in alcohol-free anhydrous

<sup>1</sup> THIS JOURNAL, 3 (1911), 312.

<sup>2</sup> W. Bein, "Zur Ausdehnung des Äthyläthers und einiger mischungen des Äthers mit Äthylalkohol" Wissenschaftliche Abhandlungen der Kaiserlichen Normal Eichungs-Kommission Metronomischen Beiträge, Heft. VIII, p. 11.

<sup>3</sup> Squibb (*Squibb's Ephemeris*, 2 (1884), 594) states that absolute ether after the addition of 0.1 per cent of "watery alcohol" does not show the faintest cloudiness upon admixture of equal volumes of oil of copaiba or carbon disulfide.

<sup>4</sup> Berthelot, *Compt. rend.*, 86, 765; also Franchimont, *Ber.*, 10, 830.

<sup>1</sup> Squibb's *Ephemeris*, 2 (1884), 594.

<sup>2</sup> Adrian, *Mon. Sci.*, 44, ii, 835.

<sup>3</sup> Wislicenus and Kaufmann, *Ber.*, 28, 1325.

<sup>4</sup> Regnauld and Adrian, *J. Pharm. et Chem.*, [3] 45 (1864), 193.

<sup>5</sup> Prof. Frankforter's valuable test (*J. Am. Chem. Soc.*, 37, 2566) for the detection of water in ether was not published until after the experimental work in this paper had been completed. A few trials indicate that it is far more delicate than the known tests. It would be desirable to make the procedure quantitative if possible.



ether by the appearance of a slight cloudiness, but the presence of a few per cent of alcohol destroys the sensitiveness of the reaction.

Tyrer<sup>1</sup> found that the amount of water present in alcohol-free "wet" ether could be accurately determined by measuring the solubility of cadmium iodide in the ether since the solubility is greatly influenced by small additions of water. The method is not applicable, however, when alcohol is present because alcohol increases the solubility of cadmium iodide considerably and after preliminary trials we abandoned it altogether.

#### REGNAULD AND ADRIAN'S RESULTS

Obviously the density of ether is influenced both by the presence of alcohol and of water, and affords no insight into the proportion in which they exist in any given sample. This proportion is dependent upon laws of distillation. At 25° C. according to our experiments, the addition of 0.1 per cent of water to pure ether increases the specific gravity about 0.0004, or four times as much as the same amount of pure alcohol. Regnauld and Adrian<sup>2</sup> determined the water from the change in density produced after absorbing the water by means of a dehydrating agent. The density of the resulting mixture which then consisted only of ether and alcohol indicated the quantity of alcohol present. They found that while potassium carbonate, which proved to be the best dehydrating agent for the purpose, removed the water completely from ether in the absence of alcohol, it was unable in the presence of alcohol to dehydrate the alcohol beyond 98 per cent by volume. This conclusion rested upon the fact that the densities of mixtures containing respectively 5 cc. of alcohol (98 per cent by volume) + 95 cc. of pure ether and 35 cc. of (98 per cent by volume) alcohol + 65 cc. of pure ether showed no change after treatment with anhydrous potassium carbonate. Since their densities were expressed only to the third place, having been taken by means of a hydrometer, it seemed desirable to test the point more accurately, especially since it can be shown that the effect of 2 per cent of water in the 5 cc. of alcohol of the first mixture is of sufficient magnitude to increase the density only about three in the fourth place.

Having convinced ourselves by some preliminary trials that potassium carbonate is insoluble in ether containing 4 per cent of absolute alcohol and that it removes water, if present, more completely than Regnauld and Adrian believed, we proceeded to test this point quantitatively. To 100 cc. of pure ether containing 2 per cent absolute alcohol, 0.5 per cent of water was added and shaken. This mixture, before the addition of the water, as will be seen from the density curve, had a specific gravity of 0.71205, ether and water both at 25° C. Forty-five grams of potassium carbonate dried for 5 hrs. at 240 to 280° were added and the mixture allowed to stand for 20 hrs. with occasional shaking, after which the specific gravity was found to be 0.71201. The experiment was repeated with ether, containing 4 per cent absolute alcohol,

which had a specific gravity of 0.71424.<sup>1</sup> One-half per cent of water was added and the mixture dried by potassium carbonate after which the specific gravity was 0.71425. It is evident that water is removed quantitatively from ether containing as much alcohol as is likely to occur in anaesthetic ethers, but Regnauld and Adrian's contention that potassium carbonate does not act quantitatively when 35 per cent of alcohol is present is true as the following experiments show.

The specific gravity of a mixture of 300 cc. of pure ether and 162 cc. of absolute alcohol (99.8 per cent) was found to be 0.7435, pycnometer full of water and ether weighed in air<sup>2</sup> at 25°. No change in the density was produced by treatment with potassium carbonate. To reduce the strength of the alcohol to about 98 per cent 2.743 g. of water were added. Carbonate of potassium in the usual proportion of 45 g. per 100 cc. of mixture was added and the mixture allowed to stand with occasional shaking for 44 hrs. The pycnometer now showed a specific gravity of 0.7447 and further treatment with potassium carbonate did not lower it. These results, however, do not agree with the statement of the above authors that potassium carbonate is unable to dehydrate the alcohol in such a mixture beyond 98 per cent by volume since the specific gravity is within 0.0012 of the original figure before the addition of water. Since 0.1 per cent of water raises the gravity in anaesthetic ether 0.0004, 100 g. of the mixture should still contain about 0.3 g. water; in other words, approximately two-thirds of the water has been removed.

#### THE DETERMINATION OF WATER

We determined the water directly by weighing the potassium carbonate although the method of Regnauld and Adrian appears to be fully as satisfactory. The procedure for determining the water is best illustrated by the following experiment:

To 94 g. of pure ether, dried over sodium, 0.7588 g. of distilled water was added by sealing the water in a glass bulb and breaking under the surface of the ether. Solution therefore contained 0.80 per cent water. Potassium carbonate was dried for 5 hrs. at 250° C. and cooled in a desiccator. About 24 g. of this were put into a glass-stoppered Erlenmeyer flask and then weighed. Seventy grams of the ether-water mixture were introduced and the flask violently shaken on a shaking machine for 8 hrs. It was then removed and allowed to stand for 28 hrs. A calcium chloride tube bent downward having been fitted by means of a cork to avoid the entrance of moisture from without, the flask was partially submerged in water at 50° C. and the ether distilled off through the calcium chloride tube. Without removing the calcium chloride tube, the apparatus was then put

<sup>1</sup> The density of this mixture does not coincide with the other points on the curve. An error was evidently made in the amount of alcohol added in making up the mixture rather than in the density determination since the density after treatment with potassium carbonate agrees with that before treatment. Such an error, however, does not invalidate the experiment since the point here involved is the removal of water.

<sup>2</sup> These determinations were not reduced to the vacuum basis, all others were so reduced.

<sup>1</sup> Chem. Soc. Proc., 27 (1911), 142-143.

<sup>2</sup> Loc. cit.

in an electric oven at 60° C. and dried for about 12 hrs. The calcium chloride tube was removed and a gentle stream of air was drawn through the flask for 30 sec. in order to sweep out the ether vapor. The flask was now stoppered and weighed after cooling in a desiccator.

The calcium chloride tube was replaced and the apparatus again heated for 3 hrs. at 60° C. Air was drawn through as before. The weight was constant to within 1 mg. The increase, due to the absorption of the water, was 0.5717 g., corresponding to 0.82 per cent found as against 0.80 per cent added.

An attempt was made to apply the same method to a similar mixture but containing in addition 3 per cent of alcohol, but no constant weight could be obtained on drying the potassium carbonate, due to the retention of some alcohol. When the temperature of the oven was raised sufficiently to drive out the alcohol, some water was lost. This difficulty was overcome by washing the alcohol from the potassium carbonate with pure anhydrous ether as the following experiment shows: To 243 g. of pure ether, dried over sodium, 2.536 g. of distilled water and 13 cc. of absolute alcohol were added corresponding to 0.99 per cent and 4 per cent, respectively.

About 20 g. of freshly dried potassium carbonate were introduced into a small flask having a long, narrow neck and a ground glass stopper. A glass wool plug was fitted into the neck and the apparatus weighed. Fifty grams of the above mixture were then run in and the flask shaken for 5 hrs. and allowed to stand over night. The ether was filtered out through the glass wool plug but did not come clear, so it was evaporated and the weight of the suspended potassium carbonate added to the calculation. The potassium carbonate was washed successively with three portions of 10 cc. each of absolute ether, introduced and expelled by alternately cooling and warming the flask. The flask was then dried at 60° C. to constant weight, air being drawn through for 30 sec. to remove ether vapor as in the previous experiments. In duplicate determinations the water found was 0.5263 g. and 0.4887 g., corresponding to 1.05 per cent and 0.98 per cent, respectively.

#### DETERMINATION OF THE DENSITIES OF ETHER-ALCOHOL MIXTURES

Having shown that the water may be determined directly by weighing the potassium carbonate, it remained to construct a curve for alcohol-ether mixtures from which, having given the specific gravity of any mixture after dehydration, the percentage of alcohol may be read off. Mixtures containing by weight 1, 2, 3 and 4 per cent were made by breaking glass bulbs containing the absolute alcohol of 99.9 per cent<sup>1</sup> under pure ether. The latter was prepared by shaking 10 liters of anaesthetic ether five times with 1/2 its volume of distilled water. The ether was then shaken with 3000 cc. of 0.5 per cent NaOH solution

in which was dissolved 2 g. of permanganate of potassium.<sup>1</sup> This was done three times, letting the permanganate stand in contact with the ether until reduced to a brown color. After separating, the ether was dried twice over  $\text{CaCl}_2$  and then over sodium-potassium alloy until no reaction was observable on the alloy. It was now distilled from the alloy through a three-section Young column, discarding the first and last 10 per cent. Before using, the pure ether was tested for peroxide with cadmium potassium iodide and for aldehyde with ammoniacal silver nitrate solution. The ether, just after preparation, was without effect upon both reagents but later it was found to contain a trace of ethyl peroxide, not more than 0.002 per cent as estimated by producing the same tint with aqueous hydrogen peroxide. Such traces are without sensible influence on the specific gravity.

The determinations of the specific gravity were made with a 50 cc. "Squibb" pycnometer having a capillary neck integral with the body. The upper end of the neck terminated in the usual enlargement provided with a ground glass stopper. The body of the pycnometer was cylindrical and about 1 in. in diameter.

Owing to the high coefficient of expansion of ether, we thought it desirable to define the temperature at which we worked quite accurately. Obviously the curve of gravities for different percentages of alcohol in ether would be of most general use if the temperatures were defined by the international hydrogen scale. For some, however, it may be easier to construct their own density curve than to reproduce in their thermostat the temperature of 25° C. on the hydrogen scale.

Since the density determinations were made in summer, it was necessary to provide a room having a constant temperature in which to place the thermostat and balance for weighing. An insulated room which was designed for cold storage purposes was provided with an iron tank filled with ice and two large electric heater lamps controlled by a four-bulb glass thermostat filled with ether electrically controlling the heating current by means of a telegraph relay. The air was circulated by an electric desk fan on a shelf in one corner and directed against the wall near the corner diagonally opposite and also toward the ceiling. The two heating lamps were placed under the fan and slightly forward so that the ascending warm air was at once distributed by the fan. The temperature of the room could be held at 25° easily within 0.5°.

An enamelled iron pot 15 in. in diameter and 12 in. deep served as the constant temperature bath or thermostat proper. It was surrounded by another vessel of galvanized iron 3 in. larger in diameter and 1 1/2 in. deeper, thus leaving a space all around of 1 1/2 in. which was packed with ground asbestos-magnesia steam pipe covering. Molten tar was poured on top of this covering to prevent the absorption of moisture. Circulation was maintained in the water by a propeller wheel revolving at high speed, driven by an electric

<sup>1</sup> Assuming that in the operation the alcohol had absorbed moisture sufficient to lower its percentage to 99.8, the effect on the percentage of alcohol in the mixture is negligible, being less than 0.5 per cent of the absolute amount of alcohol present.

<sup>2</sup> Wade and Finemore, *J. Chem. Soc. (London)*, **95**, 1846. For extreme purity further washing with water would be advisable. The ether prepared as above, however, compares favorably as to density with pure ether prepared by other experimenters. See W. Rein, *Loc. cit.*, p. 20.



TABLE I—FULL DATA FOR CURVE OF SPECIFIC GRAVITIES OF ALCOHOL ETHER MIXTURES

Per cent ether Per cent alcohol	June 1914 Temperature when weighed (Hydrogen Scale): 24.99°						December 1915 25°(a)		April 1916 24.93°	
	(Water)(b)	100 0	99 1	98 2	97 3	96 4	0.100 1	97 3	100 0	96 4(e)
Weight of full pycnometer		78.6572	64.1966	64.2492	64.3028	64.3505	64.4412	64.1928	64.3487	64.3994
		78.6571	64.1954	64.2484	64.3035	64.3515	64.4115		64.3488	64.4006
Average		78.6572	64.1960	64.2488	64.3019	64.3510	64.4113		64.3488	64.4009
Correct on for weights		+0.0007	+0.0007	+0.0007	+0.0007	+0.0007	+0.0007	+0.0008	+0.0007	+0.0007
Correction for evaporation loss			0.0005	0.0005	0.0013	0.0009	0.0009	0.0001	0.0003	0.0002
Weight empty pycnometer(c)		78.6579	64.1972	64.2500	64.3039	64.3526	64.4129	64.1937	64.3498	64.4018
		28.8665	28.8665	28.8665	28.8665	28.8665	28.8665	28.8665	28.8665	28.8665
Correction for reducing to vacuum		49.7914	35.3307	35.3835	35.4374	35.4861	35.5464	35.3272	35.4833	35.5353
		0.0530	0.0550	0.0550	0.0550	0.0550	0.0550	0.0550	0.0550	0.0550
Wt. in vac. pycnometer contents		49.8444	35.3857	35.4385	35.4924	35.5411	35.6014	35.3822	35.5383	35.5903
Volume of pycnometer = 49.9904 cc.(d)										
Sp. gr. 25°/25°										
Wt. ether + 1.040533 + 0.9970795 =										
49.8444 + 1.040550 + 0.9970770 =		0.70991	0.71097	0.71205	0.71303	0.71424	0.70985	0.71299	0.70984	0.71396

(a) These determinations were made a year and a half later in another thermostat. The thermometer, which was graduated in tenths of a degree and read by a telescope, had been compared with the standard thermometer a month previous, and this correction used to bring the thermostat to exactly 25°.

(b) Freshly boiled distilled water.

(c) After the determinations of April, 1916, the pycnometer was found to weigh within 0.2 mg. of the original weight which has therefore been used throughout for the sake of uniformity. The volume of the pycnometer was not redetermined.

(d) The volume as determined a year previous by three weighings at 25.04° hydrogen scale was 49.9914 cc. Densities of water taken from Circular 19, Bureau of Standards, Table I.

(e) The three figures recorded in this column represent successive weighings of the full pycnometer after complete emptying and refilling with fresh portions of the mixture.

motor, and forcing a current downward against the bottom of the bath, thus spreading it in all directions. The cooling due to surface evaporation was found sufficient. The heating coil was made of nichrome wire wound on mica and covered with a jacket of copper foil. The heating coil was controlled by a two-bulb regulator, filled with ether and having a side tube connected by a glass stopcock so that the approximate adjustment of the mercury level could be made by this means. The stopcock was in the portion filled with mercury and no difficulty was encountered on account of leakage. The final adjustment was made by a platinum wire contact controlled by a finely threaded screw. The surface of the mercury making the electrical contact was protected by a layer of glycerin. By means of the resistance of various sizes of incandescent lamps in the circuit, the temperature of the heating element was adjusted so that the heat was just insufficient to maintain the desired temperature in the bath. The regulator controlled, by means of a relay, an additional heating current sufficient to warm the bath slowly, slightly above the desired temperature. In this way the temperature fluctuation was small and the lag due to heat transference was reduced to a minimum.

The thermometer used was a Baudin Standard No. 17730, graduated in 0.1°, and calibrated by the International Bureau of Weights and Measures at Sevres. It was carefully adjusted to vertical position by means of a small plumb bob, and was read by a leveled cathetometer. The thermometer could be easily read to 0.002° and the variation of the bath during any determination never exceeded 0.005°. The coefficient of expansion of ether is such<sup>2</sup> that a change of 0.01° C. in the temperature changes the density a little more than 0.00001. Since it may be questioned whether the fifth decimal figure is entirely significant in the

determination of the density of such a volatile liquid as ether, it is evident that the temperature of the bath was defined with sufficient accuracy. The mercury column projected out of the water 12°. A thermometer placed close to the standard thermometer was observed not to vary more than 0.5° during the actual determination, which gives a stem correction of 0.001°C.

The details of the temperature calculation are as follows:

Thermometer reads in bath..	25.150°	.....in ice(a)	+ 0.100°
Correction for calibration.....	+0.020		—0.001
Correction, external pressure (b) (barom. = 751 mm.			
+ 159 mm. H <sub>2</sub> O).....	—0.0003	(barom. + 64 mm. H <sub>2</sub> O)	+0.0004
Correction, internal pressure..	+0.029		+0.008
Correction, zero point.....	—0.107		+0.107
	25.092		
Correction, fundamental interval.....	—0.006		
True temp. on mercury scale.	25.086		
Converting to hydrogen scale	—0.095		
Final temperature of the bath on hydrogen scale.....	24.991°		
Uncertainty for exposed stem	±0.001		

(a) The ice point was made after completing the series of weighings at the end of the second day.

(b) The barometer on the second day read 753 mm. but since a difference of 10 mm. affects the temperature reading only 0.001°, the temperature of the bath in the second decimal would not be affected. All corrections were applied as indicated in the pamphlet and tables accompanying thermometers standardized by the International Bureau.

The corrected temperature of the bath while the adjustment of the pycnometer was being made was therefore 24.99° on the international hydrogen scale for the first six columns of Table I. The check determinations in the seventh and eighth columns were made a year and a half later in another thermostat provided with a thermometer which had been compared a month previous with the Baudin standard thermometer. The thermostat was then adjusted to exactly 25°, using this correction. The thermometer could be read to 0.01 by a small telescope and the tem-

<sup>1</sup> For this degree of accuracy it was thought sufficient to read the mercury column from the front instead of taking the average of both front and back readings in order to eliminate irregularities in the thermometer stem.

<sup>2</sup> Bein, *Loc. cit.*

perature may be assumed to be defined to this degree of accuracy. For the check determination in the last two columns, the same thermostat was used without, however, adjusting to exactly  $25^{\circ}$  since the standard thermometer was employed, hence the temperatures 24.93 and 24.94 are entitled to the same confidence as 24.99 in the original series; the corrections, being similar to the above, are omitted.

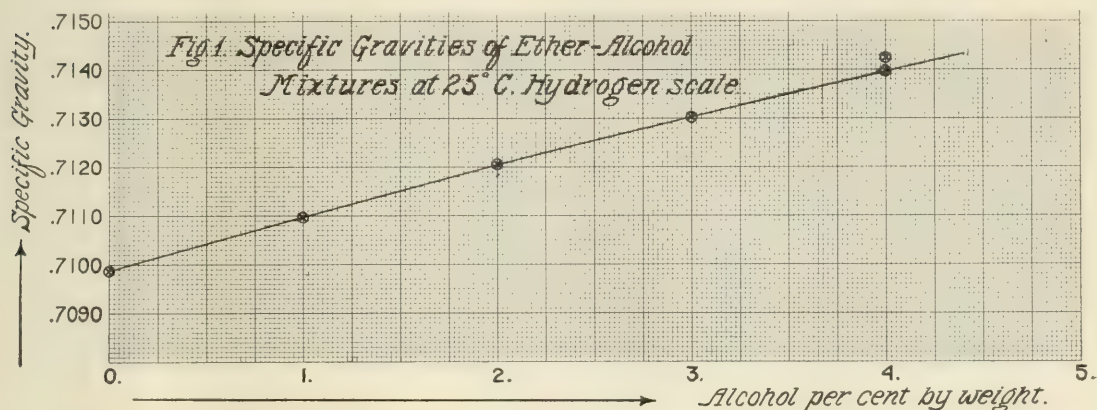
The pycnometer was filled with the ether mixture and suspended in the thermostat for 45 min.<sup>1</sup> The temperature was observed three times during this interval and if there was any variation the determination was started over. The adjustment of the pycnometer was made while it was in the bath. It was then removed, dried and weighed, taking care that the final adjustment of the rider was made exactly 10 min. after removing from the bath. After standing an additional 10 min. in the balance case, the pycnom-

eter was again weighed. The difference between the first and second weighings represents loss by evaporation in 10 min. and was added to the first weighing. The balance, being in a constant temperature room, was never more than  $0.5^{\circ}$  different for the bath. In order to ascertain if the moisture adhering to the pycnometer was different at the end of 10 min. and 20 min., respectively, two series of weighings were made on the empty pycnometer, after wetting and drying at 10, 20, and 30 min.; all weighings checked to 0.0001 g.

Table I gives the full data. As will be seen, at least two weighings were made on each mixture, in some cases three. When the amount of the sample permitted, the pycnometer was emptied, and re-filled, otherwise it was simply replaced in the bath and readjusted to the mark. Since the weighings were made at temperatures slightly below  $25^{\circ}$ , it was necessary to correct for the slightly lower densities which ether and water would have had if weighed at exactly  $25^{\circ}$ , the expansion of the pycnometer itself being negligible. The expression given makes use of the co-

efficient of expansion of ether<sup>1</sup> to calculate the volumes 1.040533 cc. and 1.040550 cc. which 1 cc. of ether at  $0^{\circ}$  would have at  $24.99^{\circ}$  and  $25^{\circ}$ , respectively, the remainder of the expression giving the densities of water at these temperatures. It applies to the first six columns. For the remaining columns the calculation is similar: these columns show determinations made at a later date to check the density of the 3 and 4 per cent mixtures since the density as first found for the 4 per cent mixture did not lie on the curve.

The original of the plot (Fig. 1) was made sufficiently large to show variations of one in the fifth place, and it was seen that the densities fell evenly upon the curve with the exception of the first determination on the 4 per cent mixture which we believe must have received more than 4 per cent of alcohol through some error in preparation. The curve is very nearly a straight line. Since a variation of 0.0001 in density,



or one of the small divisions on the coordinate paper, corresponds to 0.1 per cent of alcohol in the mixture, it is evident that the curve is of ample accuracy for the purpose of the analysis.

#### DIRECTIONS FOR THE COMPLETE ANALYSIS

The flask used (Fig. 2) was a 100 cc. Regnault pycnometer for taking the density of solids. It is best to have two and make the analysis in duplicate.

Fifteen grams of potassium carbonate dried at  $200^{\circ}$  to  $250^{\circ}$  are placed in the bulb A and accurately weighed after replacing the stem B. Remove the stem and introduce quickly 50 cc. of the ether for analysis. Replace stem and allow the flask to stand 14 hrs. with frequent shaking. By removing the stopper and holding the inverted flask in the warm hand, the ether can be filtered out through the cotton plug X. Care must be used to insure a clear filtrate, otherwise there will be a loss of potassium carbonate. Examine the filtrate after standing to see that no finely divided carbonate has separated out. Fill the upper enlargement B with absolute ether and cause it to be drawn in by pouring some of the ether over the bulb. Shake well

<sup>1</sup> A pycnometer which had a thermometer attached for taking the temperature of the liquid within, but similar in other respects when filled with ether at  $15^{\circ}$  C. and immersed in the thermostat, was found to have acquired the bath temperature in 15 min.

<sup>2</sup> The coefficient of expansion of pure ether has been used in the case of the mixtures containing alcohol since owing to the close proximity of the temperatures to  $25^{\circ}$  the error so introduced is negligible. See Ben. *Loc. cit.*, p. 15.



and expel the ether as before. Wash four times in this manner, which removes the alcohol from the salt. Now dry the flask, with cap *C* removed, at 50° until the carbonate can be shaken down into the flask. Remove the stem and replace it with a drying tube filled with carbonate of potassium to prevent access of external moisture and dry for 1 hr. at 50°. Remove the drying tube and after sweeping out the remaining ether vapor with gentle suction for 15 sec., replace the stem and cool in a desiccator and weigh. Since it does not require much ether vapor to affect the weight, care is required to secure its complete removal without introducing moisture from an excess of air. A second weighing should be made after drying again for half an hour. The weights should be constant within about 4 mg. The difference between the weights of the potassium carbonate before and after treatment with ether is the weight of water in the sample taken.

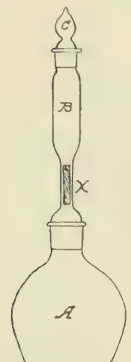


Fig. 2

For the alcohol analysis, treat 100 g. of the sample with 40 g. of freshly dried potassium carbonate for 14 hrs. in a glass-stoppered flask, shaking frequently. The pycnometer is filled with the clear ether and the specific gravity is determined at exactly 25° on the hydrogen scale. The per cent of alcohol may then be read off from the curve. Obviously if this curve is to be used, the gravity must be made in a bath at exactly 25° on the international hydrogen scale or else a new curve made by the operator at the temperature of his thermostat, which is a simple matter.

Owing to the fact that ether deteriorates with age, unless protected carefully from the effects of air and light, only fresh samples should be used for analysis. As the accuracy of this method depends to a considerable extent on the manipulation, strict adherence to the procedure, as given, cannot be too strongly recommended.

TABLE II—ANALYSES OF KNOWN MIXTURES (1 TO 13, AND 18) AND MARKET ANAESTHESIA ETHERS (14 TO 17, AND 19) BY DIFFERENT ANALYSTS

DETERMINATIONS	Analyst	No	PER CENT ALCOHOL		PER CENT WATER	
			Added	Found	Added	Found
Made in same Thermostat as used for the Density Curve	Mr. A.	1	0.82	0.85	0.22	0.258 0.234
		2	3.17	3.28	0.75	0.756 0.751
		3	2.85	2.90	0.27	0.269 0.277
		4	3.32	3.38	1.10	1.07 1.08
	Mr. C.	5	3.40	3.67	0.75	0.834
		6	3.63	3.57	0.60	0.545
		7	2.51	2.47	0.30	0.327
		8	2.01	2.00	0.21	0.229
Made in Ordinary Laboratory Thermostat	Mr. P.	9	2.94	2.93	0.46	0.39
		10	3.11	3.00	0.63	Lost
		11	2.86	2.70	0.41	0.39
		12	3.85	3.83	0.79	Lost
	Mr. A.	13	4.02	3.93	0.53	0.53
		14	..	1.42	..	1.08 1.08
		15	..	0.85	..	1.21 1.22
		16	..	0.12	..	0.12 0.11
		17	..	4.25	..	0.36 0.36
		18	1.70	1.62	1.10	1.12 1.19
		19	..	0.32	..	0.26 0.25

Table II gives the results obtained by three different experimenters in our laboratory on known mixtures and five well-known market brands of anaesthetic ethers. The compositions of these mixtures were unknown to the experimenters. Mr. C. and Mr. P. had never used the method before and worked en-

tirely from the directions as given above. Nevertheless, the agreement between the amounts found and actually added demonstrates that the method is reliable and sufficiently accurate for the analysis of anaesthetic ether.

## CONCLUSION

In his classic articles on ether, Squibb<sup>1</sup> estimated that the 4 per cent of aqueous alcohol remaining in his ether contained about 90.75 per cent of pure alcohol. It is interesting to note from the table that the water and alcohol exist in proportions which are more nearly equal than Squibb believed. This is in accordance with the experiments of Wade and Finnemore<sup>2</sup> who have shown that ether and water form a constant boiling mixture containing 1.3 per cent of water which boils 0.35° lower than pure ether. They also showed that alcohol and ether form no such mixtures, neither is this the case if all three components occur together. Consequently, the mixture rich in water is the one which distills most readily. The amount of alcohol which persistently accompanies the constant boiling mixture depends largely upon the efficiency of the fractionation process employed.

It is questionable whether ether can be made by the usual process of distillation which will comply strictly with the requirements of the present Pharmacopoeia that it shall consist of 96 per cent ethyl oxide and 4 per cent of alcohol containing a little water. Ether of such composition might be prepared by a special distillation process if it could be shown to possess any superior qualities which, in our opinion, is extremely improbable. Specimen No. 14 had the proper specific gravity but contained 1.4 per cent alcohol and 1 per cent water. Specimen No. 17 probably had had alcohol added to it.

MALLINCKRODT CHEMICAL WORKS, ST. LOUIS

## THE ANALYSIS AND COMPOSITION OF SOME CIGARETTE PAPERS

By STROUD JORDAN

Received February 4, 1916

Recent reports on cigarette papers<sup>3</sup> contain some very valuable information as to the process of manufacture, ash values and alkaloidal tests. Only a very general description is given and some of the necessary details are omitted in the foregoing papers, so that it has been thought expedient to publish some analytical results on two of the more common papers used by the manufacturers of cigarettes.

The samples reported in this article were taken from reels actually running on cigarette machines and Numbers 1, 2 and 3 represent Austrian papers of the type known as "Sunshine," made by Stefan Robitsek of Vienna. These papers come in lengths of 3900 meters to the reel, have an average width of 31 mm. and weigh from 19.4 to 22.1 g. to the square meter, corresponding to a thickness of 0.0014 to 0.0016 in. Numbers 4 and 5 were both of the French type, known

<sup>1</sup> Loc. cit., p. 596.<sup>2</sup> Ibid., p. 1850.<sup>3</sup> Paper, No. 24, 15 (1915), 19-31; Woch. Papierfabr., 45, 2296-2302, Zentr. oesterr.-ungar. Papierind., 32 (1914), 623-4; and in Bull. 2, Agr. Comm. of Ohio, Dairy and Food Div., Bureau of Drugs.

as "Vierge Egyptien" (combustible), and measure about 1560 meters to the reel. The average width of these papers is 30 mm., having an average weight of 18.75 g. to the square meter and a corresponding thickness of about 0.0014 in.

#### METHODS OF ANALYSIS

MOISTURE determinations should be made according to Bureau of Chemistry, *Bull.* 107, 14.

ASH—The sample used for moisture determination was incinerated over a Tirrill or Bunsen lamp, using a very low flame, then the ash removed to a blast flame and incinerated until no further loss in weight was observed. [This ash should show only a slight effervescence or none at all, when it is suspended in water and treated with a few drops of concentrated hydrochloric acid (absence of carbonates).]

FIBER (PULP)—10.000 g. of finely cut paper were weighed into a liter Erlenmeyer flask and 500 cc. of distilled water and 10.0 cc. of hydrochloric acid (sp. gr. 1.20) were added. The mass was boiled over a free flame for 1 hr. or until the whole was well pulped, then filtered on a Buchner funnel, using a tared, acid-washed filter, and washed with water until a drop of the filtrate showed only a slight opalescence when tested in the usual manner for chlorides. The filtrate was preserved for determination of the constituents of the ash. The pulp was washed three times with 95 per cent alcohol, packed well with a glass rod, removed to a drying oven and dried to constant weight at 105° C.

The pulp was then reduced to ash and the ash found subtracted from the weight of the pulp, along with the weight of the filter paper used, from which any ash value it might have had has been subtracted. This gives the weight of pulp by difference.

MINERAL FILLER is calculated by difference, by subtracting the combined weights of moisture, fiber and size from 100 per cent.

As a check on the determination of mineral filler, the constituents of the ash were calculated to the compounds occurring in the paper and this total weight compared with the filler as found by difference.

SIZING, COATING, KINDS OF FIBER, ETC.—These constituents were determined according to the methods laid down in Allen's "Commercial Organic Analysis," I, 473-479 (4th Ed.).

#### ANALYTICAL RESULTS (PERCENTAGES)

SAMPLE:	1	2	3	4	5
Moisture.....	4.05	4.14	3.99	4.30	4.62
Ash (as oxides).....	12.25	12.07	12.95	4.95	5.12
Fiber (pulp).....	71.07	71.35	72.57	87.08	85.74
Filler.....	24.88	24.10	23.19	8.62	9.64
Size (less than).....	1.00	1.00	1.00	0.10	0.10

CONSTITUENTS OF THE ASH—The compounds which occurred in the ash were calculated in the usual manner by the official methods as laid down in Bureau of Chemistry, *Bull.* 107, e. g., CaO (p. 15), MgO (p. 16) and (Fe + Al)<sub>2</sub>O<sub>3</sub> (p. 15).

As a check on the above ash determination, the filtrate from the fiber determination was evaporated to dryness and the acid expelled. This residue was taken up in a convenient volume of water and the compounds present determined as above.

#### COMPOSITION OF THE ASH (PERCENTAGES)

SAMPLE:	1	2	3	4	5
Calcium oxide.....	12.06	11.74	11.01	4.39	4.30
Magnesium oxide.....	0.17	0.26	1.29	0.20	0.24
Aluminum oxide.....	Trace	Trace	0.24	0.30	0.11
Iron oxide.....	Trace	Trace	Trace	Trace	Trace
Silica.....	Trace	Trace	Trace	Trace	Trace
H <sub>2</sub> S precipitate.....	None	None	None	None	None
Sulfates.....	None	None	None	None	None
Nitrates.....	None	None	None	None	None
Chlorides.....	Trace	Trace	Trace	Trace	Trace

As a check on the above results, Samples 1 and 2 were compared with the compounds found in the filtrate from the pulp determination. The following gives a comparison:

SAMPLE:	1(a)	1(b)	2(a)	2(b)
Calcium oxide.....	12.06	11.76	11.74	11.69
Calcium carbonate.....	21.52	21.00	20.95	20.87
Magnesium oxide.....	0.17	0.15	0.26	0.33
Magnesium carbonate(c).....	0.36	0.31	0.54	0.67

(a) Result from ash. (b) Result from filtrate from pulp. The other traces showed up the same in both samples. (c) 3MgCO<sub>3</sub>.Mg(OH)<sub>2</sub>.4H<sub>2</sub>O.

FIBER AND SIZING—All fibers were found to be linen. Sizing in the first three were found to be dextrine and the last two carried traces of starch but no dextrine.

#### COMPOSITION OF THE PAPER

The composition of the papers appears to be: linen fiber slightly sized with starch or dextrine and filled with the carbonates of magnesium and calcium. The filler in the first three averaged 24.05 per cent, while the last two showed an average of 9.13 per cent.

The fillers were calculated to the carbonates, while it is possible that a portion of the magnesium was added as the peroxide or oxide for accelerating the burning of the paper. This change would not affect the resulting weights appreciably.

#### SUMMARY

Nothing injurious was found in the ash, filler or pulp. The paper burns to a clean white ash which shows good combustion and the absence of compounds formed by destructive distillation. The filler is not materially changed when the paper is burned, so has no effect except to promote combustion and to make the papers "tight." No tests were found for alkaloids or alkaloidal salts. No poisonous metals were found (absence of hydrogen sulfide precipitate). No bad effect was had from the small amount of sizing, as is evidenced by the good burning qualities and the absence of compounds formed by destructive distillation.

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#### TIN IN CANNED FOODS

By W. D. BIGELOW

Received July 17, 1916

It has long been known that the acids of canned fruits dissolve more or less tin from the container, the amount depending partly on the age of the product and the temperature of storage. It is also well known that some foods having but a slightly acid reaction, such as pumpkin, string beans, and shrimp, attack tin to a considerable extent. This has been shown<sup>1</sup> to be due in some cases at least to the presence of amino bodies in the food. The tin in canned foods has usually been assumed to be in solution. Articles on this subject and reports of analytical work frequently refer

<sup>1</sup> Bigelow and Bacon, Bureau of Chemistry, *Circ.* 79.



to the tin contained in the food as "soluble tin salts." It was pointed out by the writer<sup>1</sup> some time ago that the tin in canned food was largely, sometimes chiefly, in some insoluble form.

It is a common experience in the laboratory that compounds of tin separate out from reagent solutions of tin chloride. This is ordinarily prevented by the use of strong hydrochloric acid. The same separation occurs with solutions of compounds of tin with organic acids. It appears, therefore, that the acid acts as a carrier dissolving the tin from the coating of the container and carrying it into the food where the tin separates in an insoluble form, leaving the acid free.

With nonacid or slightly acid foods of the types mentioned above, this deposition of tin in insoluble form probably occurs to a greater extent than with the acid fruits. In both cases it appears that a considerable proportion of the soluble tin salts is carried within the solid particles of food before being hydrolyzed.

It is conceivable that the higher tin content of the drained solids than of the liquor might be due to metathesis, the tin replacing calcium or magnesium, for instance, in its insoluble compounds within the solid particles of food. The property of solutions of tin salts, however, to deposit insoluble tin compounds, and especially the property of stannous solutions to yield insoluble basic stannic compounds, appears to afford a more probable explanation of the presence of insoluble in place of soluble tin compounds in canned foods. In either case the drained solids of canned foods contain a materially higher amount of tin than the liquor, and this difference increases with the age of the sample. Thus the high tin content of old canned foods is largely due to insoluble compounds of tin which are presumably less likely than soluble compounds to be absorbed from the intestinal tract.

The figures given in Table I were obtained by determining the amount of tin in drained solids and liquor, respectively, and calculating the amount of tin in the original sample from the figures thus obtained and from the weight of drained solids and liquor, respectively.

TABLE I

VARIETY OF FOOD	MILLIGRAMS TIN PER KILOGRAM IN		
	Liquor	Total sample	Drained solids
Cranberries.....	33	170	254
Raspberries.....	39	194	294
Cherries.....	52	107	163
Peaches.....	86	193	251
Pears.....	99	130	151
Plums.....	43	125	180
Shrimps.....	67	224	381
Spinach.....	35	86	131

The relation of the tin content of the drained solids to that of the liquor of certain canned foods is brought out more definitely in Table II. The samples shown in this table were taken from an experimental pack in which the various cans were as uniform as they could be made. At intervals after the food was packed, sample cans were examined to determine the tin content of the food. At least two cans were taken for each sample. The drained solids and liquor were weighed separately, the tin determined in each and

expressed in terms of milligrams per kilogram of drained solids and liquor, respectively. From these figures, the tin content of the original sample was calculated.

By a study of this data we are able to form a rough approximation of the amount of tin which is in soluble form. For this purpose it is necessary to assume that the tin of the liquor is all soluble. This is probably not the case. It is extremely unlikely that the soluble tin compounds all find their way into the solid particles of the food before the separation of the tin in insoluble form. It is much more likely that a considerable portion of the tin in the liquor is a finely divided insoluble oxide, hydrated oxide, or basic salt of tin. It is altogether probable that the amount of soluble tin in these samples did not increase after the first analyses were made, and that the subsequent increase of tin in the liquor was due to the separation of finely divided insoluble compounds of tin. The thought also suggests itself that a considerable portion of the tin that appears to be in solution is probably in colloidal form. If we assume all the tin of the liquor to be soluble, therefore, the amount of tin calculated as insoluble will be less than the amount actually present in that form and the results will at least be conservative.

TABLE II

VARIETY OF FOOD	Age of sample Yr. Mo.	MILLIGRAMS TIN PER KILOGRAM IN:		Soluble tin in drained solids(a)	Insoluble tin in drained solids(b)	Soluble tin in total sample(a)
		Total	Drained solids			
Asparagus.....	8	280	322	200	193	129
	1	5	433	489	252	248
	2	7	470	554	238	229
Lima beans.....	9	80	99	46	38	61
	2	9	173	254	40	33
	2	124	169	63	60	109
String beans.....	7	130	174	64	61	113
	1	3	299	442	97	93
	1	8	250	382	102	98
Wax beans.....	2	6	434	658	132	127
	3	93	143	39	38	105
	7	116	176	52	50	126
	10	139	251	55	53	198
	1	3	230	391	72	69
	1	8	217	359	87	84
	2	4	347	616	88	85

(a) The figures in these columns are doubtless higher than they should be as they are based on the assumption that the tin of the unfiltered liquor is all in solution.

(b) For the reason given in footnote (a), the figures in this column are doubtless lower than they should be.

The figures given in Table II in the column headed "Insoluble tin in drained solids" were obtained in the following manner, taking, as an example, the sample of asparagus which was examined 2 yrs. and 7 mos. after packing. The liquor in this sample contained 5.2 per cent of solids or 94.8 per cent of water. One kilogram of the liquor, therefore, contained 948 g. of water. Since a kilogram of liquor contained 238 mg. of tin and 948 g. of water there was in the liquor  $238 \div 948 = 0.25$  mg. of tin for each gram of water. The drained solids were found to contain 8.3 per cent of solid matter or 91.7 per cent of water. One kilogram of the drained solids, therefore, contained 917 g. of water.

Now it is fair to assume that the relative amount of water and dissolved tin in the drained solids is substantially the same as in the liquor. Figuring on that basis, the amount of soluble tin in the drained solids is  $914 \times 0.25 = 229$  mg. per kg. Since the total tin content of the drained solids was found to be 554 mg.

<sup>1</sup> Research Laboratories, National Canners' Association, *Bull.* 2, August, 1914.

per kg., it follows that  $554 - 229 = 325$  mg. per kg. must be in an insoluble form.

As stated above, this amount must be well within the truth. If any considerable amount of the tin of the liquor is insoluble, the insoluble tin of the drained solids must be considerably more than 325 mg. per kg. The remaining figures in the column marked "Insoluble tin in drained solids" were all calculated in the same manner, using average figures for the weight and water content of drained solids and liquor as the individual determinations were not made.

The column headed "Insoluble tin in drained solids" is of particular interest although, as stated above, it is believed that the figures in this column are somewhat less than the truth; the relative amount reported as insoluble tin in samples of different ages shows that the process of hydrolyzation is a continuous one.

The figures given in the last column headed "Soluble tin in total sample" were obtained by adding together the figures in the columns headed "Milligrams tin per kilogram liquor" and "Soluble tin in drained solids," after calculating these respective figures to milligrams of tin per kilogram of tin of original sample. It is interesting to note that the figures in this column are almost identical with the figures in the column headed "Milligrams tin per kilogram liquor." It is probable, therefore, that an approximate idea of the amount of soluble tin in a sample of canned food can be obtained by determining the amount of tin in the liquor of the food, although the figure so obtained will obviously include any insoluble tin which may be present in the liquor in a finely divided state and also any tin that may be present in colloidal form.

Recent workers agree that the ideas of the earlier writers on the toxicity of tin were erroneous. It is now known that the toxicity of soluble tin compounds is at least very much less than it was formerly supposed to be. It is evident, however, that the results obtained in the study of soluble tin salts cannot be used as a criterion on which to judge the toxicity of tin in canned foods. Whatever the insoluble combination in which tin occurs in canned foods it is in all probability less likely to be absorbed from the intestinal tract than soluble tin compounds. The same is true, perhaps to a less extent, of tin in colloidal form. At any rate, the need of experimental work on the toxicity of tin as it occurs in canned foods is obvious.

NATIONAL CANNERS' ASSOCIATION, WASHINGTON

### THE EFFECT OF CURING ON THE AROMATIC CONSTITUENTS OF VANILLA BEANS<sup>1</sup>

By FRANK RABAK

Received March 13, 1916

The fruit of vanilla has long been used as a flavoring agent. The plant is native to Mexico, where it is at present extensively cultivated for the production of the vanilla beans of commerce. It has been introduced into a number of other tropical and subtropical countries where it is also profitably cultivated. Among the other sources are South America (Guadaloupe),

Tahiti, Reunion, Madagascar, Comores, Seychelles, and Mauritius.

Vanilla beans as found on the market are described by the United States Pharmacopoeia<sup>1</sup> as the "cured, full grown, but immature, fruit of *Vanilla planifolia*, Andrews. (Family *orchidaceae*.)"

Vanilla is used for flavoring purposes in the form of the so-called extract or tincture of vanilla, which is prepared by extracting the coarsely comminuted beans with a hydroalcoholic menstruum varying in strength from 45 to 65 per cent.

The aroma of vanilla, to which the flavor is attributed, does not preëxist in the beans but is formed by a chemical reaction induced during the drying or curing process to which the beans are subjected after harvesting.

Behrens<sup>2</sup> states that ripe vanilla beans have little or no odor but become strong in odor by curing,



COMMERCIAL VANILLA BEANS

due to the splitting up of an existing glucoside with the formation of the compound vanillin. The above statement regarding the odor of vanilla was confirmed by Busse,<sup>3</sup> who states that vanillin is formed from a nonodorous body partaking of the nature of a glucoside.

In an extensive research with vanilla, Lecomte<sup>4</sup> found that the fruit of vanilla contained, besides the glucoside coniferin, two ferments, one an oxidase and the other a hydrolyzing agent. The latter con-

<sup>1</sup> United States Pharmacopoeia, Eighth Decennial Revision, 1900, 497.

<sup>2</sup> J. Behrens, "Ueber das Vorkommen des Vanillins in der Vanille." *Der Tropenpflanzer*, 3 (1899), 299.

<sup>3</sup> W. Busse, "Vanille—Chemie der vanille Frucht. Arbeiten aus dem Kaiserlichen Gesundheitsamte," Berlin, XV, 1898 bis 1899, p. 101.

<sup>4</sup> H. Lecomte, "Sur la formation du parfum de la vanille." *Compt rend.*, 133 (1901), 745.

<sup>1</sup> Published by permission of the Secretary of Agriculture.



verts the glucoside coniferin into coniferyl alcohol and glucose, the former oxidizing this alcohol into vanillin.

Later investigations have shown that the agreeable aroma of vanilla is not due alone to the compound vanillin but is strongly influenced by other substances of entirely different character.

Walbaum<sup>1</sup> states that the value of vanilla beans does not depend solely on the vanillin content. The oleoresinous constituents of the beans were examined and found to contain anisaldehyde and anisic alcohol besides other compounds which could not be identified, but which possessed a characteristic agreeable odor.

The presence of other odorous constituents in vanilla beans is also mentioned by Iserman,<sup>2</sup> who states that

agents which are known to impart much of the pleasant flavor to the cured beans.

#### CURING OF BEANS

As has been previously stated, the flavor of vanilla beans is brought about by a curing process with a consequent development of the true flavor upon which the efficacy of the beans as a flavoring material depends.

The curing process varies somewhat according to the source of the beans, the prime object, namely, the evaporation of the moisture and the formation of the flavoring constituents, being attained in every case. This is accomplished in a general way by a process of heating and subsequent sweating, the details of which vary in the different producing countries.

Two general methods are in vogue for the curing



LABORATORY CURED VANILLA BEANS

the special aroma and taste is probably due to vanilla resins. Busse<sup>3</sup> states that vanillin is present in the living fruits only in insignificant quantities and is mainly produced in the process of curing. Vanillin is not the sole criterion of quality and does not represent the natural aroma of the fruit. Besides vanillin there is present in the beans vanillic acid, resin, oil, sugar, mucilage, and tannin.

Up to the present time attention has been largely directed towards the vanillin content of the beans, only bare mention being made of the resinous constit-

<sup>1</sup> H. Walbaum, "Das Vorkommen von Anisalkohol und Anisaldehyde in der Früchten der Tahiti-vanille. Festschrift, Otto Wallach. Zur Erinnerung an seine Forschungen auf dem Gebiete der Terpene in den Jahren 1884-1909," p. 649.

<sup>2</sup> S. Iserman, "Vanilla Beans: Chemistry and Character of Constituents," *Western Druggist*, July, 1910, 358-362.

<sup>3</sup> H. Busse, "Studien ueber die Vanille," *Apoth. Zeit.*, 13 (1898), 894.

of vanilla beans, the dry and the hot water methods.

The dry method, in use in Mexico, consists essentially of placing the freshly gathered beans in the sun for several hours, after which they are wrapped in woolen cloths to promote sweating, and the process of heating and sweating is continued for several days until most of the moisture has evaporated. The final drying is usually completed in the shade. In unfavorable weather a drying oven is employed, in which the beans are sweated at a temperature of 60° C. The curing process is continued until the beans are soft and supple and have acquired a chocolate-brown color, the complete length of time required being frequently as long as 5 mos.

The hot water method, used in Reunion, consists in placing the beans in hot water (90 to 100° C.)

for 10 to 30 secs., after which they are wrapped in woolen blankets or placed in a box lined with blankets, where the sweating process takes place. Subsequently the beans are exposed to the sun and later the curing is completed in a drying room until the finished beans have the proper color and texture. This process requires from 1 to 2 mos. for completion.

The curing process is difficult and precarious, calling for a high degree of skill and experience. Weather conditions also have much to do with the rapidity and success of the process. The exact details of the two methods differ greatly according to locality. The general method of procedure for both processes is considerably modified in the minor details, the one object being to produce finished beans which will have the maximum amount of flavor of superior quality and at the same time will have had removed

curing vanilla beans were made. It was also desired to ascertain whether the long-continued curing as now practiced is absolutely necessary for the production of beans of commerce and whether shorter time of curing noticeably affects the percentage of vanillin in the cured beans.

A comparison of the efficacy of the two general methods of curing, namely, the dry method and the hot water method, and the effect of temperature upon the curing was sought. Furthermore, it was desired to study the effect of the various curing methods upon the formation of the oleoresins of vanilla which are present in all cured beans and which agreeably modify the flavor of the beans.

#### LABORATORY CURING EXPERIMENTS

A small quantity of green beans was obtained from

TABLE I—TREATMENT, LOSS IN WEIGHT AND CURING OF VANILLA BEANS AT ROOM TEMPERATURE AND IN THE WATER OVEN  
Immersion in water three successive times at temperature given, for periods indicated, at intervals noted

BEANS CURED AT ROOM TEMPERATURE					BEANS CURED IN WATER OVEN (40-60° C.)				
TREATMENT	No.	Per cent Loss in Weight	Curing Period Days	REMARKS	No.	Per cent Loss in Weight	Curing Period Days	REMARKS	
None	1	53.0 66.4	14 24	Curing progressed slowly for 7 days after which color developed rapidly to uniform brown; beans well cured in 14 days. At end of this time, however, beans were wrapped in wax paper and allowed to dry. Cured beans were dark brown in color, soft, pliable and possessed fine aroma.	2	32.5 67.0	8 33	Beans became uniformly brown in 6 days, sweating continuous until 8th day when beans were wrapped in waxed paper and allowed to dry until soft and pliable. Beans possessed characteristic but mild aroma.	
Temp., 40° C.	7	39.3 68.5	14 46	Curing proceeded about same as No. 1. After subjecting to sweating process for 14 days beans were uniformly brown in color. Beans wrapped in waxed paper and allowed to dry until they presented a wrinkled appearance and proper pliability. Beans possessed very fine aroma.	8	49.6 66.6	8 28	Beans all brownish color in 5 days with good odor developing. After 8 days' sweating in water oven beans were wrapped in waxed paper and allowed to dry slowly until proper texture was attained. Odor was fine vanilla-like characteristic but not especially strong.	
Period, 30 sec. Interval, 1 min.									
Temp., 60° C.	5	36.5 66.0	11 33	Beans became yellowish green after third day. After 11 days all were uniformly brown in color and had characteristic wrinkled appearance. Beans wrapped in waxed paper and allowed to dry to proper flexibility. Beans characterized by strong and exceptionally fine odor.	6	41.4 66.2	8 33	After 5 days beans were uniformly brown in color with pronounced odor and apparently curing rapidly. After 8 days' sweating beans were treated as above and dried to proper pliability. Odor was strong, vanilla-like.	
Period, 20 sec. Interval, 1 min.									
Temp., 80° C.	3	40.7 66.2	12 24	Beans assumed brown color and developed odor more rapidly than any of above. After 12 days' sweating beans wrapped in waxed paper and set aside to dry. After 12 days of drying beans possessed a most exquisite aroma, deep brown color and fine texture.	4	31.2 64.0	8 29	Uniformly brown after 4 days' sweating, curing more rapidly than any of above and becoming soft and pliable. After sweating 8 days beans treated as above. Final appearance excellent both as regards color and pliability. Odor strong.	
Period, 10 sec. Interval, 1/2 min.									
Temp., 90° C.	9	23.3 66.1	10 28	Beans were all pliable, wrinkled and brown in 10 days with odor fairly strongly developed. Allowed to dry in air for 18 days. Beans pliable and wrinkled with only faint odor and pale brown color.	10	30.0 66.3	3 25	Beans possessed a uniform dark brown color in 2 days with prominent odor developing. After 3 days' sweating beans were exposed to air and dried until proper degree of pliability was reached. Strong but unpleasant odor noted.	
Period, 10 sec. Interval, 1/2 min.									
Temp., 100° C.	11	35.2 64.0	10 18	Beans became light brown and soft on third day. Taken from towel on 10th day and allowed to dry in air for 8 days. Odor prominent but not strong. Color pale brown.	12	44.0 69.0	3 17	Beans uniformly brown but pale after 1 day's sweating. Odor only fair and color pale brown after 3 days. Beans allowed to dry sufficiently, the cured beans being very light in color with faint odor.	

from them sufficient moisture to prevent molding when the beans are finally packed for the market. As a general rule from 5 to 7 lbs. of the fresh beans are required to produce 1 lb. of cured beans.

It is stated by Ellis<sup>1</sup> that the temperature of the water into which the pods are dipped before curing has much to do with the successful curing of vanilla.

Treatment with hot water supposedly kills the pods and prevents dehiscence. It is, however, essential that the temperature be not sufficiently high to destroy the action of the oxidase which is present in the pericarp. A destruction of the oxidase would seriously interfere with the formation of the odorous constituents of the cured beans.

The object of this investigation was twofold. A number of modifications of the process now used in

Mexico through a prominent manufacturer of vanilla extract. The small ends of the beans were very slightly yellow but were practically devoid of odor.

The curing experiments were conducted with twelve lots of beans, one-half of which were cured at room temperature and the other half in a water oven at somewhat higher temperature. Each of the six lots cured at room temperature were given different treatment prior to the sweating and drying. The treatment consisted in dipping the green beans into water at various temperatures up to the boiling point. Each lot was kept wrapped in a soft towel and placed on the laboratory shelf to undergo the sweating and drying process.

The duplicate lots of beans cured in the water oven at a temperature of 40–55° C. received exactly the same treatment as those cured at room temperature.

<sup>1</sup> F. R. Ellis, "Vanilla," *The Chemist and Druggist*, 67 (1905), 593.



A description of the treatment, loss in weight, and time of curing of the green beans at room temperature and in the water oven is given in Table I.

The general treatment in the curing at room temperature and in the water oven was similar to that employed in the commercial curing of the beans. The processes of sweating and drying were applied, however, under very different conditions than those obtaining at localities where the beans are cured commercially. During the sweating process the beans were wrapped in soft towels and later in waxed paper to complete the drying.

The treatment of the two sets of samples was identical in that one sample in each set was cured without previous treatment, while the remaining five samples were subjected to the action of hot water at increasing temperatures up to the boiling point. The subsequent treatment of each sample was identical in every case.

It will be noted that the time of sweating or the length of time required to produce the brown color and the characteristic odor of the cured beans de-

waxed paper, placed in tight containers, and allowed to stand for a period of 2 mos. After this time the samples were carefully examined and compared with regard to average weight and length, also color, odor, and general appearance, with several commercial samples of cured beans, and the results tabulated, as shown in Table II.

The average weight and length of the laboratory cured beans compare very favorably with the commercially cured samples. In color and odor several of the laboratory samples were superior to the commercial samples. The presence of crystals of vanillin on the surface of the beans usually occurs when beans with high content of this constituent are kept in a confined space for a period of time. Crystals of vanillin were observed to be most prevalent in the samples cured at room temperature, an entire absence of crystals being noted in the samples cured in the water oven with one exception, that of Sample 2, on which a few crystals were observed.

A decided red-brown color was apparent in the cross section of the beans cured at room tempera-

TABLE II—GENERAL COMPARISON OF LABORATORY CURED AND COMMERCIAL CURED VANILLA BEANS

SAMPLE	CURED BEANS		BROWN COLOR	ODOR	DESCRIPTION OF WHOLE BEANS	DESCRIPTION OF CUT BEANS (CROSS SECTION)
	Av. Wt.	Av. Length				
1	4.1	19	Chocolate	Fragrant, vanilla-like	Uniformly colored, soft, pliable. A few small vanillin crystals on surface	Uniformly red-brown, inner portion redder than surface
7	5.1	19.5	Pale	Fine, fragrant	Soft and pliable, wrinkled. No crystals	Reddish brown, inner portion redder than surface
5	4.9	18	Chocolate	Fine, mild	Pliable and wrinkled. A few crystals on surface	Reddish brown, inner portion redder than surface
3	5.1	19.5	Dark	Especially fine	Nearly covered with vanillin crystals	Dark brown, somewhat lighter than surface
9	4.4	19	Light chocolate	Very mild	No crystals	Uniformly brown
11	5.2	19.5	Reddish	Lacking fineness	Not uniformly colored. A few crystals at ends	Lighter but uniformly brown
2	5.2	19.5	Dark	Good, strong	A few crystals at one end	Inner portion lighter brown than surface. Charred odor
8	5.1	20	Chocolate	Mild, fragrant	Uniformly colored. No crystals	Uniformly chocolate-brown
6	5.6	20	Pale	Prune-like	No crystals	Uniformly pale brown
4	4.7	19	Chocolate	Good, but lacking bouquet	No crystals	Inner portion paler than surface
10	4.8	18.5	Chocolate	Very mild	Not uniformly colored. No crystals	Lighter in cross section
12	4.8	18	Pale	Prune-like	Not uniformly colored. No crystals	Uniformly brown
Mex. A	5.1	23	Dark	Strong, not agreeable	Pliable, sticky. No crystals	Much lighter brown than surface. Odor somewhat tobacco-like
Tahiti	3.2	18	Dark	Strong	Conspicuous pale, longitudinal stripes	Uniformly brown. Odor somewhat tobacco-like
S. Amer.	3.9	20	Very pale	Mild, sweet	Not pliable. A few crystals	Inner portion reddish brown
Bourbon	2.7	17	Almost black	Pleasant	Very pliable. No crystals	Inner portion lighter brown than surface
Old (a)	2.5	16	Pale	Very faint	Nearly dry. No crystals	Uniformly pale brown

(a) Beans several years old.

creases with the increase in temperature of the water in which the green beans were immersed. Indications, therefore, point to increased activity of the oxidases which supposedly bring about the changes. Whether this increased activity is favorable or detrimental to the production of color and odor will be apparent later.

After the sweating process, the time required for drying to the proper appearance and texture varied somewhat according to the previous treatment with hot water. The beans were dried until the proper pliability was obtained, or until the loss of moisture was from 64 to 69 per cent. In a general way the drying increased in rapidity as the temperature to which the beans were originally subjected was increased.

The formation of the brown color as well as the vanilla odor was seemingly most rapid in the samples subjected to the hottest water. These changes were also most marked and rapid in the samples sweated in the water oven at a temperature ranging from 40 to 60° C.

The various lots of cured beans were wrapped in

ture, with a decreasing tendency as the temperature of the water increased into which the beans were immersed.

Physical tests being insufficient and inadequate to determine accurately the quality of beans cured by the various modifications of the methods, a chemical examination was necessary. Not only was it desired to ascertain the respective qualities of the beans with regard to vanillin content, but also the oleoresin content, which is considered an important adjunct to the flavor of the beans.

#### PREPARATION AND PROPERTIES OF EXTRACTS

In order more advantageously to judge the quality of the cured beans and to make a thorough comparison of the various samples with the commercial beans, extracts were made from the samples according to the directions in the United States Pharmacopoeia<sup>1</sup> for the preparation of tincture of vanilla. The resulting extracts afforded an excellent means for com-

<sup>1</sup> United States Pharmacopoeia, Eighth Decennial Revision, 1900, 484.

paring the general physical and chemical properties of the individual samples with those prepared from commercial vanilla beans. These comparisons are shown in Table III.

The general physical properties of the extracts from the samples cured at room temperature were superior to those cured in the water oven at somewhat higher temperature. The colors of the former were distinctly more red and brownish red than the latter. All the laboratory extracts were more attractive in color than the extracts from the commercial beans. The deeper color of the extracts from the laboratory cured beans was perhaps due to the presence of vanilla resins which possess a color of deep red to brown.

The odor and taste of the extracts from the beans cured at room temperature were superior to those from the oven cured beans. The presence of a distinct flowery or fruity odor and taste was apparent. Extracts from the commercial beans seemed lacking in this respect.

In vanillin content less difference is noted between the extracts from the commercial beans and the laboratory cured beans. The extracts from the beans cured at room temperature assayed considerably higher in

ples were next in order, followed by the Tahiti and the old sample.

In order partly to obtain more expert judgment and partly to verify the writer's judgment of the samples, a sample of each extract was submitted to a prominent manufacturer of flavoring extracts, who, without having any knowledge of the identity of any of the 18 samples submitted, made the following report on the color, odor, and taste:

COLOR—South American, the best.

ODOR—Nos. 3, 5, 1 and 7 ranked highest; Tahiti, No. 11, and South American, next; Mexican A, Nos. 9, 8, and 2, Bourbon, 4, 6, 10, and 12, Mexican B and old sample follow in order.

TASTE—Nos. 1, 2 and 3 ranked first; South American, Nos. 11, 7, 9, and 8, were next in rank, followed by Tahiti, Mexican A, No. 2, Bourbon, Nos. 4, 6 and 10; No. 12, Mexican B, and old sample were stated to contain a foreign taste.

According to the report the color of the extract from the South American beans was considered best. This is in close accordance with the colors as described in Table III. Extracts 1 and 3 possessed about the same color as the South American, namely, a bright wine-red, while Nos. 5 and 7 were slightly darker. The remainder of the laboratory extracts possessed an admixture of brown, this color being more prominent in some than in others.

TABLE III—PHYSICAL AND CHEMICAL COMPARISON OF VANILLA EXTRACTS FROM LABORATORY CURED AND COMMERCIAL BEANS

SAMPLE	PHYSICAL PROPERTIES OF EXTRACTS			PER CENT VANILLIN
	COLOR	ODOR	TASTE	
1	Wine-red	Pleasant, fruity, very fragrant	Very agreeable, fruity, lasting	0.255
7	Deep wine-red	Pleasant, fruity	Agreeable, vanilla-like	0.253
3	Very deep wine-red	Pleasant, less fruity	Mild, characteristic, pleasant	0.210
5	Wine-red	Very pleasant, flowery	Very pleasant, fruity	0.317
9	Wine-red, slight brownish tint	Pleasant, vanilla-like	Agreeable, not fruity	0.212
11	Wine-red, slight brownish tint	Mild, pleasant	Agreeable, slight	0.212
2	Wine-red	Pleasant, agreeable	Mild and pleasant	0.215
8	Brown with reddish tint	Strong, pleasant	Strong, lasting	0.252
12	Light wine-red, brownish tint	Mild, lacking fragrance	Characteristic, pleasant	0.228
4	Brown with only trace of red	Pleasant, fragrance lacking	Pleasant, lasting	0.201
10	Wine-red, distinct brownish tint	Mild, characteristic	Characteristic, less agreeable	0.239
12	Wine-red, distinct brownish tint	Mild, agreeable	Pleasant, slightly prune-like	0.225
Mex. A	Light brown	Pleasant, characteristic	Agreeable, not fruity	0.259
Mex. B	Wine-red with brownish tint	Strong, vanilla-like, lacking fragrance	Strong, harsh, not fruity	0.291
Tahiti	Very pale brown	Strong, extract-like, lacking fragrance	Strong, unpleasant, licorice-like	0.200
S. Amer.	Wine-red	Pleasant, agreeable, vanilla-like	Strong, agreeable, vanilla-like	0.268
Bourbon	Wine-red, with brownish tint	Pleasant, agreeable, vanilla-like	Characteristic, not fruity	0.248
Old	Brown	Mild, vanilla-like	Mild, not agreeable	0.196

general average than from the beans cured at higher temperatures.

Considerable variation in vanillin content exists, however, in samples prepared from the beans which had received the hot water treatment before curing. It is very probable that the effect of this treatment as regards composition of the beans will be more pronounced in other constituents than in the vanillin.

To the writer the laboratory cured beans and also the extracts appeared to possess a better odor and taste than any of the commercial beans or extracts. The color of the extracts in every case also distinctly excelled in color those from the beans cured at higher temperatures.

Judging from a purely physical standpoint of color, odor, and taste, the extracts from Samples 1 and 3 were considered the finest, followed by Samples 5, 7, 9 and 11. Samples 2, 8, 6, 4, 10 and 12 were all lower in color estimation and slightly inferior in odor and taste. Of the extracts from the commercial beans, the South American sample was distinctly superior to the others in every respect and more nearly corresponded to Samples 1 and 3 of the laboratory cured beans. The Bourbon and Mexican sam-

Not only was the rating of the various samples by the manufacturer with respect to odor and taste in close accordance with the writer's selections, but it is a singular fact that three of the laboratory cured samples were stated to excel in point of odor and taste the extracts from the commercial beans and in nearly all cases the beans cured at room temperature were superior to those cured in the water oven.

In order to ascertain whether the various modifications of the curing process produced any effect upon the composition of the beans, an analysis of the residues remaining from the preparation of the extracts was examined.

#### EXTRACTION OF THE RESINS

Since it is generally conceded that resins or oleo-resins tend strongly to modify the agreeable odor of vanilla beans, it is very probable that the superior aroma and flavor of several of the cured samples of beans were due to the presence of these odorous resinous substances. These substances are for the most part soluble in alcohol, to a less extent, however, in hydroalcoholic solutions. In preparing the extracts described 65 per cent alcohol was used. Not all of the resinous constituents of the beans were dis-



solved by alcohol of this strength but it is assumed that approximately the same percentage of these constituents was extracted from each sample. Provided that more resinous constituents were present in some samples than in others, and granting that the 65 per cent alcohol extracted only a small portion of these constituents, the residues from the preparation of the extracts still contained much of the unextracted resinous substances.

These residues were therefore subjected to extraction with 94 per cent alcohol in order to obtain the residual resins. The residues remaining from the alcohol extraction were further extracted with ether. The percentages of alcohol and ether extracts, and descriptions of each, are given in Table IV.

The quantity of alcohol-soluble constituents remaining in the beans after the preparation of the extracts is considerable. While a number of constituents are no doubt present in these extracts, a large portion probably consists of vanilla resins, together with some vanillin.

The percentage of alcohol extracts from the samples of beans cured in the laboratory at room temperature is uniformly higher than from those cured in

#### EXAMINATION OF RESINS EXTRACTED WITH ALCOHOL

In order to obtain further knowledge of the alcohol extracts obtained from the residues, the chemical constants, acid, ester, and saponification numbers were determined. The results are shown in Table IV.

Considerable variation exists in the acid, ester, and saponification values of the alcohol extracts obtained from the residues of the laboratory cured beans. The general average of these constants is higher than that of the commercial beans, as was also the percentage of extract. The content of free acid constituents of the resinous extracts is high in nearly all instances, signifying the presence of considerable resin acids. The ester values are likewise high, showing the presence of saponifiable resinous compounds. The resin acids and the combined saponifiable resins seem to have been formed to a greater extent in the beans cured in the laboratory than in the commercially cured samples. Provided these substances tend to add fragrance to the odor of the vanilla bean and therefore also to the extract made from the beans, it would seem that methods which would insure a high percentage of these resinous substances should be preferred. Doubtless a certain percentage of these

TABLE IV—ALCOHOL AND ETHER EXTRACTS FROM VANILLA RESIDUES

SAMPLE	ALCOHOL EXTRACT OF VANILLA RESIDUES				CHEMICAL CONSTANTS OF RESIDUES				ETHER EXTRACT OF VANILLA RESIDUES			
	DESCRIPTION				ALCOHOL EXTRACT OF RESIDUES				DESCRIPTION			
	Per cent	COLOR	STATE	VANILLA ODOR	Value	Acid	Ester	Sapon.	Per cent	COLOR	STATE	ODOR
1	19.23	Dark red	Semi-solid	Fine	13.4	170.5	183.9	4.14	Red-brown	Oily	Fatty	
7	27.25	Brownish red	Nearly solid	Fine	27.0	182.3	209.3	4.50	Brownish red	Oily	Balsamic	
5	18.22	Brownish red	Nearly solid	Fine	14.3	169.0	183.3	5.34	Pale brown	Oily	Fatty (a)	
3	20.80	Reddish brown	Semi-solid	Mild	14.6	180.0	194.6	3.73	Pale brown	Oily	Fatty (a)	
9	21.41	Reddish brown	Semi-solid	Pronounced	39.0	161.4	200.4	3.71	Pale yellow	Oily	Slight fatty	
11	16.07	Brownish red	Nearly solid	Fine	36.0	167.5	203.5	3.88	Pale brownish red	Oily	Mild, pleasant	
2	23.19	Pale brownish red	Partly liquid	Yes	34.3	124.6	158.9	4.86	Pale brown	Oily	Slight balsamic	
8	13.30	Reddish brown	Nearly solid	Pronounced	34.0	132.0	166.0	3.33	Brownish red	Oily	Slight vanilla	
6	17.18	Brownish	Semi-solid	Paint, agreeable	60.1	126.1	186.2	4.99	Pale brown	Oily	Nearly odorless	
4	21.28	Pale brown	Nearly solid	Mild	48.3	134.5	182.8	4.33	Pale yellow	Oily	Faint vanilla	
10	13.11	Brownish	Semi-solid	Paint	53.2	127.3	180.5	4.38	Pale brown	Oily	Faint	
12	15.50	Brown	Partly liquid	Faint	40.0	142.2	182.2	3.70	Pale brown	Oily	Faint	
Mex. A	19.60	Brown	Liquid	Faint, fatty	25.8	145.6	171.4	4.01	Red-brown	Oily	Fatty (a)	
Mex. B	12.76	Brown	Semi-solid	Yes	12.9	155.3	168.2	4.11	Dark brown	Oily	Fatty	
Tahiti	6.43	Pale brown	Solid	Faint	39.7	85.0	93.4	6.03	Dark red-brown	Oily	Faint balsamic	
S. Amer.	27.20	Dark red-brown	Semi-solid	Pleasant	8.4	85.0	93.4	2.81	Dark brown	Oily	Slight vanilla	
Bourbon	19.75	Dark brown	Nearly solid	Good	38.2	155.0	193.2	4.46	Yellow	Oily	Faint	
Old	13.35	.....	.....	.....	28.2	134.2	162.4	4.22	Pale brownish	Oily	Faint	

(a) Fatty taste as well as odor.

the water oven. Likewise those extracts were considerably deeper and richer in color. It would seem, therefore, that curing at room temperature is more conducive to the formation of vanilla resins and coloring matter.

The highest percentage of alcohol extract (vanilla resins) in the commercial beans was in the South American sample. This sample also produced a vanilla extract with the deepest color. The residues from the Mexican and Bourbon beans also contained a high percentage of alcohol-soluble substances, and likewise a highly colored extract. These facts are significant of the effect of curing upon the color of prepared extracts and also of the comparatively large quantity of flavoring resins which remain in the residues.

The ether extracts were found to consist largely of fatty oil and were nearly devoid of odor. Some of the less soluble resinous constituents are doubtless present in these extracts. The percentages of ether extract seem to bear no direct relationship as regards treatment during curing. Some variation is apparent, however, among the samples from different sources.

substances are extracted by the hydroalcoholic menstruum used in preparing the extracts of commerce, the quantity in solution depending largely upon the strength of the alcohol employed.

#### CONCLUSIONS

From the results reported herein it may be said in general that the curing process as at present commercially applied to vanilla beans is unnecessarily long and extended, requiring on an average several months for the transformation of the green to the cured beans.

In the laboratory experiment conducted it has been shown that the beans can be cured in a much shorter time by means of a much less tedious process. It has further been demonstrated that the process is simplified to the advantage rather than to the detriment of the aromatic constituents. In order to produce uniformity in the composition of the beans, and thereby insure more uniform extracts, the importation and curing of the green beans are suggested.

While the amount of vanillin in the beans was not increased appreciably, as compared with commercial beans, it may be stated with assurance that the beans

cured in the laboratory were in most cases superior in vanilla resins and coloring matter. This is significant since vanilla resins and coloring matter are considered important adjuncts to the quality of vanilla beans. The superior flavor of the extracts prepared from the laboratory cured beans may therefore be ascribed to the resinous constituents. A considerable proportion of the vanilla resins are left unextracted when the menstruum is less than 65 per cent alcoholic strength.

Curing the green beans at room temperature either without previous treatment or after treatment with water up to 90° C. for a short period of time apparently produces beans of the best quality, as judged by the flavoring extracts prepared from the samples.

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### A STUDY OF THE STEREO-ISOMERISM OF A FERMENTATION LACTIC ACID

By STANLEY JUDSON THOMAS

Received December 21, 1915

Investigations of the isomerism of lactic acid soon followed Pasteur's famous work with tartaric acid. In 1890, Lewkowitsch<sup>1</sup> showed that ammonium lactate when exposed to the action of *Penicillium glaucum* for several weeks became optically active. In 1892, Professor T. Purdie proved, by direct analytical evidence, that commercial lactic acid can be resolved into two oppositely active isomeric acids.<sup>2</sup> The results of experiments of various writers on the kind of lactic acid formed in naturally soured milk do not agree. Some found inactive acid, some dextro-, and some laevo-rotatory acid. Dr. P. G. Heinemann cleared up most of this conflicting testimony by showing that different bacteria produce different kinds of acid. As a summary to an excellent paper on the subject, he says: "Racemic lactic acid is the result of the formation of pure dextro acid and pure laevo acid by at least two different species of microorganisms. Racemic (inactive) lactic acid is not known to be the product of one species only."<sup>3</sup>

The object of this paper is to discuss the kind of lactic acid present in Matzoon, an Armenian artificially soured milk, and to give the results of an investigation of its optical powers.

Matzoon is a beverage prepared from cows' milk with the aid of an appropriate ferment. From this ferment, or "starter," the author isolated a bacillus, a streptococcus, and a yeast. The bacillus was determined as a member of the *B. bulgaricus* group, corresponding more closely to *B. caucasicus* (Flügge) than to any other member. The streptococcus isolated was *Str. kefir* (Kuntze), a member of the *Str. lebenis*<sup>4</sup> group. The yeast was determined as *Saccharomyces kefir*; this organism is unable to ferment milk or lactose, excepting a slight production of alcohol.

Lactic acid was discovered by Scheele. It exists

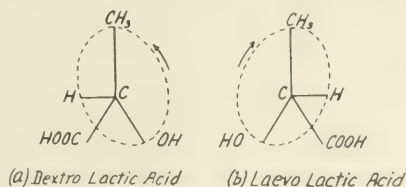
in sour milk, human gastric juice and in muscle. It has been found in the vegetable kingdom in the peduncles of *Solanum dulcamara*.<sup>1</sup> There are four lactic acids, three having the formula  $\text{CH}_3\text{CHOH}\cdot\text{COOH}$ , and one the formula  $\text{CH}_2\text{OH}\cdot\text{CH}_2\text{COOH}$ . Inactive or ethylidene lactic acid ( $\alpha$ -hydroxy propionic acid) may be prepared by treating  $\alpha$ -chloropropionic acid with potassium hydroxide: it forms a zinc lactate that crystallizes with three molecules of water of crystallization. Sarco- or dextro-lactic acid ( $\text{CH}_3\text{CHOH}\cdot\text{COOH}$ ) is found in meat: the zinc lactate made from this acid crystallizes with two molecules of water of crystallization.

Laevo-lactic acid ( $\text{CH}_3\text{CHOH}\cdot\text{COOH}$ ) differs from the dextro acid only in its optical powers: its zinc lactate crystallizes with two molecules of water of crystallization.

Beta hydroxy propionic acid (hydracrylic or ethylene lactic acid) has the formula  $\text{CH}_2\text{OHCH}_2\text{COOH}$ . When heated it liberates water and forms an unsaturated acid, acrylic acid,  $\text{CH}_2\text{CHCOOH}$ .

Thus we have three lactic acids having the same structural formula but different properties. This is known as stereo-isomerism, physical isomerism, or optical isomerism. Ethylene lactic acid,  $\text{CH}_2\text{OHCH}_2\text{COOH}$ , is inactive under all circumstances. Ethylidene lactic acid,  $\text{CH}_3\text{CHOHCOOH}$ , on the other hand, may exhibit optical activity. On close examination the latter is found to contain a carbon atom in its molecule which holds four other atoms or groups of atoms, all different from each other. Optically active substances, without exception, contain one or more such carbon atoms in their molecules, and the property of turning the plane of polarization bears a close relation to the structure of a substance. Optical activity is, therefore, due to the presence of a carbon atom in a molecule which holds four dissimilar groups with its four bonds. Such a carbon atom is known as an asymmetric carbon atom. Furthermore, an optically active substance may show dextro-rotation, that is, turn the plane of polarization to the right; or laevo-rotation, that is, turn the plane of polarization to the left. A closer examination of the lactic acid molecule may show why the acid exhibits both dextro-rotation and laevo-rotation.

Let us now examine the lactic acid molecule. If we attempt to draw a picture of the molecule in space we may have:



The difference between these formulae is only that of an object and its image in a mirror. If *b* be superimposed upon *a*, we will find that the OH group

<sup>1</sup> Standard Dispensatory.

<sup>1</sup> Ber., 16, 2720.

<sup>2</sup> J. Chem. Soc., 1892, 754.

<sup>3</sup> J. Biol. Chem., 2, 612.

<sup>4</sup> Freudenreich, Landw. Jahrb. d. Schweiz., 10 (1896), 1.



of *b* will lie on the COOH group of *a*. If we take the groups in order, CH<sub>3</sub>, H, OH, we find that in the first (*a*) they travel counter-clockwise, while in the second (*b*) they travel clockwise.

As we may see, if these two active lactic acids are mixed in equal proportions, inactive lactic acid will result. If we make lactic acid synthetically from symmetrical substances we always get the inactive lactic acid. Thus propionic acid evidently yields an intimate mixture of dextro- and laevo-rotatory acids and the product is therefore inactive.

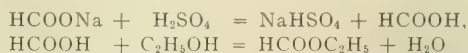
Among the earliest methods of obtaining lactic acid on a commercial scale was that proposed by Beusch:<sup>1</sup> 6 lbs. of cane sugar and 1/2 oz. of tartaric acid (which serves to convert the cane sugar into dextrose) are dissolved in 26 lbs. of boiling water. After 2 days, 2 lbs. of chalk are added, together with 4 oz. of putrid cheese suspended in 8 lbs. of sour milk. The mixture is then set aside at a temperature between 30 and 35° C. and well stirred every day until, in the course of 6 or 8 days, it is converted into a thick paste of calcium lactate. This paste is boiled for 1/2 hr. with 1/2 oz. of quicklime and 20 lbs. of water, the solution strained through cheesecloth and evaporated to a syrup. The crystalline mass which first forms is pressed by itself, then three or four times after having been each time stirred up with 1/10 part of cold water, and the lactate of calcium thus purified is dissolved in twice its weight of boiling water. To 32 parts of the solution of the calcium salt is added a mixture of 7 parts of sulfuric acid and 7 parts of water. The lactic acid thus formed is strained through linen while still hot to separate it from the sulfate of lime, and boiled with 1 3/8 parts of zinc carbonate for 15 min. Lastly, one part of the zinc salt is dissolved in 7 1/2 parts of boiling water and treated with sulfuretted hydrogen until zinc sulfide ceases to precipitate. The filtrate, containing the pure lactic acid, is evaporated on the water bath.

The method used in this experiment was as follows: A synthetical culture medium was prepared consisting of asparagin 10 g., magnesium sulfate 0.2 g., dipotassium phosphate 1 g., sodium chloride 0.5 g., potassium nitrate 0.2 g., dextrose 20 g. to each liter of distilled water: to this solution were added 15 g. of pure calcium carbonate per liter. To the medium thus prepared, was added a small amount of previously prepared Matzoon as a starter, and the mixture allowed to incubate at 37.5° C. for 2 wks. At the end of that time the fermentation product was filtered and washed. A residue of unused calcium carbonate together with a slight amount of calcium oxalate remained. The filtrate contained the calcium salts of volatile and nonvolatile organic acids. This filtrate was barely acidified with sulfuric acid, heated, and filtered to get rid of the calcium as calcium sulfate. The filtrate was then distilled to one-half volume, and steam passed through the residue in the flask so as to separate the volatile acids from the non-volatile acids.

**TESTS FOR VOLATILE ACIDS**—The distillate was treated with sodium hydroxide (care being taken to avoid an excess) and heated gently. The solution was evaporated on the water bath and the crystals of the sodium salts of the volatile acids were obtained.

**FORMIC ACID** was tested for in four ways: (1) To a small portion of the dry residue in a test tube was added a little sulfuric acid. The mixture was heated gently while the mouth of the tube was covered. Carbon monoxide would be liberated during the heating if formic acid were present. Carbon monoxide burns with a characteristic blue flame. The reaction which takes place is:  $\text{HCOONa} + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{H}_2\text{O} + \text{CO}$ . (This test should be tried in a dark room.) Where a large amount of formic acid is present it is not necessary to heat the mixture.

(2) To a small portion of the salt were added a little alcohol and a drop of sulfuric acid. If formic acid were present ethyl formate would be formed which has a characteristic odor. The following reactions show what takes place:



(3) To a solution of the salt was added a little silver nitrate. On heating, a formate, if present, would reduce the silver nitrate to free silver.

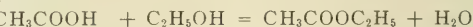
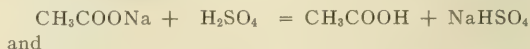
(4) A little of the dry formate was mixed with soda lime (CaO + NaOH) and the mixture heated. Hydrogen would be liberated were a formate present, as



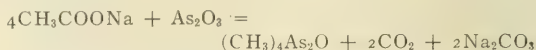
By none of these tests could the author show the presence of formic acid.

**ACETIC ACID**—Since no formic acid was present, acetic acid was tested for by the following methods:

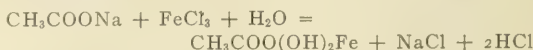
(1) A small portion of the solid was just acidified with sulfuric acid and a drop of alcohol was added to the mixture. Acetic acid was shown to be present by the odor of ethyl acetate which was given off. The odor is similar to that of bananas. The reactions which take place are:



(2) The cocodyl test. A little of the dry salt was mixed with arsenious oxide (As<sub>2</sub>O<sub>3</sub>) in a hard glass tube and heated to a high temperature. A strong garlic-like odor of cocodyl oxide shows the presence of acetic acid:



(3) A small amount of the solution of the sodium salt was treated with a drop of ferric chloride and the mixture boiled. A red-brown precipitate of basic ferric acetate formed which showed the presence of acetic acid:



*Propionic* and *butyric acids* were found to be present by the following method: A rather large amount

<sup>1</sup> Ann. Chemie Pharm., 61, 174.

of the distillate after the first treatment with the sulfuric acid was neutralized with baryta water and evaporated to dryness. The residue was heated to boiling with 80 per cent alcohol, by which process the barium propionate and butyrate were dissolved, leaving the barium salts of the lower acids which are insoluble. The alcoholic solution was evaporated, the residue dissolved in water and decomposed by silver sulfate by boiling. After filtering, the silver salts were dissolved in concentrated sulfuric acid which liberated the pure propionic and butyric acids. They appeared as minute oily drops on the sulfuric acid. No attempt was made to separate the propionic and butyric acids.<sup>1</sup>

After testing for the volatile acids the author continued the purification of the lactic acid. After the volatile organic acids were removed the residue contained lactic acid, succinic acid and some calcium sulfate which continued to separate out on concentration. This latter substance was very hard to remove: repeated filtrations, washing regularly to keep the succinic acid in solution, and concentrating on the water bath, were necessary. After all the calcium sulfate was removed, the residue was a very dark syrupy liquid (lactic acid and charred organic impurities) containing a white, crystalline solid (succinic acid). The succinic acid was removed by filtration with suction, and its melting point determined as 183° C. (very sharp): a large amount of succinic acid was formed due to the use of a derivative of this acid—*asparagin*—in the original culture medium.

The lactic acid, which still contained a large amount of charred organic matter, was diluted to about four times its volume with distilled water and purified by boiling, under a return condenser, with animal charcoal. The charcoal and its occluded organic compounds were filtered off under suction and a clear solution of lactic acid remained. The colorless liquid obtained was diluted with distilled water and neutralized with zinc carbonate, thus:



The zinc lactate obtained was crystallized, washed and recrystallized several times to obtain as pure a salt as possible. The zinc was removed by hydrogen sulfide, filtered off, and the optical properties of the lactic acid determined by means of the polariscope.

The lactic acid obtained from Matzoon proved to be of the usual inactive variety. The problem now presented itself to resolve this acid into its active components. The method proposed by Purdie and Walker<sup>2</sup> was the one used:

150 cc. of the lactic acid solution were neutralized with strychnine. This required slightly over 28 g. of strychnine. Since strychnine unites with lactic acid in molecular proportions,<sup>3</sup> there must have been about 8.5 g. of pure lactic acid present in the 150 cc. of the diluted acid. The liquid was then subjected to systematic fractional crystallization, the crystal-

line solid in each case being separated as far as possible by the aid of suction and recrystallization being carried out in a vacuum desiccator.

After several successive crystallizations the less soluble crystals were dissolved in water and the strychnine was precipitated by the addition of ammonium hydroxide. The filtrate was evaporated and a slight excess of ammonium hydroxide added to completely precipitate the strychnine. After again filtering the solution, it was tested in the polariscope in a 220 mm. tube. It gave a rotation of +0.9°. The mother liquor was then treated in the same way with ammonium hydroxide, filtered and tested. It gave a rotation of -0.9°. In this way it was proved that lactic acid obtained from Matzoon was capable of being resolved into its active components.

#### CONCLUSIONS

I—Matzoon, an Armenian lactic acid food, owes its peculiar properties to the Bulgarian bacillus together with *Streptococcus lebanis* and *Saccharomyces kefir*.

II—Fermentation lactic acid may be separated and purified by the method described in this paper.

III—The acid produced by Matzoon in a synthetic culture medium is optically inactive, but this inactive acid is capable of being resolved into active components.

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#### PLANT FOOD DEFICIENCIES OF COASTAL PLAIN AND PIEDMONT SOILS<sup>1</sup>

By C. B. WILLIAMS  
Received May 1, 1916

In approaching the solution of this kind of a problem for any section, it is necessary to conduct experimental field work on the soils of known types which occur in the area and which are important ones agriculturally in the sections. These facts may be determined by a soil survey which had best precede, if possible, the taking up of field studies to determine the plant food deficiencies of soils of the section. After the mapping has been finished in the soil survey, a trained and experienced man is sent over the area to draw representative samples of soil and subsoil for analyses from each type occurring in the area. These are sent to the chemical laboratory for a determination of the total amount of nitrogen, phosphoric acid, and potash present.

#### WHAT CHEMICAL ANALYSES WILL SHOW

From such an examination it will be possible to calculate the total amounts of these plant food constituents actually present in the soil, but it will not be possible from such an examination to determine the availability of these for plant growth. This can be satisfactorily done only by well planned and carefully conducted fertilizer experiments with different crops on each type of soil, and carried on a sufficient length of time to eliminate seasonal and other factors that might occur to interfere with a fair deduc-

<sup>1</sup> See Fresenius, "Qualitative Analysis," p. 419.

<sup>2</sup> J. Chem. Soc., 61, 754.

<sup>3</sup> Ibid.

<sup>1</sup> Presented at the 52nd Meeting of the American Chemical Society, Urbana-Champaign, Ill., April 17 to 21, 1916.



tion from one or two years' results. Below are tabulated the average amounts of nitrogen, phosphoric acid and potash contained in the leading types of soil occurring in the Coastal Plain and Piedmont regions in which field work has been conducted. In the Coastal Plain, the Norfolk series embraces decidedly the most important soils of the whole South Atlantic States, while in the Piedmont section the Cecil series occupies the greatest area and are the soils of the greatest importance agriculturally. The data show very strikingly that the total amounts of phosphoric acid and nitrogen present in all the different types of soil on which the experimental fields are located are each much smaller than is the amount of potash. From these facts alone, with reference to the different types under consideration, the only inferences that could safely be made would be that potentially most of the soils are fairly well supplied with potash, but that the amounts of phosphoric acid and nitrogen, one or the other, or both, are at present, or soon will be, limiting factors in the production of large crops.

AVERAGE LBS. PLANT FOOD IN SURFACE 6 $\frac{1}{2}$  IN. OF SOIL PER ACRE OF SOME OF THE LEADING SOILS IN THE COASTAL PLAIN AND PIEDMONT REGIONS

Type and Location of Soil	N	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	Experimental Field
<b>COASTAL PLAIN</b>				
Portsmouth Fine Sandy Loam.....	1660	590	7051	Pantego
Portsmouth Silt Loam.....	1131	555	28884	Edenton
Norfolk Sand.....	1275	298	1978	Greenville
Norfolk Fine Sandy Loam.....	912	546	8873	Edgecombe
Norfolk Sandy Loam.....	639	1439	4552	Goldsboro
<b>PIEDMONT</b>				
Cecil Clay.....	1285	1430	17743	Charlotte No. 1
Cecil Sandy Loam.....	801	571	49260	Gastonia
Cecil Loam.....	865	1512	27702	Charlotte No. 2
Iredell Loam.....	909	2238	4247	Iredell

The economical increase of the nitrogen supply of all these soils for the production of general crops like corn, cotton, or oats will have to be brought about largely by the growing of leguminous crops in rotation with these and possibly other general field crops and turning a part of these into the soil for soil improvement. By this means, not only can the nitrogen supply of the soil be kept up, wholly or largely, but the soils will be kept in good physical condition by the organic matter turned into them. It will probably be necessary, with many of our soils, where this practice is followed, to add lime in fairly liberal amounts at intervals of 4 to 6 years. On the other hand, in the case of phosphoric acid, its supply for plant growth will have to be kept up in most cases by additions of some material carrying the plant food constituent in more or less readily available form (e. g., acid phosphate, basic slag, phosphate rock or ground bone) if large crops are expected to be produced. In some of the leading types of soil occurring in the South the total amount of phosphoric acid is very low. Potentially soils of the Iredell and Houston series are some of our richest in phosphoric acid supply. This has been brought out both by chemical examination and by field experiments.

#### WHAT FERTILIZER EXPERIMENTS IN FIELD SHOW

For the Coastal Plain section and the Piedmont section the following general deductions which will have wide application throughout the Southern States, may be made from data obtained in field experiments:

**COASTAL PLAIN SOILS** With *Portsmouth fine sandy loam* the chief deficiency is generally for nitrogen in available form. Next in importance to be supplied are lime and phosphoric acid.

For the *Portsmouth silt loam* type, plant food constituents producing the greatest returns when added to the soil are phosphoric acid, nitrogen and lime in the order given.

For the *Norfolk sand* type of soil, the chief deficiencies are shown by our results to be *first*, nitrogen; *second*, lime; and *third*, potash. For the *Norfolk fine sandy loam* the main deficiencies of the soil have shown up to be *first*, nitrogen; *second*, potash; and *third*, phosphoric acid and lime. This type of soil is one of the largest in extent and importance of all the Coastal Plain soils. Field observation on the *Norfolk sandy loam* soil has shown that the chief plant food requirements are for nitrogen, lime and potash in the order given. Phosphoric acid, when used, seems to have on an average caused a decrease in yield of all the crops except in the case of cotton. Ordinarily with all the Norfolk series of soils of the Coastal Plain Region, phosphoric acid and potash give little or no increase in crop yields until nitrogen has been added to the soil.

**PIEDMONT SOILS**—The chief deficiencies of the *Cecil Clay* type of soil have been shown by the field results to be nitrogen, lime and phosphoric acid. The chief plant food requirements of the *Iredell Loam* type of soil have been shown to be *first*, nitrogen decidedly; and *second*, potash. On an average, phosphoric acid has seemed to decrease rather than prove beneficial when applied to this type of soil. Nitrogen, phosphoric acid and lime have been shown to be the chief requirements of the *Cecil Sandy Loam* of this field.

In the production of grain and seed cotton on average *Cecil Loam* soil, phosphoric acid was found to be the chief deficiency while applications of nitrogen gave the greatest response when hays were grown. Practically no grains on an average were secured from the use of lime and potash, except in the case of lime, in the growing of oats for hay, and in the case of potash in growing red clover for hay.

Taking the results as a whole for the leading soils of both the Coastal Plain and Piedmont sections, which no doubt have wide application to soils throughout the South Atlantic States, it will be seen that the chief needs for plant growth in the Coastal Plain Region are generally, *first*, for nitrogen, and *second*, for potash and lime. Those soils of chief importance and extent in the Piedmont Region show a lack *first*, for phosphoric acid and *second*, for nitrogen. Without the addition of these deficient plant food constituents, it will be impossible to grow large crops for any great length of time, for, with most of the types of soil of these two regions of the South, the growth of 2500- to 3100-bu. crops of corn would require an amount of phosphoric acid and nitrogen equal to the total amount of these two constituents contained in most of the Coastal Plain and Piedmont soils.

## LABORATORY AND PLANT

### THE PRINCIPLES OF COUNTER-CURRENT EXTRACTION

By W. K. LEWIS

Received May 2, 1916

A large number of processes in chemical engineering practice involve the transfer of some substance from one to the other of two bodies. This process is in general spoken of as extraction. For the sake of clearness we shall designate the body bringing into the system or process the matter which it is desired to transfer to some other body as the "carrier." The matter which the carrier brings into the system and which is to be transferred to some other body shall be called the "solutum."<sup>1</sup> The body which is to absorb the solutum from the carrier and thus take it out of the system, shall be called the "extractor." It is therefore the function of the extractor to absorb from the carrier, in general as completely as possible, the solutum, either for the purpose of recovering the solutum in the extractor or for removing the solutum from the carrier, or in certain cases for both. To secure efficiency of extraction the principle of the counter-current must be employed, *i. e.*, fresh carrier entering the system must be treated first not with fresh extractor, but with extractor which is already nearly saturated with solutum from contact with previous batches of carrier, while toward the end of the system fresh extractor as free as possible from solutum must be used for final removal of solutum from the carrier.

The calculation and design of systems for counter-current extraction is at present a matter of empiricism. Several years ago this laboratory undertook the study of the problem and a large amount of work has been done upon it. The problem is by no manner of means an easy one and especially from the experimental side the verification of the methods of calculation developed has been a difficult matter, but our results, while even yet incomplete, are sufficiently definite to justify us in presenting our methods of calculation and our data, especially in view of the fact that these things are greatly needed by the profession.

We first present the formulas which we have developed and later the experimental evidence which we have accumulated indicating the validity of our methods of calculation. The derivation of the formulas we shall add separately.

#### GENERAL CONSIDERATIONS

If a carrier and extractor be brought into contact any solutum present will distribute itself between the two and ultimately an equilibrium will be attained. The concentrations of solutum in carrier and extractor will at equilibrium bear a certain relation to each other and this distribution of solutum between the two phases will usually follow, at least approximately, one or the other of two laws. If we

<sup>1</sup> This term, the word formerly used for solute, is employed because the thing transferred, especially when a material substance, can usually be conceived as in solution; the use of the word *solutum* rather than *solute* will indicate that a transfer from one phase to another is under consideration, that the separate phases need not be solutions in the ordinary sense, and that the thing transferred may be either energy or matter.

call the concentration of solutum on the carrier  $x$  and in the extractor  $y$ , we shall have either  $x = \alpha y$  or  $x = \alpha y^{1/n}$ . In the first case the solutum is said to be linearly distributed between carrier and extractor, while in the second case the solutum is spoken of as adsorbed upon the carrier. The nature of the extraction process is decidedly different in the two cases.

When carrier and extractor are brought together this equilibrium is not immediately set up, but, on the other hand, solutum passes from one phase to the other at a rate depending upon the specific case and conditions involved. It is exclusively this rate of interchange of solutum between carrier and extractor which determines the capacity of any industrial system.

Both the equilibrium conditions and the rate of transfer of solutum from one phase to the other are subject to the influence of a number of variables such as the nature of both carrier and extractor, the temperature, the pressure, the concentration of solutum in both phases, the viscosity of the phases, etc. On the other hand, most of these variables are fixed by the nature of the case. For example, if we are extracting tannic acid from hemlock bark the extraction must be carried out with water as an extractor. The distribution of tannic acid between hemlock bark and water is itself influenced by both temperature and concentration, but inasmuch as extraction is always more rapid the higher the temperature, we shall employ in extraction the highest temperature possible. The temperature may be limited by the boiling point of the solution obtained, by deterioration of the tannin extract, or by the extraction at too high temperatures of excessive amounts of non-tannin material. In any case, however, the temperature of extraction is dictated by considerations which are not under control of the designer of the extraction system. While it is also true that the concentration influences the distribution and the extraction, the initial concentration of the tannin on the bark is determined absolutely by the tannin content of the bark available for extraction, and furthermore, even the concentration of tannin left on the bark is dictated by the necessity of securing as high a tannin recovery as possible, so that the initial, and to at least a degree, the final concentration are not subject to variation. On the other hand, the concentration of the tannin in the extract obtained can be varied by the designer within wide limits by the use of larger or smaller quantities of water for the extraction. The rate of extraction will be greater the greater the concentration difference between carrier and extractor, and it is therefore primarily this which can be varied in a given system. If this concentration difference becomes small so that the two phases are nearly in equilibrium, the rate of transfer of solutum will become negligible and to secure an appreciable transfer will require an excessive time. The two variables



which the designer of a counter-current system can control are in general the ratio of extractor to carrier and the size of the extraction system, or what is equivalent to the same thing, the time of contact between carrier and extractor. In the following discussion we shall assume that all other variables such as the nature of extractor, carrier and solutum, the temperature and pressure of extraction, the distribution law between the phases, etc., are beyond the control of the designer and are therefore fixed for the given case. The following treatment is a study of the influence of the time of contact and ratio of extractor to carrier upon any extraction system.

In all extraction systems either carrier or extractor is a fluid: *i. e.*, either a liquid or a gas. Furthermore, either one or the other of these phases is finely divided, the separate particles being more or less completely separated from each other and offering a large surface of contact, while the other phase, which is always a fluid phase, fills the voids between the particles of the first. For example, in the extraction of solids such as tan bark, pyrites cinder, black ash, and the like, with liquids, the solids are always divided and completely immersed in a continuous liquid medium. In the washing of gases, *e. g.*, benzol and ammonia from coal gas, the washing liquid is separated in the form of either a spray or exposed in a large surface for contact with the gas. In any case it is probable that the extraction process consists primarily in the diffusion of the solutum through a stationary layer of fluid which envelops separate particles of the finely subdivided phase. The fluid in immediate contact with the separate particles is probably nearly in equilibrium with them and the diffusion process is determined by the difference in concentration between the saturated solution on the very surface of the separate particles of the dispersed phase and the main body of the solution around those particles but outside of the stationary surface film. Our formulas are derived upon the assumption of this mechanism.

Assuming the nomenclature given in the list below, our formulas are as follows: For the case of the extraction of solids by liquids,

$$\log \left[ 1 + \frac{c_1}{x_0} (\rho - \alpha) \right] = \frac{\beta u V}{\alpha A^2} (\rho - \alpha).$$

For the case of transfer of solutum from a gas to a liquid or *vice versa* they become,

$$\log \frac{x_0 - \alpha c_0}{x} = \frac{K V}{u} (\rho - \alpha),$$

for apparatus in which the velocity of gas past the liquid is constant (spray washers), or

$$\log \frac{x_0 - \alpha c_0}{x} = \frac{\beta U l}{\rho A} (\rho - \alpha),$$

for apparatus in which the absorbing liquid forms a film over a stationary surface.

#### DERIVATION OF FORMULAS

The mechanism by which the solutum is removed from the carrier by the extractor is assumed to be as follows: The more fluid medium (either liquid or gaseous) forms a film on the surface of the other phase,

which is practically stationary. Let us consider first the extraction of a solid carrier by a liquid extractor. In immediate contact with the carrier, on the interior of this film, the extractor is saturated with solutum, the equilibrium between the carrier and the extractor being practically perfect at this particular point. The concentration of the solutum in the body of the extractor is, however, considerably lower than this, and the solutum diffuses through this stationary film according to ordinary diffusion laws. A more complete discussion of the factors governing diffusion will be given later.

In considering the extraction we may look at the matter from either one of two points of view. Either we may consider the decrease in concentration of solutum on the carrier or the increase in concentration in the extractor. The total amount of solutum given up by the one must of course be equal to that taken up by the other. If we designate, by  $t$ , the time of contact of extractor with carrier, leaving the exact formulation of this quantity,  $t$ , for later discussion, we may write the equations

$$(1) \quad \frac{dc}{dt} = k(c' - c), \text{ and } (2) \quad \frac{dx}{dt} = K(c' - c),$$

$c$  being the concentration of the solutum in the liquid extractor at any particular point in the apparatus,  $x$  the concentration of the solutum on the carrier at the same point, and  $c'$  the concentration of solutum in the extractor in immediate contact with the surface of the carrier, and therefore, from what has been said above, in equilibrium with the solutum on the carrier. The two constants  $k$  and  $K$  will not necessarily be identical, but there will exist between them a proportionality which will be developed later.

The value of  $c'$  is a function of  $x$ , two cases requiring consideration. In the first of these quantities in the two phases are proportional and we may write

$$(3) \quad x = \alpha c'.$$

In the case we are considering, namely, the extraction of a solid by a liquid, this relationship probably never rigidly holds. On the other hand, in many cases of this type this equation is a very close approximation of the facts and enables us very satisfactorily to calculate the behavior of extraction systems. The two most important cases are, first, those in which the solid carrier is a porous material and holds the solutum in it merely as a solution contained in its pores. Such is the case in the extraction of copper sulfate from pyrites cinder, of grease from wool, and of various substances from organic fibers by the use of organic solvents, etc. The second case is that of a solutum held in a gel, as for example salt in skins. In both these cases diffusion out of the carrier is experimentally found to be nearly proportional to the difference in concentration of the solutum in the extractor held within the pores of the material in the one case, or within the gel in the other, and the concentration in the main body of the extractor. In the second case we have adsorption of the solutum from the liquid upon the carrier, and in that case

it is experimentally found that the relationship existing between  $c'$  and  $x$  is

$$(4) \quad x = \alpha c'^{1/n},$$

$\alpha c'$  and  $n$  being constants, the latter greater than unity, usually having a value between 2 and 20.

In either case we may substitute in (1) the values given for  $c'$  and obtain, when  $x = \alpha c'$ ,

$$(5) \quad \frac{dc}{dt} = k \left( \frac{x}{\alpha} - c \right), \quad \text{and} \quad (5a) \quad \frac{dx}{dt} = K \left( \frac{x}{\alpha} - c \right);$$

when  $x = \alpha c'^{1/n}$

$$(6) \quad \frac{dc}{dt} = k \left( \frac{x^n}{\alpha^n} - c \right), \quad \text{and} \quad (6a) \quad \frac{dx}{dt} = K \left( \frac{x^n}{\alpha^n} - c \right).$$

The integration of these differential equations gives us the solution of the problem in hand.

Let us now apply the principle of the equality of input and output in any continuously operating process. Let us call the weight of carrier passing any section per unit time equal to  $U$ , and likewise the weight of extractor per unit time equal to  $u$ . Call the concentration of solutum on the carrier and in the extractor, at one end or the other of the system, in general, at that end where the fresh extractor enters the system, equal to  $x_0$  and  $c_0$ , respectively. Usually  $c_0$  will be equal to zero. The equality of input and output requires that

$$(x - x_0)U = (c - c_0)u.$$

For the usual case where  $c_0 = 0$ ,

$$(7) \quad x = x_0 + \frac{uc}{U}.$$

Inserting this value in the above equation we obtain

$$(8) \quad \frac{dc}{dt} = k \left( \frac{x_0}{\alpha} + \frac{uc}{\alpha U} - c \right)$$

or

$$\frac{dc \left( \frac{u}{\alpha U} - 1 \right)}{x_0 + \frac{uc}{\alpha U} - c} = k dt \left( \frac{u}{\alpha U} - 1 \right).$$

Integrating,

$$\log \left[ \frac{x_0}{\alpha} + \left( \frac{u}{U\alpha} - 1 \right) c \right] = kt \left( \frac{u}{\alpha U} - 1 \right) + \text{const.}$$

The limits are as follows:

$$\left. \begin{array}{l} l = 0 \quad t = 0 \quad c = 0 \quad x = x_0 \quad \text{constant of inte-} \\ l = l \quad t = t \quad c = c_1 \quad x = x_1 \quad \text{gration} \end{array} \right\} = \log \frac{x_0}{\alpha}$$

$$(9) \quad \left[ \frac{x_0}{\alpha} + \left( \frac{u}{U\alpha} - 1 \right) c_1 \right] = kt \left( \frac{u}{\alpha U} - 1 \right) + \log \frac{x_0}{\alpha}$$

#### ADSORPTION

If  $x_0 + \frac{uc}{U}$  be substituted for  $x$  and  $\rho = \frac{u}{U}$  in Equation (6) we obtain

$$(10) \quad \frac{dc}{dt} = k \left[ \left( \frac{x_0}{\alpha} + \rho c \right)^n - c \right]$$

or

$$(11) \quad \int_{c=0}^{c=c} \frac{dc}{\left( \frac{x_0}{\alpha} + \rho c \right)^n - c} = kt.$$

This equation may be integrated graphically but will not be further discussed here. In consequence of its importance we shall treat this case at some future time.

#### NATURE OF DIFFUSION PROCESS

The constants  $k$  and  $K$  are in reality diffusion constants, representing the rate at which diffusion will take place under conditions of unit difference of concentration and unit distance of flow. These constants will depend upon the solutum involved, upon the fluid medium through which the flow takes place (i. e., upon the extractor), upon the temperature, and perhaps also upon still other variables. On the other hand, in general all these variables will be fixed by the conditions necessarily imposed upon the engineer; e. g., in the extraction of grease from wool, petroleum naphtha is the only solvent available on account of the greater expense of other materials. Furthermore, the temperature to be employed for the extraction will be limited rigidly by the boiling point of this material unless the system be kept under pressure, and in that case by the allowable pressure in the system. In the same way in all cases the extractor which must be employed, the highest temperature which it is possible to utilize, and other such variables will not be at the discretion of the engineer, but beyond his control. If in any case these things are capable of modification, each new possible modification must really be considered as a separate problem, to be solved by the methods outlined in this discussion.

This being the case, the only factors which the engineer can control are, in the first place, the time of contact of the carrier with the extractor and, in the second place, the amount of extractor used per unit amount of carrier treated. It will be developed later that the velocity with which the extractor flows past the carrier is also an important factor, which is to a greater or less extent under the control of the engineer.

The discussion of the matter of time of contact now becomes necessary. If we consider a single particle of the carrier passing through any given system, that particle will remain in the system a certain length of time, and that time is the time of contact of that particle of solid carrier with the extractor, and such we might define it to be. On the other hand, if we consider a drop of the liquid extractor flowing through the system, this drop of extractor will also be in the system a certain length of time, depending upon its linear velocity and the length of the system. This drop will not, however, be in contact with the carrier throughout the whole of its path. Indeed, it is practically impossible in this case to define contact at all, but if we agree to consider the drop as in contact with the carrier during any time when it is within a certain maximum distance of the carrier surface, the drop will be in contact with the carrier a certain definite fraction of the total time the drop remained in the system, that fraction depending in general upon the amount of carrier in the system and being proportional to that amount. Thus, if in extracting wool, in one case we pack into an extraction tank twice as much wool as in another case, a drop of solvent passing through this tank will have twice the chance to come in contact with the fiber,



and its time of contact will thus in a very real sense be twice as great as under the second assumption. The actual value of the time of contact of the drop of extractor with the carrier will depend upon our arbitrary assumption as to the limiting distance between carrier and drop beyond which contact is neglected. Inasmuch as this assumption would be an entirely arbitrary one, it is allowable and advisable to omit this particular factor altogether and to define arbitrarily the time of contact of the liquid with the carrier as the average time which any particular drop of liquid remains in the system. This time must be multiplied by the amount of carrier per unit volume of the system unless this quantity, as is usually true, is constant.

Another factor influencing the time of contact is the surface which the carrier exposes to the action of the extractor. Thus the more finely divided the carrier, the greater its surface per unit amount, and in case the influence of surface, or what is the same thing fineness of subdivision of the carrier, is to be taken into consideration, the time of contact must be defined as proportional to the surface per unit weight of the carrier. On the other hand, this quantity is usually fixed, owing to the fact that the carrier is either not subdivided at all to avoid the expense of grinding, or else is subdivided as far as possible without causing packing of the material in the extraction tanks, resulting in interference with the extraction process. This matter of surface exposure of the carrier is therefore generally not one which is varied in a given extraction system.

It must be realized that these definitions of time of contact are arbitrary ones, the time of contact being really proportional to the factors which we have mentioned, but inasmuch as the proportionality constant cannot possibly be determined except by making arbitrary assumptions, the simplest thing to do—and a thing entirely admissible—is to make the proportionality factor equal to unity. Time of contact may therefore be defined as the time the extractor or carrier, as the case may be, is in the system, times the weight of carrier per unit volume of the system, and also times the surface of the carrier per unit weight. Usually these last two terms are omitted provided they are not subject to variation.

If the carrier per unit volume of the system be constant, the voids between the particles of carrier will also remain unchanged, and the time of contact will therefore be proportional to the total volume of the extraction system, divided by the amount of carrier or extractor per unit time. We shall therefore limit ourselves throughout to this definition of time of contact, *i. e.*,

*Time of contact of carrier* =  $\frac{\text{total volume of system}}{\text{amount of carrier per unit time.}}$

*Time of contact of extractor* =  $\frac{\text{total volume of system}}{\text{amount of extractor per unit time.}}$

Returning again to the diffusion constants  $k$  and  $K$ ,

and indicating the time of contact of the carrier by  $t_x$  and of the extractor by  $t_c$ , Equations (5) and (5a) become,

$$\frac{dc}{dt_c} = k \left( \frac{x}{\alpha} - c \right), \text{ and } \frac{dx}{dt_x} = K \left( \frac{x}{\alpha} - c \right).$$

Dividing,

$$\frac{dc}{dx} = \frac{k}{K} \frac{dt_c}{dt_x}.$$

However, from the equation

$$(x - x_0)U = (c - c_0)u,$$

$$\frac{dc}{dx} = \frac{U}{u} = \frac{k}{K} \frac{dt_c}{dt_x}.$$

Integrating, remembering that zero contact for carrier must also be zero contact for extractor,  $\frac{U}{u} = \frac{k}{K} \frac{t_c}{t_x}$ .

This equation represents the relationship which must exist between the constants  $k$  and  $K$ , the ratio of carrier to extractor, and the times of contact,  $t_x$  and  $t_c$ . The constants  $k$  and  $K$  are in reality diffusion constants, as previously pointed out, and it is desirable to have them numerically identical. They will be numerically the same provided  $ut_c = Ut_x$ . By definition we have arbitrarily chosen to place

$$t_x = \frac{V}{U}, \text{ and } t_c = \frac{V}{u}.$$

It is evident that these definitions meet the above requirement, so that with these definitions of time of contact the diffusion constants are the same no matter whether carrier or extractor are under consideration.

It will be shown later that the diffusion constant,  $k$ , increases with increasing velocity of extractor. The data on this point is inadequate, but seems to justify as a preliminary assumption the relationship,

$$k = K = \beta \left( \frac{u}{A} \right)^2,$$

where  $A$  is the cross section of the extraction system, and  $\beta$  a constant the value of which depends entirely upon the carrier, extractor, and solution involved, the *fineness* of the particles of carrier, the temperature of the extraction, etc. The value of  $\beta$  must be determined for each specific case.

Inserting these values in (9) there results,

$$(9a) \quad \log \left[ 1 + \frac{c_1}{x_0} (\rho - \alpha) \right] = \frac{\beta u V}{\alpha A^2} (\rho - \alpha).$$

#### INTRODUCTION OF NEW TANKS

The calculation of a counter-current system for extracting a solid carrier with a liquid extractor is rendered complicated by the fact that it is impossible to realize perfect counter-current conditions. To secure absolute counter-current flow both carrier and extractor must enter the system at a uniform rate. In the extraction of a solutum from a solid carrier, the carrier is usually put into a tank, and at definite intervals of time, tanks of fresh carrier are introduced into the system. The system is then run with continued addition of extractor, but without the addition of further carrier until the next tank is inserted into the system. To allow for this lack of continuity in

extraction, in any exact way, would be very difficult, but an approximation can readily be made, which will introduce no greater error than the other assumptions we have been compelled to use. When a new tank of fresh carrier is inserted into the system, the inflow of extractor at the other end of the series is changed from that tank which is most nearly extracted and into which fresh extractor has been running, to the next in the series, and the extractor continues to flow into this tank until the next change of tanks in the system, *i. e.*, throughout one cycle of operations. At the beginning of this cycle the top of this tank is the head of the system. At the end of this cycle the top of the next tank becomes the head of the system, and therefore it will not involve serious error if we assume that during this cycle the average position of the head of the system has been at the middle of this tank. In other words, during this cycle only one-half of this tank has really been an effective part in the counter-current extraction system.

Considering now the tank which has just been inserted into the series, at first, extract from the previous tanks flows into this tank until all the voids have been filled; until this stage is reached this tank is not in any way a part of the real counter-current system. When this state is reached the tank becomes active in a sense, but, on the other hand, during a large part of the rest of the time the liquid in this tank is merely being displaced by inflowing liquid and no extraction in the tank starts until this displacement is completed. It is possible to estimate when this displacement is finished, but, on the other hand, in general, this tank will be for so slight a time a really effective part of the counter-current system that in general the whole tank may be neglected. If we do this, this means that both this tank and one-half of the first tank are not in actual operation, and the net length of the counter-current system may be approximated by subtracting from the total number of tanks in operation 1.5. Inasmuch as one tank is out of the system entirely, being refilled, this means that 2.5 less than the total number of tanks in the system are in effective operation at any one time.

Furthermore, the liquid obtained as effluent from the last tank of such a system cannot be considered as having the same concentration as that which is obtained from the true counter-current system itself.

The reason for this is that the liquid flowing from the real counter-current system into the tank of fresh material first mixes with that material, dissolves the solutum from that material, and then delivers the product of the system as a whole before a new tank is inserted into the series. While the product of the counter-current extraction system is not of constant composition on account of the discontinuity of operating conditions, we may without serious error, assume it to be of a definite *average* composition which we shall call  $c_1$ . The composition of the liquid in the fresh tank obtained by admixture of the fresh charge with the liquid necessary to fill the voids flowing upon this charge from the true counter-cur-

rent system we shall call  $c'$ . The concentration of the solutum on the carrier as it enters the system originally is  $x'$  and of the solutum on the carrier as it enters the counter-current system from the last tank  $x_1$ . We shall now assume that there is no adsorption of solutum on the carrier, but that the solutum is held in the voids within the carrier itself. As soon as the extractor from the true counter-current system enters a new tank of carrier which has just been inserted into the series, this extractor completely dissolves all the solutum in the carrier and forms a solution which we shall assume to be homogeneous both in the voids of the carrier itself, and in the voids between the particles of carrier in the tank. Unquestionably, in the majority of cases this is practically what happens, and the following equations apply only to these cases. The equations are merely an expression of the equality of input and output to the last tank in the series and to the series as a whole.

$S$  = volume of product

$P$  = volume of each tank actually filled by solid carrier

$Q$  = volume of each tank occupied by voids in carrier

$R$  = volume of each tank occupied by voids between carrier

$P + Q + R$  = the total volume of each tank not including excess space above the top of the mixture

$D$  = wt. of solid carrier per unit volume of the carrier itself

$d$  = wt. of liquid extractor per unit volume of the solution

In each cycle the total carrier entering the system is enough to furnish the product,  $S$ , and fill the voids within the carrier  $Q$ . The ratio  $\rho$ , of extractor to carrier, is therefore

$$(a) \quad \rho = \frac{(S + Q)^1}{PD}$$

If equilibrium exists between carrier and extractor, the concentration,  $c$ , of solution in all the voids both within and around the carrier will be the same. The amount of solutum in the voids within the carrier will therefore be  $dQc$ , the corresponding weight of carrier itself being  $PD$ . Since, however, the concentration,  $x$ , of solution in the carrier is to be expressed as parts by weight of carrier, it must be true that

$$DPx = dQc, \text{ or } \frac{DPx}{dQ} = c, \text{ or if } \frac{DP}{dQ} \text{ be called } \alpha, \\ (b) \quad c = \alpha x.$$

Equations (a) and (b) hold in all cases.

Three cases arising in industrial practice must now be differentiated:

CASE 1,  $S=R$ : When a tank of fresh carrier is inserted into a series the cycle through which it passes before the insertion of another tank can be divided into two stages: in the first, liquid entering from the previous tank fills all the voids in the charge. This liquid enters at a concentration  $c_1$ , bringing in an amount of solutum  $d(R + Q)c_1$ , and dissolves all the solutum on the carrier,  $PDx'$ , filling all the voids with a uniform solution of concentration  $c'$ . Hence

$$(c) \quad (R + Q)dc' = (R + Q)dc_1 + PDx' \\ \text{or} \\ d(R + Q)(c' - c_1) = PDx'.$$

All of the solutum extracted from the carrier during the total

<sup>1</sup> At this point one must keep clearly in mind the distinction between motion of both carrier and extractor past a section of constant concentration and motion of carrier and extractor relative to each other. The first is the essential in determining  $\rho$ . In the case under discussion the carrier remains stationary, so that motion of the extractor past a fixed point in the apparatus is greater than the value of  $\rho$  would indicate.



process is equal to DP multiplied by  $(x' - x_0)$ , the difference in the concentration of the solutum on the carrier at the beginning and at the end of the operation. The solutum extracted is also equal to  $dS$  multiplied by  $(c' - c_0)$  the difference in the concentrations of the solutum in the extractor at the beginning and the end of the operation. The concentration of the solutum in the extractor is generally zero at the start of the extraction; therefore,

$$(d) \quad dSc' = DP(x' - x_0).$$

CASE 2,  $S > R$ : In this case during a cycle a fresh tank passes through three stages: *First*, a volume of effluent from the true counter-current system sufficient to fill the voids enters at a constant concentration  $c_1$ , bringing in a weight of solutum  $dc_1(R + Q)$ , dissolving the solutum on the charge  $x'DP$ , and producing a solution of concentration  $c'$ , such that, as before,

$$(c) \quad d(R + Q)(c' - c_1) = DPx'.$$

*Second*, after the tank becomes full the product begins flowing from the tank, and a volume,  $R$ , is collected at the concentration  $c'$ . *Third*, in order to make up the total product,  $S$ , further volume,  $S - R$  is removed as product at the concentration  $c_1$ . The solution removed as product is therefore the sum of the two, or,

$$(d) \quad c'dR + c_1d(S - R) = PD(x' - x_0).$$

This equality represents the equality of input and output in the extraction system as a whole

CASE 3,  $S < R$ : In this case, during a cycle a fresh tank also passes through three stages. When the tank enters the series the solution of concentration  $c'$  has not been completely displaced from the previous tank. There therefore enters the tank a volume,  $R - S$ , at concentration  $c'$ , and the tank is then filled with a solution  $Q + S$  at concentration  $c_1$ , giving

$$(c) \quad (R - S)dc' + (Q + S)dc_1 + DPx' = (Q + R)dc', \text{ or} \\ d(c' - c_1)(Q + S) = DPx'.$$

Inasmuch as the product has a constant concentration,  $c'$ ,

$$(d) \quad dc'S = DP(x' - x_0).$$

By means of these equations one can estimate the conditions at both ends of any counter-current system for which sufficient data are available.

#### WASHING OF GASES

We have now completed the consideration of the extraction of a solid carrier by a liquid extractor. It will be remembered that we pointed out that the extraction of a gaseous carrier by a liquid extractor was in all essentials similar. The calculations in this latter case are indeed simplified by the fact that true counter-current conditions are usually realized in industrial practice.

The equations expressing the rate of extraction of a gas by means of a liquid are very similar to those previously derived for the counter-current extraction of a solid by means of a liquid.

$$(14) \quad \frac{dc}{dt_c} = k(p - \alpha c), \quad (15) \quad \frac{dx}{dt_x} = -K(p - \alpha c).$$

$\alpha$  is the solubility constant,  $\frac{1}{u}$ , the ratio of the partial pressure in the vapor to the concentration in the liquid.

If the pressure in the apparatus be chosen as unity then

$$p = \frac{x}{1 + x}.$$

$\frac{x}{1 + x}$  is the mol fraction of absorbable component in the gas at any point in the system.

If  $x$  be small in comparison with  $1 + x$  we may assume  $p = x$ .

The equality of input and output requires that  $(x - x_0)U = (c - c_0)u$ .

Inserting these values in Equation (14) and integrating we obtain,

$$\log \frac{x_0 - \alpha c_0}{x - \alpha c} = \log \frac{x_0 - \alpha c_0}{x_0 - \rho(c_0 - c) - \alpha c} = \log \frac{x_0 - \alpha c_0}{\rho(c - \alpha)} = \log \frac{p_0 - P_0}{p - P},$$

or as for  $V = V_1$ ,  $c = 0$

$$(16) \quad \log \frac{x_0 - \alpha c_0}{x_0 - \rho c_0} = \frac{kV_1}{u} (\rho - \alpha).$$

Experimentally it is found that  $k = \frac{\beta U^2}{A^2}$ .

$$(16a) \quad \log \frac{x_0 - \alpha c_0}{x_0 - \rho c_0} = \frac{\beta VU}{\rho A^2} (\rho - \alpha) = \frac{\beta Ul}{\rho A} (\rho - \alpha) = \log \frac{x_0 - \alpha c_0}{x}.$$

If  $\alpha = 0$ , without neglecting  $x$  in the denominator of the mol fraction,

$$(17) \quad \log \frac{x_0(1 + x)}{x(1 + x_0)} = \frac{\beta UV}{A^2} = \log \frac{f_0}{f} = \frac{\beta Ul}{A},$$

where  $f$  may be either the fraction or the per cent of the absorbable gas at the points indicated. This is the equation to use where chemical combination of solutum with extractor occurs, *e. g.*, for the absorption of  $\text{NH}_3$  by  $\text{H}_2\text{SO}_4$ .

Equation (16a) becomes indeterminate for  $\rho = \alpha$ . In this case, and indeed whenever  $\rho$  and  $\alpha$  are nearly equal, (16a) simplifies to

$$(16b) \quad \frac{c_0}{x} = \frac{kV}{u} = \frac{\beta Vl}{\rho A}.$$

The equation for the washing of gases can be written as follows:

$$\log \frac{P_0 - p_0}{P - p} = kV \left( \frac{1}{U} - \frac{\alpha}{u} \right)$$

But from (7),  $U(P - p_0) = \frac{u}{\alpha}(p - p_0)$

$$\text{whence } \frac{1}{U} = \frac{\alpha}{u} \left( \frac{P - P_0}{p - p_0} \right).$$

$$\text{Hence } \log \frac{P_0 - p_0}{P - p} = \frac{kV\alpha}{u} \left( \frac{P - P_0}{p - p_0} - 1 \right) = \frac{kV\alpha}{u} \left( \frac{P_0 - p_0 - P + p}{p - p_0} \right) = kV \frac{[(P_0 - p_0) - (P - p)]}{u(c - c_0)}; \\ \text{or } u(c - c_0) = kV \frac{[(P_0 - p_0) - (P - p)]}{\log \frac{P_0 - p_0}{P - p}},$$

or the amount extracted per unit time equals the diffusion constant  $k$ , times the volume of the apparatus  $V$ , times the logarithmic mean of the pressure differences of the solutum in gas and liquid at the two ends of the apparatus.

We have, therefore, the amount of solutum transferred proportional to the logarithmic mean of the pressure difference, an expression strikingly similar to the law for the flow of heat between bodies, in which case the logarithmic mean should also be employed. It is helpful to consider an extraction system as in all respects similar to a system for the transfer of heat, and indeed apparatus for the transfer of heat from one body to another which embodies the counter-current principle can be looked upon as a counter-current extraction system in which the solutum is not matter but energy in the form of heat.

It is very important to keep in mind the fact that the equations developed from the differential expression involving the rate of transfer of solutum from carrier to extractor—and involving therefore the diffusion

constants  $k$  and  $\beta$ —are equations having to do only with the velocity of interchange of solutum from one phase to the other. They are, therefore, the equations which determine the *extraction capacity per unit volume* of the system in question. If a given system is operating entirely satisfactorily from this point of view of capacity per unit volume, and it is merely desired to change extraction capacity of the system as a whole not by changing the concentration relationships at different points in the system, but by enlarging the system proportionally at every point, it is unnecessary to involve any of the equations containing the constants  $k$  or  $\beta$ . Equations involving the constants  $k$  or  $\beta$  are necessary only where it is desired to modify the performance of the system by changing the concentration relationships at comparable points within the system.

Where, therefore, a given system is operating satisfactorily and it is merely desired to build a larger or smaller system to accomplish the same purpose on a correspondingly larger or smaller scale, it is merely necessary to see to it that in the new system the values of time contact  $t_x$  and  $t_c$ , the ratio of extractor to carrier, and the velocity of the liquid phase through the system, *i. e.*,  $u/A$  in the case of the extraction of a solid by a liquid, and  $U/A$  in the case of the washing of a gas, remain constant. It would be unnecessary to maintain the velocities constant were it not for the fact that these velocities so greatly change the value of the extraction constant  $k$ .

To avoid misunderstandings in the use of the preceding formulas, the following tables of definitions of the quantities involved are appended.

## NOMENCLATURE

SYMBOL	SIGNIFICANCE	DEFINITION FOR EXTRACTOR OF Gas by a Liquid
$ca$	Carrier	
$so$	Solutum	
$ex$	Extractor	
$c$	Concentration of $so$ in $ex$	Ratio of weight of $so$ to weight of $ex$ in which it is held at any point in the system
$x$	Concentration of $so$ on $ca$	Ratio of weight of $so$ to weight of $ca$ on which it is held at any point in the system
$p$	Partial pressure of $so$	Partial pressure of $so$ in the liquid $ex$ , total pressure in the apparatus being taken as unity
$\alpha$	Solubility constant	Defined by the equation $x = \alpha c$ which holds when $so$ on $ca$ and $ex$ are in equilibrium. (Does not hold for adsorption)
$u$	Velocity of $ex$	Weight of $ex$ per unit of time
$U$	Velocity of $ca$	Weight of $ca$ per unit of time
$V$	Total volume of extraction system	Units of volume
$t_c$	Time of contact of $ex$	$t_c = V/u$
$t_x$	Time of contact of $ca$	$t_x = V/U$
$\rho$	$Ex$ employed per unit amount of $ca$ treated	$\rho = u/U$
$\beta$	Diffusion constant	$\beta = kA^2/u^2$
$K$	Diffusion constants	Where $k$ and $K$ are identical; value depends on the particular system
$k$	Volume of product	Units of volume
$S$	Volume of apparatus filled by carrier	Partial pressure of $so$ in the gaseous carrier, total pressure in the apparatus being taken as unity
$Q$	Volume of apparatus filled by voids in $ca$	Units of volume
$R$	Volume of apparatus occupied by voids between carrier	Units of volume

It will be apparent that throughout this discussion the functions of carrier and extractor will be reversed if the concentration or pressure differences be of opposite sign.

## EXPERIMENTAL INVESTIGATION

Preliminary work was carried out by Mr. A. W. Kenney in the spring of 1913. The system employed consisted of porous coke saturated with sodium hydrate solution. Work with this indicated in a qualitative way the lines which the investigation would have to pursue, but no quantitative results of value were obtained. During the next year Mr. Kenney<sup>1</sup> followed up the work with a study of a counter-current extraction system, removing  $SO_2$  from a gaseous mixture by the use of water as an extractor. At first mixtures of  $SO_2$  and air were employed, but the oxidation to sulfuric acid was excessive and vitiated the results. Finally mixtures of  $SO_2$  and  $CO_2$  were used. A great deal of difficulty was encountered in obtaining satisfactory concentration gradients; this was ultimately traced to variations in temperature. The solubility of  $SO_2$  in water changes very rapidly with the temperature and very slight temperature changes profoundly influence the shape of the concentration curves. It was ultimately found necessary to maintain the whole extraction system at constant temperature by air jacketing and to saturate the gas entering the tower with moisture by bubbling through a wash bottle in order to avoid the cooling effect due to water evaporation into the dry gas which otherwise occurs. The results obtained are given in tabulated form below, but at the time it was impossible to get satisfactory constants from these results by any method of calculation, and the problem seemed almost hopeless. Nevertheless, during the next year the work was taken up by Mr. V. A. Stewart, who studied the absorption of  $CO_2$  by solutions of caustic soda in excess, using the same absorption system as that employed by Mr. Kenney. The results of Mr. Stewart's<sup>2</sup> work are also given in tabular form and again it was found impossible to reconcile the results and to obtain from different runs constants in any way concordant. During the last year a careful study of Stewart's results called our attention to the fact that the absorption was much more rapid the higher the velocity of the gas through the system. In all previous calculations no allowance had been made for variations in gas velocity, but this was now taken into consideration and it was found that the absorption coefficient  $K$  was proportional to the square of the velocity of the gas. Recalculating both the results of Kenney and of Stewart on this assumption we obtain the constants shown in the last column of each table. Realizing that these constants were obtained by methods of calculation, the significance of which was not appreciated until more than a year after the data were collected, and that the variations in conditions in the absorption system were very

<sup>1</sup> Thesis submitted in partial fulfillment of the requirements for the S.M. degree at the Massachusetts Institute of Technology, 1914.

<sup>2</sup> Thesis submitted in partial fulfillment of the requirements for the S.B. degree at the Massachusetts Institute of Technology, 1915.



wide, the degree of coincidence is remarkable. We believe that the results of this work substantiate the accuracy of our assumptions and the reliability of our method of calculation.

TABLE I—REMOVAL OF CO<sub>2</sub> FROM AIR BY EXCESS NaOH

Number of Sections	Mol. fraction CO <sub>2</sub> $\frac{x}{1+x}$	Mols Air per hour U	V	$\beta$
0	0.205			
1	0.045	27.48	260	0.000092
2	0.010		340	0.000080
0	0.083	15.60		
1	0.030		260	0.000109
0	0.252			
1	0.164	11.34	260	0.000063
2	0.082		340	0.000072
0	0.152			
1	0.065	11.88	260	0.000120
2	0.015		340	0.000141
0	0.150			
1	0.093	12.30	260	0.000065
2	0.024		340	0.000108
0	0.124			
1	0.046	12.72	260	0.000130
2	0.034		340	0.000074
0	0.080	16.98		
1	0.030		260	0.000097

TABLE II—REMOVAL OF SO<sub>2</sub> FROM CO<sub>2</sub> BY WATER

U	$\mu$	$c$	T	$\alpha$	$x_0$	% loss	Volume	$\beta$
3.05	0.702	0.0988	21	0.532	0.0625	12.5	0.260	....
..	..	0.0955	..	..	..	..	0.340	....
..	..	0.0870	..	..	..	..	0.320	0.000162
2.23	0.555	0.1057	24	0.531	0.0624	22	0.260	....
..	..	0.1012	..	..	..	..	0.340	....
..	..	0.0917	..	..	..	..	0.320	0.000201
3.86	0.621	0.1160	25	0.535	0.0635	1	0.260	....
..	..	0.1083	..	..	..	..	0.340	....
..	..	0.1000	..	..	..	..	0.320	0.000166
2.89	0.711	0.1106	21	0.531	0.0665	9	0.260	....
..	..	0.1080	..	..	..	..	0.340	....
..	..	0.0922	..	..	..	..	0.320	0.000216
3.40	0.577	0.1150	22	0.532	0.0677	11.5	0.260	....
..	..	0.1110	..	..	..	..	0.340	....
..	..	0.1010	..	..	..	..	0.320	0.000124

At the same time another investigation was being carried on by Mr. T. C. Pond<sup>1</sup> on the extraction of sodium carbonate solution from wood pulp as is necessary in the soda pulp process. One of the concentration gradient curves obtained by Mr. Pond is given here. The experimental points represent the values as determined by Mr. Pond; the dotted curve connecting those points represents the actual concentration gradient and the full curve represents the concentration gradient as calculated from our equation. Mr. Pond had only four tanks in series in his system so that the insertion of a new tank into the system introduced decided variations in the concentration gradient, the flattening out of the curve being emphatically shown in the divergence of the actual from the theoretical curve in the fresh tanks in the series. This divergence, while very large in the fresh tanks in which the concentration gradients have not yet been established, is negligible in the rest of the system where the concentration gradient is relatively unaffected by the introduction of a new tank. In a longer system divergence would be much less than in the short system employed by Mr. Pond.

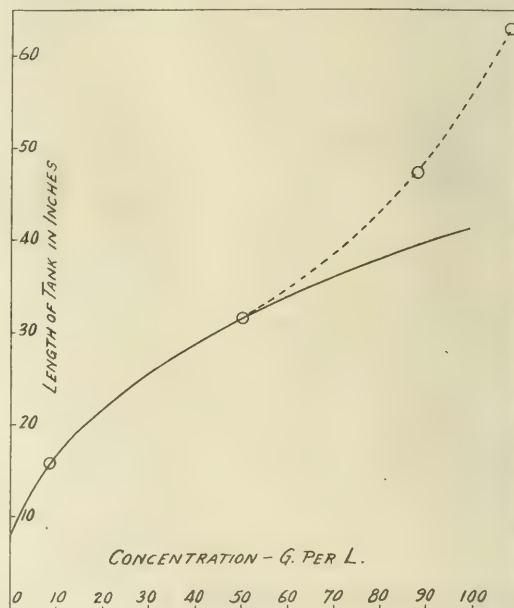
#### UTILITY OF EQUATION

We believe that these figures offer experimental justification of our method of calculation. On the other hand, it cannot be too strongly emphasized that under ordinary operating conditions it is almost impossible to get a concentration gradient

<sup>1</sup> Thesis submitted in partial fulfillment of the requirements for the S.B. degree at the Massachusetts Institute of Technology, 1915.

which satisfies our expression. The reason for this is that the concentration gradient is very sensitive to changes in conditions such as temperature, rate of flow, etc., and these must be carefully controlled if theoretical results are to be obtained. None the less, our equations do indicate the nature of the process involved and while they are not applicable directly to the concentration gradient existing in commercial systems they should and in our opinion do apply to the average conditions existing in any continuously operated system. The diffusion constant K for our equation must therefore be determined from the known results of a system operating under commercial conditions, taking for the concentrations the average values obtained for a relatively long period of time. In order to determine the constant in our equation it is unnecessary to determine the concentration gradient through the system, but average values of the constant will be obtained from the known average performance of the operating system. Using these constants it will be possible to predict the effect of change in the performance of the system resulting from increase in size, change in velocity of flow, or variation in the amount of extractor employed.

It will be noted that the average value of the constant from Table I is 0.000096, and from Table II, 0.000174. In the first case, however, the inert gas was air and in the second CO<sub>2</sub>. Evidence points to the assumption that the thickness of stationary film is determined by the weight of gas passing the surface, rather than by its linear velocity, *i. e.*, to compare the results in the first case with those in the



second the constant should be multiplied by the square of the ratio of the molecular weights  $(44/29)^2$ . Since, however, diffusion of a gas is inversely proportional to the square root of its molecular weight, a

further correction factor of  $\sqrt{44/64}$  must be applied. Corrected in this way, the constant in the first table becomes 0.000183 as compared with 0.000174 in the second. In other words, it is apparently possible to use a single constant for the rate of absorption in two such diverse cases as  $\text{SO}_2$  in water and  $\text{CO}_2$  in  $\text{NaOH}$  solution, even with different diluent gases, provided differences in the densities and diffusion velocities be allowed for. While too much weight must not be put upon the checking of these two constants, it is still confirmatory of the correctness of our assumptions and method of calculation.

If data are to be obtained in the laboratory for the design of commercial systems as is of course necessary when new processes are under investigation, the laboratory conditions must duplicate on the small scale, as nearly as is possible, the conditions which it is anticipated will obtain in actual operation. We do not, however, recommend the laboratory method for determining the value of the diffusion constant in our equation where it is possible to get data from a large system in actual commercial operation. The main value of our equations will be to predict the effect of adding new tanks to the system, of increasing the rate of flow of extractor through the system, of using more extractor, and of all such changes in commercial operation.

#### EFFECT OF VELOCITY

The most striking fact brought out in this investigation is the marked influence of velocity on the rate of extraction. Throughout our work on extraction for those cases where the distribution of solutum between carrier and extractor is linear, we have found that the coefficient of diffusion  $K$  in our formulas is proportional within the experimental error to the square of the gas or liquid velocities. This means that the more rapidly the extractor is forced through the system the more rapid and indeed the more perfect will be the extraction. This statement would not apply to a gas washer using a spray, inasmuch as the drops of spray are carried with the gas and the relative velocity of the spray past the gas remains practically unchanged, whatever the velocity of the gas. In any system in which the carrier is stationary our results should apply. This means that in the design of counter-current extraction apparatus where gas washers or ordinary extractors are used, provision should be made to have the relative velocity of carrier and extractor as high as it is possible to make it. We do not claim that this rule, that rate of extraction is proportional to the rate of the velocity of the extractor, holds under all conditions. It is merely the empirical result of our experimental work, but it is in keeping with our concept of the extraction process. If the rate of extraction be limited by diffusion through a stationary film on the surface of the carrier, then high velocity should tend to remove this film and make it thinner, thereby greatly increasing diffusion. This result is in striking accord with all we know regarding the influence of velocity upon flow of heat and diffusion processes in general, but the proportionality between  $K$  and the square of the velocity is probably limited in its application.

#### ILLUSTRATIONS

A single illustration of the method of employing these equations will suffice. Assume that a part of the  $\text{SO}_2$  is being removed from waste sulfur gases by washing with water. The tower used is 50 ft. high. The gases enter with 10 per cent  $\text{SO}_2$  at  $77^\circ \text{F.}$ , and at present one-half the  $\text{SO}_2$  is removed. The tower at present treats 70,000 cu. ft. of inert gas per hour, using therefor 30,000 gals. of water. How much higher would it be necessary to build this tower to recover 70 per cent of the  $\text{SO}_2$  instead of 50?

The equation to be employed is

$$\log \frac{x_0 - \alpha c_0}{x} = \frac{kl}{u}(c - \alpha) = (\text{const.})l.$$

The latter form may be used because it is not proposed to modify the velocity of gas through the apparatus nor the amount of water used to dissolve the gas.

Where the gases enter the system the ratio of  $\text{SO}_2$  to inert gas, or  $x_0$ , is 10 : 90, or  $x_0 = 0.1111$ . At present half the  $\text{SO}_2$  is removed, or at the other end of the tower  $x = \frac{0.1111}{2} = 0.0556$ .

From the solubility tables it is found that at the average concentration and temperature in the tower the partial pressure of  $\text{SO}_2$  is such that a solution of 1 g. mol per liter exerts 0.530 atmospheres. 1 g. mol per gram, which is the same as 1 pound mol per pound, the unit of concentration in these equations, will therefore exert a thousand times as much, or  $\alpha = 530$ .

The tower is treating 70,000 cu. ft. of inert gas or 10/90ths as much  $\text{SO}_2$ . Multiplied by the ratio of the absolute temperatures,  $(460 + 32)/(460 + 77)$ , the volume of  $\text{SO}_2$  is reduced to standard conditions. Divided by the pound molecular volume under standard conditions, 359 cu. ft., gives the pound mols of  $\text{SO}_2$ , 1/2 of which is recovered.

This  $\text{SO}_2$  recovered, divided by the pounds of water used, 30,000 times the pounds per gallon,  $8\frac{1}{3}$ , gives the concentration,  $c_0$ , of the solution obtained.

$$c_0 = \frac{(70,000)(10)(492)}{(90)(537)(359)(2)(30,000)(8.33)} = 0.0000397$$

Hence,

$$(\text{const.})(50) = \log \frac{0.1111 - 530(0.0000397)}{0.0556} = 0.210$$

$$(\text{const.}) = 0.0042.$$

Under the proposed conditions,  $x_0$  and  $\alpha$  will remain the same, but  $x$  will fall to 0.3  $x_0$  while  $c_0$  will rise in the ratio of 7 to 5, as 70 per cent of the  $\text{SO}_2$  will now dissolve in the water which at present takes up but 50 per cent. Therefore

$$\log \frac{0.1111 - 530(0.0000397)^{\frac{7}{5}}}{0.3(0.1111)} = 0.0042l,$$

whence  $l = 93$  ft., or the tower must be made 43 ft. higher.

#### SUMMARY

We have developed formulas which show the influence of the size of any extraction system, the amount of extractor employed per unit amount of carrier treated, and the velocity of flow of carrier past extractor in any counter-current system for the extraction of solids by liquids or of liquids by gases or *vice versa*, and we have presented experimental evidence which we believe demonstrates the applicability of these formulas and justifies us in recommending their use in the interpretation of data collected in the study of any extraction system and in the design of new systems which it is desired to construct.



# A COMPARISON OF THE RELATIVE EFFICIENCY OF LABORATORY REFLUX CONDENSERS

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Further than statements based upon qualitative separations, such as that made by Clowes,<sup>1</sup> in which he mentions that there is a considerable loss of ether when it is heated under a Liebig condenser used as a reflux, there has not been, so far as is known to the authors, any systematic comparison of the efficiency of different kinds and lengths of condensers.

Much important chemical work demands the use of this apparatus, and it seemed worth while to compare the efficiency of those most commonly used. The aim of this work is not to obtain great accuracy of results, but rather to gather data under the ordinary laboratory conditions which will aid in the choice of a reflux condenser, when it is necessary to heat a low-boiling liquid for some length of time. When fat is extracted by means of a Soxhlet apparatus, the ether is boiled for about 16 hrs. Should the condenser used show an efficiency of 98 per cent per hr. (that is, if 2 per cent of the total ether were lost in 1 hr.),  $\frac{1}{3}$  of the total ether used would be lost in the experiment. It is very obvious that an efficiency of even a fraction of 1 per cent per hr. in the condenser is well worthy of consideration.

Not long since, one of us was asked to select a condenser for use with the Soxhlet apparatus and no preference could be given. Many indeed are the claims for great efficiency of the various types now in use. At that time the various kinds at hand were roughly tested, using gasoline as the volatile liquid. One hundred grams were boiled for 1 hr. under different condensers. The source of heat was then removed and the flask allowed to cool and reweighed. The efficiency of the condenser was calculated as the per cent of gasoline remaining after the experiment.

TABLE I—EFFICIENCY OF REFLUX CONDENSERS (GASOLINE)

Gentle Boiling. Flow of Water 375 Cc. per Min. Temperature at inflow = 20° C.; at outflow = 24° C.									
CONDENSER	Allihn	Liebig	Metal	Allihn	Liebig	AIR CONDENSER			
Length, cm.	30	80	Ball	15	48	Glass	150	100	(coil)
Efficiency per hr.	98.69	97.64	96.8	94.65	91.96	89.4	86.4	42.6	

It is apparent that the length of the condenser makes considerable difference in its efficiency. In order to condense any large proportion of the gasoline vapor, the longest of the Allihn or Liebig condensers must be used. This method of comparison is, however, too crude, and in order to obtain results that show comparative values of the various condensers now on the market, more accurate methods of work were devised.

Experiments were made comparing the refluxing efficiencies of the following kinds and lengths of condensers: Liebig, 5 lengths; Allihn, 3; Spiral, 3; Hopkins, 2; Davies, 3; and Friedrichs, 1. The simpler form of the last named variety was used, not that having an outer as well as an inner water jacket.<sup>2</sup>

In each determination, 100 g. of liquid were boiled in a 250 cc. Erlenmeyer flask standing upon a concave

asbestos wire gauze and heated from beneath by means of a ring burner. This burner and gauze insure equal distribution of heat upon the bottom of the flask. After boiling for  $\frac{1}{2}$  hr., the burner was removed and an asbestos board slipped under the flask. It was allowed to cool for 5 min. before weighing, the water still flowing through the jacket. Duplicate determinations were made in every case.

A Woulfe bottle, carrying a thermometer, was placed between the water tap and the condenser, so that the temperature of the water flowing through the jacket might be observed. This temperature during all of these experiments did not vary more than about 3° (from 16 to 19° C.). The water was allowed to flow at the rate of approximately 500 cc. per min. The rubber stopper carrying the condenser was covered with tin foil to prevent any solvent action by the liquid.

It was found necessary, in every case, to bevel the lower end of the condenser tube so that the size of the drop and the rate of drop-back might be kept more nearly uniform. It was also found early in the work that the only way in which comparable results could be obtained, was to count the drop-back of the liquid used, as a measure of the rate of boiling.

The Liebig, Spiral and Allihn condensers were kept in a vertical position. The Davies, Friedrichs and Hopkins varieties were inclined slightly, because in these types the vapor traverses a space between an inner and outer jacket: this construction caused a drop-back when the condensers were held in a vertical position, both from the bottom of the inner jacket, and from the bevelled end of the tube. By tilting the whole apparatus, this drop from the bottom of the inner tube is made to fall upon the inner surface of the outer tube and run down to the bevelled tip, thus making the drop returning to the flask more nearly of the same weight as that in the case of the other condensers.

In order to obtain sufficiently accurate values, it was found necessary to correct for the amount of liquid remaining in the condenser after cooling. To estimate roughly the ether adhering to the walls of the tube, it was boiled under a reflux condenser which had been previously dried and weighed. (No water was allowed to flow through the jacket during these determinations.) When the vapor escaped freely from the top, the flask was allowed to cool for 5 min. and the condenser was again weighed as rapidly as possible. The sources of error in this crude method of procedure are at once obvious. The results given below are taken into account in Table V and seem sufficiently accurate for practical purposes.

TABLE II—CORRECTIONS FOR ETHER IN VARIOUS CONDENSERS

CONDENSER	Friedrichs	Davies				Liebig				Spiral	Allihn	Ball (Cop)
Length, cm.	18	15	19	30	15	20	32	9	25	29		
Ether, g.	0.07	0.06	0.07	0.06	0.01	0.03	0.09	0.06	0.04	0.06	1.7	

A few trials were made, allowing the four liquids—water, chloroform, alcohol and ether—to drop back in equal quantities by volume. The number of drops

<sup>1</sup> *J. Soc. Chem. Ind.*, **16** (1897), 979.

<sup>2</sup> *Z. angew. Chem.*, **23** (1910) 2425.

giving the same volume at the temperature of the boiling point of each were calculated from the respective surface tensions and densities given by Castell Evans<sup>1</sup> using the formula given by Findley.<sup>2</sup>

$$\frac{V_1}{V_2} = \frac{N_2 d_1}{N_1 d_2} \quad \text{or} \quad N_2 = \frac{V_1 d_2 N_1}{V_2 d_1}$$

where  $V_1$  and  $V_2$  = surface tension;  $N_2$  and  $N_1$  = no. drops;  $d_1$  and  $d_2$  = densities.

It is evident that different liquids could not be compared in the same condenser by using the same rate of drop-back in each case. The size of the drops is different for each liquid at a given temperature, the attraction of the glass varies, etc. Five drops of ether per second were here taken arbitrarily as a standard and the number of drops of the other liquids having the same volume, compared to this. These numbers are included in Table III.

TABLE III—EFFICIENCY WITH DROP-BACK IN EQUAL QUANTITIES BY VOLUME (LIEBIG CONDENSER)

No account was taken of the quantity of substance adhering to condenser tube

SUBSTANCE	Drop Rate		PER CENT EFFICIENCY		
	B. P. 20 cm. ° C. Jacket		20 cm.	24 cm.	38 cm.
Ether.....	34	5	Very low	98.4	98.76
Chloroform.....	61	7.6	93.6	88.5	98.16
Alcohol.....	78	4.5	97.9	98.5	98.42
Water.....	100	1.77	98.78	99.0	99.42

The percentage efficiencies in Table III indicated too great an apparent loss in the case of chloroform. Ether, boiling as it does at a lower temperature, would be expected to escape in larger quantities if conditions were in every way comparable.

When it was found that correct results could not be obtained by refluxing equal volumes of the respective liquids, a comparison was made by weight. In order to determine the number of drops of each liquid having the same weight, the respective weights of one drop of each were determined, the temperature being as near the boiling point as was practicable. Twenty drops were in each case drawn from a given orifice and weighed. The weight of one drop of water, divided by the weight of one drop of any of the other liquids, gives the number of drops of each having the same weight. These values appear in Table IV, Column 1,

TABLE IV—RELATIVE EFFICIENCY OF LIEBIG CONDENSERS OF DIFFERENT LENGTHS

SUBSTANCE	Drop-back	B. P.	PER CENT EFFICIENCY			
			15 cm.	20 cm.	24 cm.	37 cm.
Water.....	1	100	98.8	98.17	99.15	99.42
Alcohol.....	2.5	78	97.3	97.9	98.9	98.4
Chloroform.....	2.3	61	97.0	97.3	98.8	99.0
Ether.....	3.34	34	94	94.3	96.4	97.0

Table IV shows the influence of the length and also the influence of the boiling point of the liquid upon the efficiency of the Liebig condenser. As would be expected, the longer the condenser, and the higher boiling the liquid, the greater the efficiency. It is noteworthy, too, that the values are very largely dependent upon the rate of boiling. There are many sources of error in the above method. A small error in counting the rate of drop-back may account for the irregularity in the efficiency of the 37 cm. Liebig shown in Table IV for chloroform. There is also an

irregularity in this table in the values for efficiency in the case of ether. Slight changes in external conditions such as draughts, etc., cause considerable variation in the efficiency of the shorter condensers. It was found by trial, that if a small plug of glass wool was placed in the upper end of the 24 cm. Liebig, the efficiency was changed from 96.4 per cent up to about 98.7 per cent. Considerable saving of ether in the Soxhlet or similar apparatus can be effected if air currents are prevented, as these which carry away the vapor.

The relative efficiencies of a number of condensers have been compared at two different rates of drop-back, *viz.*, 3.3 and 5 drops per second. Results at the latter rate are given to show that with a rapid rate of boiling the very short condensers cannot be used to advantage. As might be expected, our results checked best at the lower rate of drop, partly no doubt because it is rather difficult to count accurately, drops at the rate of 5 per second or 25 in 5 seconds. The results in Table V express the total *condensing efficiency* of the condensers enumerated.

TABLE V—A COMPARISON OF RELATIVE EFFICIENCY OF VARIOUS KINDS OF CONDENSERS FOR ETHER

Rate of Drop-back, 5 drops per second				Rate of Drop-back, 3.3 drops per second			
CONDENSER	Length Cm.	Per cent Efficiency	Price	CONDENSER	Length Cm.	Per cent Efficiency	
Hopkins	37	99.03	\$3 to \$4(?)	Hopkins	30	98.82	
Friedrichs	18	98.98	\$5.00	Graham	9.5	98.7	
Liebig	37	98.87	\$1.20	Allihn	29	98.60	
Graham	25	98.80	\$2.40	Allihn	20	98.58	
Davies	30	98.14	\$6.00	Friedrichs	18	98.5	
Hopkins	27.5	98.02	\$1.75	Graham	16	98.5	
Allihn	29	97.74	\$1.50	Hopkins	27	98.48	
Davies	20	97.64	\$5.00	Hopkins	37	98.4	
Liebig	32	97.63	\$1.00	Graham	25	98.3	
Davies	15	97.0(?)	\$4.50	Liebig	32	98.17	
Allihn	20	97.16	\$1.20	Liebig	37	98.0	
Graham	16	97.12	\$1.35	Liebig	20	97.86	
Graham	9.5	97.0(?)	....	Liebig	15	97.78	
Ball	(a)	96.64	\$3.20	Liebig	20	97.60	
Liebig	20	73.23	\$0.75				
Liebig	15	0.00	....				

(a) Drop-back 3.2 per second. Highest rate attainable with this metal condenser.

The weight of a drop of ether in the case of the copper ball condenser was not determined. Apparently it is larger than in the case of glass tubes; therefore the efficiency of this condenser may be greater than is at first sight apparent, *i. e.*, the ether may be boiling much faster than is necessary to obtain, in the case of glass, a rate of 5 drops per second.

Evidently, at a slow rate of boiling the lengths of these condensers is of little moment. The rate of boiling, rather than the length or kind of condenser, seems to be the determining factor in efficiency.

## CONCLUSIONS

I—It has been found that in order to obtain comparable results, the rate of drop-back of the liquid must be in approximately equal weights per second.

II—In order that drops of equal weight may return to the flask the end of the condenser tube must be bevelled so that the drop returns from one point only.

III—The rate of boiling has very marked influence upon the efficiency of the condenser.

IV—The bore of the condenser tube has influence upon the efficiency of the condenser, as has also a

<sup>1</sup> "Physical Chemical Tables," 2 (1911), 725, Chas. Griffin & Co., London.

<sup>2</sup> "Practical Physical Chemistry," 1914, p. 94, Longmans, Green & Co., New York.



narrowing at the tip or a constriction anywhere in the tube. (Noticed in the spiral type where the spiral is fused on to the inner tube.) These conditions tend to cause choking and when this occurs the loss is always disproportionately great.

V—The length of the condenser is a factor in its efficiency (especially in the case of the Liebig) for low-boiling liquids. In the case of the other forms the length of the jacket has less influence than seems to be commonly supposed.

VI—In experiments where a long condenser can be conveniently used, the Liebig seems to be preferable because it is a much less costly condenser and can be easily cleaned. Where a short condenser is required, the Friedrichs seems best.

VII—The short Liebig or Allihn can be used to advantage only when the rate of condensation is not greater than from 2 to 3 drops per second, or when some means is used, such as a glass wool plug in the top of the condenser or a test tube inverted over the top of the condenser to prevent too rapid a carrying away of the vapor by air currents.

DEPARTMENT OF CHEMISTRY  
UNIVERSITY OF MISSOURI, COLUMBIA

### CHAIN SCREEN DOORS

By HENRY H. WIEGAND  
Received June 14, 1916

Whenever the ordinary door of an oven or furnace is opened a stream of intensely heated gases pours out of the upper part of the opening, while at the bottom an equivalent volume of cold air rushes into the furnace, chilling contents and walls, entailing damage thereto and loss of heat. Time is also lost, as the interior must again be raised to the requisite temperature.

Many makeshifts have been devised to avoid the adverse conditions arising from the opened furnace door, but until the advent of the ingenious Wiegand chain screen door, nothing properly served the purpose. What was demanded was a door or shield that would permit a clear, unhampered view of the interior of the furnace or oven; would not in any way interfere with the free manipulation of the tools required to care for the interior; yet a door that would keep the heat in and the cold air out; in other words, a door which should possess at the same time the qualities of opaqueness, transparency and penetrability. This was a seeming impossibility until the chain door was devised by a Baltimore inventor.

These chain screen doors, in the form used mostly around metal, glass and chemical furnaces, consist of a multitude of freely hanging individual strands of steel chain suspended close together from a bar in a manner to form a continuous sheet or curtain of chain, not unlike the familiar Japanese screen. This curtain of chain, hung before the uncovered opening to a furnace and looking like a coat of mail, effectively hinders the heat, glare, gases and sparks from leaving the furnace and checks the entrance of cold air. The loosely hanging strands of light chain are parted with ease and pressed aside by the tools or other objects projected

into the furnace, only to fall together again when entrance has been effected. The interstices in the links of chain permit an unhampered view of the interior—in fact a better survey may be obtained than under ordinary conditions, as the glare is toned down and the effect is similar to looking into a furnace through a piece of wire gauze. This is particularly noticeable with those installed on electric furnaces.

In some plants, when it is necessary to work in front of the naked fire, the workmen are obliged to stand back a great distance from their work and protect their bodies from the heat and glare with large sheet-iron shields which are supported by one hand while the other manipulates the tools. This seriously handicaps the workman and cuts his efficiency in half. In some industries the men are obliged to protect their eyes with dark goggles and their bodies and hands with extra heavy coverings. All such devices impede the men in the performance of their work. In those plants where the new chain screens have been employed the workman has both hands available for his work and may, with comfort, freely manipulate his tools while standing within a few inches of his work.

In glass working, the heat of the uncovered furnace is intense. Measured on the thermometer it shows a temperature of 600 to 1000°, yet when one of these chain screens is placed in front of the opening the temperature is lowered to such an extent that the bare hand may be held without danger or discomfort within an inch or so of the protecting transparent screen.

In a boiler room where the Wiegand chain doors have been employed for about three years, experiments were made to obtain an idea of the effectiveness of the device in avoiding the losses arising from the frequently opened stoking door. A thermometer was fixed on a standard in the fire room at a point opposite this door and 10 in. therefrom. This position was chosen as being near to the one usually taken by the fireman when stoking or cleaning the fire. When the ordinary fire door was thrown open and the incandescent fire bed exposed, as is the case whenever the furnace is coaled or cleaned, the thermometer rose to 400° F. On covering the furnace opening with the auxiliary "chain door," the temperature dropped to 135° F., and the bare, unprotected hand could be held anywhere in front of the screened opening without discomfort. This drop of 265° on the application of the screen indicates that a great quantity of heat lost by radiation and convection, through the ordinary uncovered furnace opening, may be saved by the employment of such a device.

These chain screens have a great field of usefulness in connection with glass furnaces, porcelain ovens, pyrites roasters, chemical, shrapnel and annealing furnaces, and cupolas for melting iron and other metals. Their use around the electric furnace has added much to the comfort of the operatives, when pouring.

Chain screen doors are supplied in "automatic" and "non-automatic" forms. The automatic is employed

mostly on boiler furnaces and is so constructed that the opening of the fire door trips a catch, which permits the screen to unroll from a cylinder, and fall in front of the furnace opening. When it is desired to close the fire doors again, the screen is rolled up on its cylinder, which is permanently mounted above the furnace opening. The "non-automatic," much used on ovens and other furnaces that are not so frequently opened, is much simpler in construction. The chains forming the screen are suspended from a bar and may be raised out of the way by a hand chain running through a pulley overhead. When needed the screen is lowered into supporting brackets fixed at the sides of the opening. In some plants, whose furnaces are provided with vertically moving doors, the chain screen is permanently attached to the bottom of the ordinary vertical door. When the latter is raised to uncover the entrance, the chain door rises and takes its place.

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### EXAMINING COMMERCIAL BROMINE

By ELWYN WALLER

Received June 7, 1916

Recently a sample of commercial bromine was brought to the writer's laboratory for examination. The impurities likely to be present are not very numerous. If the material has been recovered from by-products in the manufacture of substances from aromatic and other organic compounds, a material amount of organic substance may be present, *e. g.*, Reyman<sup>1</sup> mentions finding 10 per cent bromoform in one case. Ordinarily, only a small amount of grease, wax or paraffin, which has been used in sealing the container, is all of the organic impurity present. The presence of  $\text{SO}_3$  or  $\text{H}_2\text{SO}_4$  is possible, but the amount is usually insignificant. The presence of Br hydrates may perhaps occur, but that branch of the subject does not seem to have been investigated. The occurrence of Cl is naturally the chief impurity, both on account of the association in nature, and also on account of the usual methods of manufacture.

In testing, some manufacturers determine the purity by taking the specific gravity in a specially constructed apparatus, and by reference to a table (made up, I know not how) read off what they claim is the true per cent of Br in the sample. Apparently it is assumed, in the construction of the table, that Cl is the only impurity. The possible influence of other impurities would seem to render this method a rather uncertain one, especially as the authorities<sup>2</sup> are not altogether in accord, varying from 2.966 to 3.1872.

The sample referred to showed sp. gr. at 5-6° C. . . . . 3.0286  
A sample marked C. P. from a well-known dealer at 25° C. . . . . 3.0135  
at 25° C. . . . . 3.1021

Titration of a known quantity with standard  $\text{Na}_2\text{S}_2\text{O}_3$ , is one method recommended by many. The objection to it is that this permits of working on only a

small quantity, and the assumption must also be made that only Br and Cl are present.

Friedheim and Meyer<sup>1</sup> suggest the application of Dechan's process,<sup>2</sup> which was devised for the examination of brines, mineral waters, etc. It depends on the following: With a mixture of bromides and chlorides, addition of a large excess of  $\text{K}_2\text{Cr}_2\text{O}_7$  and positive acidification with  $\text{H}_2\text{SO}_4$ , on boiling gives off Br but no Cl unless it is allowed to become very concentrated, when  $\text{CrO}_2\text{Cl}_2$  may distil over. By the aid of a current of steam passed through the boiling solution, all the Br can be driven into the distillate, and in the residual solution the Cl can be determined with  $\text{AgNO}_3$ . To apply the process in the case of commercial Br, 0.5 to 1 g. of the sample is weighed out in a thin glass bulb, which is broken under the surface of NaOH solution. When all Br has been taken up, 50 cc. of a 3 per cent solution of  $\text{H}_2\text{O}_2$  is added, and the excess boiled out. Transfer to a distilling flask, add 10 g.  $\text{K}_2\text{Cr}_2\text{O}_7$  in crystals, and 20 cc.  $\text{H}_2\text{SO}_4$  (1 : 1 by vol.). Distil until the distillate gives no reaction for Br, avoiding a concentration beyond what would be equivalent to 8 cc. concentrated  $\text{H}_2\text{SO}_4$  in 100 cc. of liquid. Then dilute the contents of the flask, and precipitate an aliquot portion with  $\text{AgNO}_3$ .

The process was tried but proved unsatisfactory. To obtain the necessary reagents absolutely free from chlorides, is, at this time especially, a difficult matter. It was also found that unless the concentration is brought to a certain point, no Br whatever will distil over, though much still remains, consequently constant attention is necessary to keep the degree of concentration in the flask between the proper limits. The results obtained were irregular and not concordant.

Erchenbrecher<sup>3</sup> treats 6 g. of the sample with 25 cc. of  $N/5$  solution of KBr or NaBr, evaporates on the water bath, finally in a weighed dish, ignites gently and weighs. The Cl of the sample displaces the Br of the salt, and by use of a table the proportion may be found.

To weigh out precisely 6 g. or any other prescribed quantity of Br is a troublesome operation, so that the use of a table would hardly seem to be of advantage in this connection. The principle involved can, however, be applied as will be seen later.

Kubierschky<sup>4</sup> applies the same principle by shaking 25 cc. of the sample in a flask with 25 cc. of  $N$  KBr, settling and taking the specific gravity of the supernatant aqueous solution. With pure Br he states the specific gravity should be 1.227, and he has made a table showing the gravities corresponding to different percentages of Cl.

The application of the above principle proved to be a convenient mode of conducting the test. The method pursued was to weigh out 6 to 8 g. of the sample in a small stoppered flask. This was then poured and rinsed into a 350 cc. beaker containing about 70 cc. of water. The object in using so large a beaker

<sup>1</sup> *Z. anorg. Chem.*, **1**, 407.

<sup>2</sup> *J. Chem. Soc.*, **49**, 682.

<sup>3</sup> *Z. angew. Chem.*, **1894**, 636.

<sup>4</sup> *Loc. cit.*

<sup>1</sup> *Ber.*, **8**, 792.

<sup>2</sup> Judging from the statements in Watts' Dictionary, I, 676.



was to avoid loss when boiling out the Br. To this was then added, by means of a pipette, 20 or 25 cc. of a solution of pure NaBr of 7 to 10 per cent strength. At the same time, *using the same pipette*, the same amount of NaBr solution was pipetted into a weighed dish to serve as a blank.

The beaker containing the Br was placed on the boiling water bath, and allowed to remain there until the Br had all boiled off, and most or all of it had been expelled from the solution, when the solution of mixed bromide and chloride was transferred to another weighed dish, and both that and the blank were evaporated to dryness, the last traces of moisture expelled by heating in air bath at about 130° ignited gently and weighed. The salts obtained from the "mixed" is less than that from the "blank" by an amount equivalent to the difference between the combining weights of Cl and Br.

In other words, Blank — Mixed = Diff., and since (Br) 79.92 — (Cl) 35.46 = 44.46

$$44.46 : 35.46 = \text{Diff.} : \text{Cl present.}$$

For most purposes, 80 per cent of the difference in weights gives the Cl.

The contents of the dishes should be dissolved separately, and each diluted to some convenient bulk (say 250 cc.), and aliquot portions tested by titration with standard AgNO<sub>3</sub>. The halogen equivalent in the two masses of salts should be the same if no losses have occurred.

Applied to the sample submitted the results were:

Taken	Wt. of "Blank"	Wt. of "Mixed"	Diff.	= Cl	% Cl
6.7249	1.5884	1.3206	0.2678	0.21364	3.18
7.2330	1.3983	1.1257	0.2726	0.21747	3.06
8.4340	2.0737	1.7434	0.3303	0.26349	3.12

Material from a dealer in laboratory supplies marked as Bromine C. P. was found to contain 0.19 per cent Cl.

159 FRONT STREET, NEW YORK CITY

### A NEW TYPE OF EXTRACTOR

By JAMES B. McNAIR

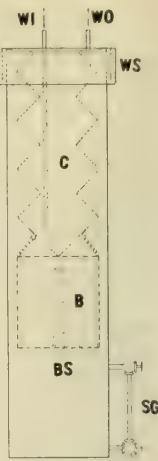
Received May 22, 1916

The accompanying diagram illustrates an original type of extractor which has been used successfully in extracting plant material with 86° Bé. gasoline. Like many other extractors, it consists of three main parts, *viz.*: a container for the solvent, a container for the material to be extracted, *B*, and a condenser for the solvent *C*. This machine, however, has advantages (which the illustration makes apparent) over some other extractors; it is easily cleaned, lacks complications, retains almost all of the solvent, etc. The diagram is drawn proportionally for a machine which has been efficiently used with 86° Bé. gasoline. The use of another solvent, due to a different specific heat, etc., might necessitate a re-proportioning of the parts, *e. g.*, a greater proportionate condensing area or the use of a different variety of substance in the condenser (in this case, copper).

The container is a long copper cylinder with a water boiler gauge, *SG*, attached to its vertical side near the base. Surrounding the top of the

cylinder is a gutter to serve as a water or mercury seal. This water seal tends to prevent explosions and the escape of the solvent. The bucket, *B*, for the material to be extracted, has a siphon, *BS*, and an inside wire gauze bucket nearly the same size as *B*. The bucket is suspended by chains to hooks attached to the lower part of the condenser, *C*. The condenser, *C*, consists of a series of truncated cones attached (as illustrated) to a lid. The water inlet is a small pipe, *WI*, and the water outlet a shorter pipe, *WO*.

In operating the machine the solvent is first poured into the container; then the condenser with its attached bucket is lowered into the container. Heat is applied at the bottom of the container. The number of extractions may be observed by the variations in the level of the liquid in the solvent gauge, *SG*.



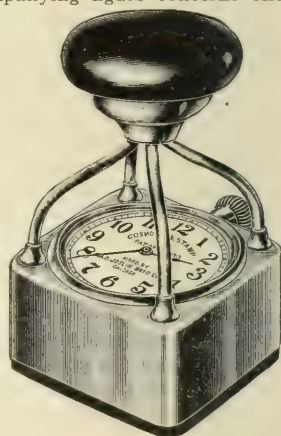
RUDOLPH-SPRECKELS PHYSIOLOGICAL LABORATORY,  
UNIVERSITY OF CALIFORNIA, BERKELEY

### A SIMPLE AUTOMATIC TIME RECORDER

By MAX MORSE

Received February 4, 1916

No one appreciates more than the laboratory worker any device which eliminates the personal responsibility when many determinations are running at the same time. The accompanying figure concerns one such device, namely, an instrument which accurately keeps account of the recording of time of beginning experiments, the receipt of samples, etc. The clock, mounted in a nickel frame, operates a rubber dial on the back. Being rubber, there is little incentive to damage the clock, as happens sometimes with those bearing copper dies by jamming the works when making an impression. Dials are furnished either in 12- or 24-hr. cycles. A key is furnished, operating the setting and winding, so that one may wear it on his chain or bunch of keys and have sole access to the clock as to winding and setting, for the key is individual. The low cost of the apparatus, as compared with the ordinary cumbersome, non-portable type of recording clock—a difference of \$27.50—is an item for the budget. The clock has been used to advantage in this laboratory.



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## ADDRESSES

### INTERPRETATION OF COAL ANALYSIS: WITH SPECIAL REFERENCE TO NONCOMBUSTIBLES<sup>1</sup>

By E. G. BAILEY

The purpose of a test on coal or any other material is to arrive at definite conclusions by a short cut, and yet with sufficient accuracy that the results of the test may form the basis of comparison for the purchase or use of the material tested. The old saying "The proof of the pudding is in the eating thereof" strictly applies to the burning of coal. There is no test, nor, can there be any test, that will replace results obtained from actual practice. But it is impossible to burn two coals under the same conditions at the same time, and it is unnecessary to state that in actual practice conditions do vary, so that comparisons based upon actual service results alone are often unfair to one coal or the other, or at least they lead to indefinite conclusions.

Another kind of test where the operating conditions are more nearly under control is a road test, where a great many data covering operating conditions are accumulated in addition to the consumption of coal per ton-mile, so that should the conditions vary from one test to another, certain allowances can be made. No criticism can be made of carefully conducted road tests, but they require time and are very expensive, and it is desirable to have some quicker and cheaper method of checking up the comparative values of different kinds of coal or different shipments of coal from the same company.

For this purpose, the chemical analysis of coal has been very widely used during the past ten or twenty years by practically all coal consumers in the country.

The purpose and value of coal analysis should be better understood. The chemist, as a rule, passes his figures on to the purchasing agent or superintendent of motive power with little or no comment or interpretation. The man who is responsible for the buying or burning of the coal is most interested in making a comparison of it with other coals which he has used or which are available. He accepts the figures from the chemist for the purpose of such comparison, and proceeds to draw certain conclusions as to the relative value of the two coals, based upon one or two constituents, such as the percentage of ash, sulfur or B. t. u., according to his own ideas of what the chemist's figures really mean. Very often these conclusions are not borne out by the practical road tests or the actual use of the coal in regular service. That theory and practice do not always agree, has often been repeated when the results obtained in the actual burning of the coal did not bear out the figures of the chemical analysis as interpreted by the person making the comparison. But theory and practice should and do agree when they are both right. Too often one is based upon erroneous data, incomplete results, or else failure to duplicate conditions.

It is regretted that too often the results of the chemical analysis are wrong, not by insignificant fractions of one per cent, but by several per cent or several hundred B. t. u. Very frequently the trouble is in the sampling, where the original sample is not large enough to be truly representative, or else it may not have been properly reduced and pulverized. The sampling question is of much greater importance than it has usually been considered. This phase of the subject will not be treated here except to impress upon each person who has any occasion to depend upon coal analyses, that no matter how sure he may feel that his present method is right, he should look up the methods of sampling and analysis recently proposed by committees

of the *American Society for Testing Materials*<sup>1</sup> and the *American Chemical Society*. One of the most obstinate hindrances to progress along any line is the characteristic of human nature for people to feel confident that their own way is the best. It may be all right for a poet or a musician to have distinctive peculiarities of his own, but it does not work out well in chemistry nor in the sampling of coal. The best standards should be rigidly followed.

#### HEATING VALUE

In the case of coal used for the generation of steam, whether in stationary, locomotive or marine practice, the primary factor is the heating value of the coal. In other words, all coal for these purposes has as its principal object the generation of heat to evaporate water. The matter of primary consideration is to evaporate a given amount of water at the lowest cost; and it should be remembered that the cost of fuel alone is not the entire item, for the character of the fuel has a great deal to do with the cost of repairs to grate bars, furnace linings and arches; and of very great importance in the case of locomotive practice is the question of the capacity which can be obtained.

With the introduction of calorimeters for determining the heating value of coal, many chemists considered that the whole question of fuel value was summed up in the one item of B. t. u., and consequently comparisons were drawn between different coals upon the B. t. u. basis, allowing no consideration for their other characteristics. It was soon learned, however, that such results do not always agree with results of practice, consequently many practical men have become skeptical of the value of coal analysis for giving them the dependable information which they desire.

A more careful insight into this problem shows that the real cause of the difficulty was that the comparison was limited to the one factor of heating value. While this may be the item of primary importance, yet the effect of the noncombustibles upon the action of the coal in the firebox had such a modifying influence that very frequently the coal with the higher heating value gave the poorer results. Anyone who has depended upon coal analyses without the proper interpretation, and has not given full weight to the effect of the impurities which accompany the heat-producing elements, has not been able to secure very much benefit from coal analysis.

The usual analysis of coal gives the percentage of moisture, volatile, fixed carbon, ash and sulfur, in addition to the heating value. The ultimate analysis, dividing the constituents up into their elements, gives carbon, hydrogen, oxygen, nitrogen, sulfur and ash. This is very seldom used, first because the analysis is more expensive, and second because the analysis really gives less information than the usual proximate analysis. Let us therefore confine our attention to a study of the proximate analysis.

The moisture is of course a noncombustible. It produces no heat, but is, on the other hand, an absorber of heat, as it must be vaporized and sent from the boiler as superheated steam at the stack temperature. Assuming a stack temperature of 700°, the total heat required to vaporize and superheat 1 per cent of moisture amounts to only  $\frac{1}{10}$  per cent of a 13,000 B. t. u. coal. This of itself is not a serious matter, so that the principal importance of moisture is that it acts as so much inert matter, which is paid for at the same price as coal. This applies only to the moisture which is in the coal at the time of its being weighed. It must be remembered that the percentage of moisture as shown by the usual analysis does not in-

<sup>1</sup> Presented before the 8th Annual Meeting of the International Railway Fuel Association, Chicago, May 15 to 18, 1916.

<sup>1</sup> *Proceedings American Society for Testing Materials*, Vol. XV, Part 1; also Year Book 1915





will not stand the lowest furnace temperature without melting into a clinker. In the case of coal ash, some ash has such a high fusing temperature that there are practically no fuel bed conditions that will produce troublesome clinker from it. Another ash with a little lower fusing temperature will sinter together and form a porous, spongy clinker which does not form a serious obstruction to the flow of air, nor is it difficult to remove. The ash with a still lower fusing temperature, say  $2,100^{\circ}$ , will not only become melted in the average firebox, but it will be heated several hundred degrees above its melting temperature, in which case it runs down like overheated iron until it spreads out in a thin sheet over the grate bars.

To a certain extent the action of a clinker depends upon its fusing temperature, but equally important is the temperature to which the ash is subjected. When a coal is burned, the ash is not entirely liberated until it reaches the lower part of the fuel bed, where the incoming air keeps a lower temperature than in the zone 4 to 6 in. above the grates. So it is often possible to get satisfactory results from a coal having a fusing temperature of 2,300 and yet carrying a fuel bed temperature of 2,500. Some clinker, of course, will be formed, but it is not of the extremely objectionable character if the firing is properly done. Clinker accumulates gradually, and is more or less open and does not obstruct the air beyond the critical limit. But if another fireman should handle the same coal differently, slicing or working the fire, and causing the ash, which has already been liberated from the coal in the lower and cooler part of the fuel bed, to be again thrown up into the hotter zone, it will melt into a very fluid mass and spread out over the grates in a thin sheet, and obstruct the air flow to a serious extent.

**SULFUR**—Many people have considered that the percentage of sulfur was a true indication of the clinker property of a coal. The sulfur determination, however, is one of the ideas that has been passed on from the steel chemist. In his case sulfur was extremely detrimental, but in the case of steam coal it is of minor importance. It is true that in some coal fields the variation in the clinkering property of coal received from different mines does follow the percentage of sulfur to a certain extent. Sulfur is an indirect cause, however, for it is really the iron which has the effect upon the fusing temperature, and the percentage of iron usually increases or decreases with the sulfur. There are so many exceptions to the relation between sulfur, or even iron, and the clinkering property of coal, however, that a dependence upon either is apt to lead to erroneous conclusions.

One of the very lowest sulfur coals in the United States is found in Rhode Island, where the percentage of sulfur will run less than one-quarter of 1 per cent, yet the fusing temperature and the clinkering property of this coal class it among the very worst in this respect.

#### FUSING TEMPERATURE OF ASH

Several of the largest stationary power plants in the country are making fusing temperature determinations in addition to the regular analysis on each shipment of coal. In many respects the clinker problem is of more serious consequence in railroad practice than it is in stationary boilers. The matter of fusing temperature determination has not as yet been standardized from a laboratory standpoint to the extent that the regular analysis and B. t. u. determinations have been. The value of this determination has been demonstrated so conclusively that there is now under way a definite movement to work out the fundamentals of this problem and decide upon a method which can be adopted as standard for comparison. It is the writer's opinion that the method which will ultimately prove most valuable for this determination is the one which stays closest to practice, so far as duplicating the actual fuel bed conditions is concerned.

One of the big difficulties with the whole question of coal analysis has been that the chemist was carried away with the idea of getting scientifically accurate results. The percentages of the various constituents and the determinations which he made were largely a matter of tradition, passed on to him from the needs of an entirely different line of work, and he has left the interpretation of these results to the person interested in the purchase or use of the coal. The original form of analysis did not fill the bill, and the next step was to include other factors, such as the B. t. u., and later on the fusing temperature of the ash, in an effort to strike the key to the situation that would give the factor essential for comparing the relative values of different coals. It is doubtful if there ever will be found any one factor that can be depended upon in drawing conclusions regarding a substance so complex as coal that is used under the severe conditions that exist in a locomotive firebox. It is therefore essential that the most important factor be taken as a basis of comparison, and consider the other factors as having modifying influence.

While the heating value of a coal may be considered the essential element, yet it means very little unless the percentage and character of the impurities existing in the coal are fully considered. It is therefore necessary to determine the amount and nature of these impurities. After they have been determined and allowed for, it is found that the heating value per pound of combustible is practically uniform for all coals from any one district, practically the only exception being in the case of crop coal.

Therefore it would seem in comparing one shipment of coal with another from the same district, that the determination of the heating value was the least important; the percentage of moisture is often beyond control, and it is very difficult to determine accurately at the time the coal is weighed, so the question resolves itself largely into the percentage of ash and its clinkering property, as being the critical factors to be considered in comparing the commercial value of different fuels of the same character.

When it comes to comparing coals of different character, taking lignite and semi-bituminous coals as extremes, it is practically impossible for a safe conclusion to be drawn from any chemical analysis, no matter how complete. In such cases practical tests are the only reliable means of arriving at comparative results, and then comparative information regarding different shipments of coal from any one region can best be obtained from the percentage of ash and its fusing temperature.

BAILEY METER COMPANY  
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#### COAL-TAR PITCH

By JOHN MORRIS WEISS

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Much has been written on the subject of coal-tar pitch, largely in Germany, but most of the extant publications are very restricted in scope and consider only a method of testing, a specification for some particular purpose, or a description of a particular grade of material. To make a complete review of the literature would be a difficult task and would be of little practical value for the purpose the writer has in mind. The object of this article is: (1) To treat in a rather general way the crude material for, and the manufacture of, coal-tar pitch; (2) to present the known physical and chemical characteristics of coal-tar pitch in a somewhat concise and definite form; (3) to consider the present uses of the material in industry—all from the point of view of United States practice.

#### MANUFACTURE OF COAL-TAR PITCH

Coal-tar pitch is the residual product from the distillation of coal tar, and tars are ordinarily distilled with the character of residue obtained as the primal object. The tar is taken in a



horizontal, sometimes vertical, steel still fired by coal, oil, or gas (depending on local conditions), and distilled with air, steam, or mechanical stirring. Light oil and water are first separated, then carbolic oil and finally creosote oil. The distillation is continued until the residue in the still is of the desired degree of consistency. Sometimes, where the pitch is being run very hard, anthracene oil is also separated toward the end of the creosote run, but this is exceptional, any anthracene oil obtained going for the most part along with the creosote oil. American practice has been very well set forth in an article by R. P. Perry<sup>1</sup> and the writer would refer to this paper, for a more complete and exhaustive study of manufacturing methods.

The characteristics of pitch are mainly dependent on two factors: The character of tar with which the still is charged, and the percentage of total distillate removed. The more oil removed, the higher melting the pitch becomes. Factors such as type of still setting and method of running also affect the character of the pitch, but to a minor degree compared to the first two mentioned variants.

Crude coal tars may vary widely depending on the coal used for carbonization, the type of installation in which the carbonization takes place and the degree of superheating to which the developing tar vapors have been subjected. In a paper by S. R. Church, read before the Southern Gas Association,<sup>2</sup> there are given comparative analyses of a number of typical coal tars and it can be readily seen that there are wide differences in the characteristics of crude tars.

#### ANALYSES OF TYPICAL TARS

(All tests on dry tar)

	GAS RETORT			COKE OVEN			
	Horizontal	In- clined	Vertical	United Otto	Semet- Solvay	Kop- pers	
Sp. gr. at 15.5° C.	1.266	1.293	1.238	1.153	1.207	1.188	1.186
Free carbon (insol. in C <sub>6</sub> H <sub>6</sub> )....	28.9	37.5	24.3	....	13.3	10.7	6.8
Sp. viscos. (Engler at 100° C.)..	21.8	30.0	14.9	2.1	3.4	3.0	2.1
Oil to soft pitch 60° C., m. p. (% by vol.).....	13.2	....	14.3	28.8	21.2	21.8	35.3
Refractive index at 60° C. (taken on oil).....	1.5932	....	1.5807	1.5755	1.5987	1.6122	1.6139
Sulf. res. (% taken on oil).....	0.4	....	2.4	4.3	0	0	0
Tar acids (% taken on oil)....	14.0	....	21.0	29.0	12.0	4.0	0
Pitch res. 60° C., m. p. (% by vol.).....	86.8	....	85.7	71.2	78.8	78.2	64.7

These variations are in turn imparted to the pitch produced and are largely dependent on the nature of the basic tar bitumens.

It may be set forth as an axiom that grades of pitch suitable for all purposes cannot be produced from a single source of tar. An admirable product for a particular purpose may be produced from each single tar but in general it is safe to say that the best results are obtained by blending tars from various sources and altering the still mixtures to suit the purpose for which the residual pitch is designed.

#### PROPERTIES OF PITCH

In considering the properties of coal-tar pitches it may be said that all the testing methods, peculiar to the tar industry, have been given in detail by S. R. Church<sup>3</sup> and any references

to specific properties not specially noted may be taken as determined by the methods given in this article.

#### PHYSICAL PROPERTIES

(1) MELTING POINT—The term "melting point" is really a misnomer. Bitumens, such as pitch, which consist of a complex mixture of hydrocarbons cannot be said to have a melting point in the sense that this term is usually applied to pure compounds. When pitch is heated it gradually softens, passing by imperceptible degrees from the solid to the liquid phase and the so-called melting point is merely an arbitrary figure taken for commercial purposes and representing the temperature at which a cube of pitch softens sufficiently to drop from a wire, when heated at a prescribed rate and under rigidly controlled conditions.

The melting points of coal-tar pitch vary from 37.5° C. (100° F.) in water up to 174° C. (345° F.) in air. These are really the practical limits of manufacture. A material melting below 37.5° C. (100° F.) could hardly be called a pitch, but would rather come under the class of distilled tars, where the distillation has merely removed the water, light oil and possibly a small portion of the carbolic oil fraction. Very hard pitches can be manufactured if desired, but ordinarily the hardest pitches made have an air melting point of not over 130° C. (266° F.).

(2) SPECIFIC GRAVITY—The specific gravities of coal-tar pitches vary from about 1.200 to 1.290 at a melting point of 37.5° C. (100° F.) and from 1.250 to 1.350 at a melting point of 88 to 93° C. (190–200° F.). Specific gravity is of comparatively little importance of itself. When an unknown pitch is examined, the specific gravity determination may give an indication of adulteration with pitches from other sources such as oil or water-gas tars. These are of lower specific gravity for the same melting point than coal-tar pitches and any considerable adulteration will usually be reflected in the figure found.

(3) EFFECT OF HEATING—The effect of heating and melting of coal-tar pitch is at most a slight hardening due to volatilization of oil. Trials on various grades at temperatures up to 205° C. (400° F.) showed only minor changes and there was no evidence of cracking and decomposition. Pitches that have been hardened by frequent heating, unless badly overheated, can readily be brought back to the original consistency without altering their essential properties, by fluxing with a high-boiling creosote oil.

(4) SOLUBILITY—Coal-tar pitches are soluble in benzol, carbon bisulfide, chloroform, carbon tetrachloride and glacial acetic acid. Of course the free carbon does not dissolve but can be brought into suspension by shaking. Coal-tar pitches are only partly soluble in petroleum naphthas, turpentine, grain alcohol and wood alcohol and any solution of coal-tar pitch in one of the materials which dissolve it, may be partially precipitated by the addition of an excess of one of the later named solvents. This is of considerable importance in the thinning of paints containing a coal-tar pitch base.

(5) TENACITY AND DUCTILITY—In the examination of bitumens these two properties are usually determined simultaneously. A cylinder of material of definite cross section is pulled apart under rigidly controlled conditions. The force necessary to do this is taken as a measure of the tenacity, and the lineal extension before rupture occurs as a measure of the ductility. These properties vary with the melting point of the pitch and the temperature at which the material is tested. To give detailed tests would take up much space and carry the writer outside the scope of this paper. The two properties are somewhat in inverse proportion. As tenacity increases, ductility tends to decrease. However, comparing coal-tar pitch with other bituminous materials of like tenacity, it is almost invariably of markedly greater ductility.

<sup>1</sup> THIS JOURNAL, 5 (1913), 151; reprint from *Proc. 8th Intern. Congr. Appl. Chem.*

<sup>2</sup> *Gas Age*, May 15, 1913.

<sup>3</sup> THIS JOURNAL, 3 (1911), 227; and 5 (1913), 195.

(6) **ADHESION**—This quality of pitch is its faculty to adhere to other materials such as stone, felt or wood, and it possesses this in a very high degree. This is of prime importance in many of the practical applications of pitch.

(7) **COMPRESSIBILITY**—It is well known that pitches will flow under pressure. Recent tests made in our laboratory by subjecting discs of bitumens to a smooth even pressure under rigidly controlled conditions of temperature have shown that coal-tar pitches show more compressibility at lower temperatures than other bitumens which apparently are less susceptible to changes of temperature as evidenced by the ordinary testing methods. Harder pitches will flow at temperatures considerably below their brittle points. They give under the smooth even pressure and do not splinter and crack as might be supposed.

(8) **ELECTRICAL PROPERTIES**—Tests made in our laboratories show the puncture voltage of pitch to be from 80,000 to over 100,000 volts per inch. Other tests showed the specific resistance to be so high that accurate measurements could not be obtained, the results varying from 168,000 megohms for 1 in. thickness, to infinity.

#### CHEMICAL PROPERTIES

(1) **CONSTITUTION**—Very little is known of the actual nature of the compounds making up coal-tar pitches but it is a generally accepted fact that these belong to the aromatic series. It is undoubted that some coal-tar pitches contain oxygenated hydrocarbons and all have some sulfur-containing bodies as part of their make-up. Nitrogen bodies are also present. It is possible that the nitrogen and oxygen contained in pitches are present in the form of higher homologues of the basic and phenolic bodies found in coal-tar creosote oils. C. R. Downs<sup>1</sup> has published some ultimate analyses of briquette pitches in which one of the three pitches tested showed a notable amount of oxygen and all, considerable quantities of nitrogen and sulfur. There is always a greater or lesser percentage of carbon, which is apparently not present in combination but which is in the free state and is therefore called "free carbon." This is usually considered as the portion of the pitch insoluble in hot benzol and toluol. This insoluble matter is not pure carbon but is very largely made up of this element. The nature of "free carbon" has been very extensively considered by the writer in a previous article.<sup>2</sup> The amount of free carbon in a pitch materially affects its physical properties but no definite quantitative relation can be shown. It has been held by some that the free carbon not only affects the pitch *per se* but also by virtue of the nature of the bitumens which normally make up a low or a high carbon tar. The percentage of free carbon may vary from 10 to 50 per cent in various pitches. If a coal-tar pitch is ignited there is left but a small quantity of mineral ash, almost invariably under 1.0 per cent and usually under 0.2 per cent.

(2) **RESISTANCE TO ACID**—Concentrated nitric and sulfuric acids char and decompose coal-tar pitch. Dilute sulfuric acid up to a strength of 40° Bé. seems to have very little action. Dilute nitric acid has more effect, but weak solutions are very slow in disintegrating the material. Hydrochloric acid, concentrated or dilute, is very well resisted by coal-tar pitches, and heating the acid has little effect, provided the heat is not sufficient to melt the pitch. Glacial acetic acid dissolves coal-tar pitch, the solution being purely physical, more dilute solutions not affecting it.

(3) **RESISTANCE TO ALKALI**—Most coal-tar pitches resist the action of caustic soda, caustic potash, lime and ammonia. A very few, derived from tars of high phenoloid content seem to be somewhat attacked by alkali, apparently due to the withdrawal of material soluble in this agent. For purposes requiring alkali-resisting strength it is always possible to obtain a coal-tar pitch derived from tars, which does not present this feature.

(4) **AIR AND WATER**—These two common reagents have practically no chemical effect on coal-tar pitches even after prolonged exposure. In the case of softer pitches exposed to the weather there is a gradual drying out of oil and consequent hardening. In a paper by S. R. Church and the writer<sup>1</sup> the results of a year's exposure of pitches to atmospheric conditions are given, and it is shown that the alterations due to this exposure are of little importance.

(5) **OTHER CHEMICALS**—Coal-tar pitches have been shown to resist very well the action of concentrated bleaching powder solutions and solutions of many inorganic salts. In general, it is a very resistant material so far as inorganic chemicals are concerned and is not readily oxidized.

In the paper by S. R. Church and the writer,<sup>1</sup> experiments are presented which indicate that coal-tar pitch is affected to a lesser degree than bitumens from other sources by illuminating gas and gas drips. Illuminating gas from leaky mains frequently affects bituminous pavements, and both the gas itself and the liquid condensate have a serious effect on bituminous waterproofing below city streets.

(6) **COMBUSTIBILITY**—All coal-tar pitches are inflammable, but have such high flash points that risk from this source is comparatively small. Coal-tar pitches of 135° F. melting point have flash points of above 193° C. (380° F.) and fire points upward of 243° C. (470° F.) when tested in an open dish on a sand bath. These high flash and fire points mean that there is a negligible risk in handling coal-tar pitches at the temperatures necessary for the application of the material.

#### USES OF COAL-TAR PITCH

(1) **ROOFING**—The use of coal-tar pitch for roofing purposes is too well known to give it more than passing mention. A roof composed of coal-tar saturated felt with coal-tar pitch mopped between the plies and surfaced with coal-tar pitch and gravel or slag has stood the test of time, has been approved by the Underwriters' Laboratories as a fire-retardant roof, and has been adopted as a standard high-class roofing by architects and engineers throughout the United States. Its resistance to atmospheric conditions, its impermeability to water and its adhesive qualities are of prime importance in this field.

(2) **WATERPROOFING**—Pitch is also used for underground waterproofing, on bridges, and in tunnels in very much the same way that it is used on roofs, that is, mopped between and on the surface of the plies of saturated felt. This use is also well known to architects and engineers, and coal-tar pitch waterproofing has been used widely with markedly favorable results. The qualities required here are about the same as for roofing purposes, but owing to the fact that such high temperatures are not generally encountered, a softer grade may be used. In this connection, the comparative resistance of coal-tar pitch to gas drips and illuminating gas is of considerable advantage.

(3) **PAVING**—Coal-tar pitch has found wide application in the construction of pavements of various types. Probably the most important, although of comparatively recent development, is the use of very soft pitch as a binder in the construction of bituminous concrete and tar macadam roads. In brick pavements, granite block pavements and wood block pavements, the proper grades of coal-tar pitch have found wide application, both as a filler between the blocks, and as an expansion joint at the curb line. Many municipalities have issued specifications covering the quality of pitch to be used for these purposes. Pitch for this work is usually somewhat softer than that used for roofing materials.

The ability of pitch to give under pressure is of advantage, especially in its use as a filler in wood block pavement. With expansion of the blocks the pitch squeezes out and does not crack and allow moisture to penetrate the joints of the pavement.

<sup>1</sup> THIS JOURNAL, 6 (1914), 206.

<sup>2</sup> *Ibid.*, 6 (1914), 279.

<sup>1</sup> "Experiments on Technical Bitumens." *Proc. A. S. T. M.* (1915).



In general the adhesion of pitch to all sorts of surfaces makes it very valuable as a joint filler.

(4) BRIQUETTING—The use of coal tar pitch for briquetting fine coal or coke breeze has been developed abroad further than in the United States. There are two types of briquetting processes, one where the coal or coke is mixed hot with the pitch and the other in which the pitch is ground and mixed cold with the coal before pressing. In the first case a soft pitch is used which can be readily melted and in the second process the pitch must be sufficiently hard to be readily pulverized. For this purpose the binding strength and waterproofing effect of the pitch makes it particularly advantageous.

(5) CORE COMPOUNDS—This serves as an outlet for harder pitches than are used in briquetting work. Here the pitch is used as the binder for sand cores used in making castings of iron and steel. For this purpose a bituminous binder of low ash content is desirable and coal-tar pitch serves the purpose admirably.

(6) PAINTS AND PROTECTIVE COATINGS—Solutions of coal-tar pitch in tar solvents comprise the main ingredients of the best tar paints. These are used for the protection of structural iron and steel, for waterproofing of interior walls, where it is desired to plaster directly over the paint, for acid-proofing and alkali-proofing paints and many other diverse uses. The reputation of tar paints has suffered much by poorly and improperly made materials. If properly compounded they are the equal if not the superior of many more expensive preparations for many purposes. That they can be completely ruined by thinning with noncompatible thinners, is referred to in an earlier part of this paper.

(7) MISCELLANEOUS USES—Other uses which may be given passing mention are as a pipe dip, in the manufacture of ready roofings, as a cement in the joints of stoneware pipe, and as a constituent of various rubber and other compounds used for insulating purposes. Hard pitch is also used in the manufacture of electric light carbons and in the manufacture of "clay pigeons" or "flying targets." Of more recent development is the use of ground-hard pitch as a fuel in the same manner as powdered coal. This has been found of advantage in some metallurgical processes.

It is probable that an intimate knowledge of all the industries of the United States would develop many other important uses for this class of bitumens. Wherever a bituminous or plastic substance is used there is the possibility of the advantageous substitution of coal-tar pitch. Because of the great diversity in the nature of the crude tars it is possible to vary the characteristics of the residual pitches so as to make them cover a wide field of usefulness. In all chemical industry there is the possibility of its use and it may be that only the unfamiliarity of many chemists and engineers with the real properties and characteristics of coal-tar pitch, has prevented its wider application in our industrial establishments.

THE BARRETT COMPANY  
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## THE HIGH CHARACTER OF THE MANUFACTURED FOODS OFFERED THE PUBLIC TO-DAY<sup>1</sup>

By A. V. H. MORY

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In view of a disposition in certain quarters to weaken the confidence of the people in the food they eat, it is thought that a summary showing the character of the foods examined during the past few years in the laboratory of a food distributing house, might be of interest.

To begin with, it should be pointed out that the attitude of

the chemist who would safeguard the reputation of his house must of necessity be different from that of the food official who would successfully prosecute violators of the law. The official is under the necessity of proving his case in court, which means that very fine distinctions may not ordinarily be taken into account; the food house chemist is seldom justified in overlooking any discrepancy, no matter how small, since he cannot be sure that somewhere in the country there may not be some one who would take exception to what appears to him to be a very small matter.

With the fact clearly in mind that the examinations made were thorough and the criticisms hair-splitting, the following may be of interest:

Out of the 585 samples of miscellaneous manufactured foods analyzed, representing prospective purchases as well as samples taken from stock, there were found, all told, 497 samples, or 85 per cent, which were entirely free from any form of adulteration or misbranding.

Of the 15 per cent of adulterated or misbranded samples about one-sixth, or 2.7 per cent of the whole number, might be held to be deleterious to health. These possibly deleterious samples represented the following products: Flour bleached with oxides of nitrogen, catsup containing sodium benzoate, junket tablets preserved with boric acid, and dried fruits and gelatine bleached with sulfur dioxide. The rest of the 15 per cent were found wanting for the most part because they gave constants not in full accord with the U. S. Department of Agriculture *Circular 19*, though probably not enough out of line to warrant a charge of proved adulteration. There were also a few cases involving fraud only.

These 585 samples represent the output of many producers from different parts of the country, and while it must be admitted that in almost every case these producers are well known and reputable, still, since the most of them are also very large producers, their output represents a considerable part of the manufactured food of the country.

The point must not be lost sight of that the above data were mostly obtained from the examination of products known to be more likely to be found deficient. If uniformly frequent examinations had been made of all varieties of food products sold, the showing would be many times as good as that indicated by the above figures.

It would thus appear that among manufacturers of food products who are considered reputable, the number of cases representing adulteration and misbranding is very small and the number representing a serious menace to health is practically negligible.

The fact is that for some years past about the only service the laboratory of the distributing house referred to has been able to render, is that of helping the expert buyers to select the best from among a number of perfectly legal and wholesome products submitted for consideration. And this in spite of the fact that evidences of adulteration and misbranding have been carefully and persistently sought.

It is a serious question whether the production of food products has not reached a plane far above that of other lines equally susceptible of sophistication, and approached very near to the point where the criminally inclined, who always have taken and always will take chances in the violation of law, are about the only offenders.

This encouraging state of affairs has plainly come about through our food laws, the enforcement of which has enabled the majority, inclined naturally toward fair dealing, to compete on a higher plane with the less scrupulous minority. Efficient law enforcement has thus found a ready champion in the reputable producer and distributor, whose influence is bound to be favorable to even greater efficiency in law enforcement and to a continued improvement in the character of our food supply.

SEARS, ROEBUCK & COMPANY  
CHICAGO, ILLINOIS

<sup>1</sup> Read at the 52nd Meeting of the American Chemical Society, Urbana-Champaign, April 18-21, 1916.

RESEARCH, SCIENTIFIC AND INDUSTRIAL IN THE COAL-TAR DYE INDUSTRY<sup>1</sup>

By BERNHARD C. HESSE

The coal-tar dye industry as it stands to-day is the result of the methodical and systematic following up of a side-issue of a scientific research in 1856. It is the composite result of the coordination of science, industry and merchandizing. The purpose of this paper is to consider the contribution of chemical research to this net result and to compare, in some manner, the contributions of investigations in institutions of learning with those of investigations in industrial establishments.

## POPULAR VIEW OF COAL-TAR DYE RESEARCH

Chemical research is, without doubt, the real underlying source of the origin, development and growth of this industry; on account of the great brilliancy of the intellectual achievement in synthetically producing on a commercial scale a thing theretofore derived wholly from vegetable sources, namely, alizarin, and of producing so many beautiful and useful things from such an unsightly mess as coal tar, the part played by research in this development has come to be regarded by the public as distinctive of and peculiar to this industry and naturally this has lost nothing in the retelling; so it is not to be wondered at that research in coal-tar dyes came to be spoken of by both laymen and scientists as something of an extraordinary nature. This view has become very wide-spread and deep-rooted. From the time I first became acquainted with coal-tar dye chemistry at the University of Michigan in 1888, until I was graduated from the University of Chicago in 1896, I somehow acquired from the literature and from my instructors the idea, amounting almost to conviction, that there was something almost uncanny about coal-tar dye research and the methods employed in it.

## GERMANY AND THE UNITED STATES

Directly after graduating from the University of Chicago in 1896, I entered the employ of the largest coal-tar dye works in the world at its plant in Germany and indeed in one of its research laboratories. This was my first trip outside the United States and it was, of course, an event of the first magnitude for me to be in Europe, and, as a chemist, to be in Germany, in a German coal-tar dye plant, and to cap it all in its research laboratory—a real *sanctum sanctorum* for chemists. In a short time the daily routine wore the novelty off my experience and I then settled down to calm analysis and dispassionate appraisal of my surroundings and to compare what was actually before and around me with my expectations. I found that the general laboratory equipment was no better than what I had been accustomed to; that my colleagues had no better fundamental training than I had enjoyed nor any better fact—or manipulative—equipment than I; that those in charge of the work had no better general intellectual equipment nor any more native ability than had my instructors; in short, there was nothing new about it at all, nothing that we did not have back home, nothing—except the specific problems that were engaging their attention, and the special opportunities of attacking them. Those problems were of no higher order of complexity than those I had been accustomed to for years, in fact, most of them were not very complex from a purely intellectual viewpoint. There was nothing inherently uncanny, magical or wizardly about their occupation whatever. It was nothing but plain hard work and keeping everlastingly at it. Now, what was the actual thing behind that chemical laboratory that we did not have at home? It was money, willing to back such activity, convinced that in the final outcome, a profit would be made; money, willing to take university graduates expecting from them no special knowledge other than a good and thorough grounding

in scientific research and provide them with opportunity to become specialists suited to the factory's needs. However, we then had numerous men at home, who put their money behind investigational enterprises but they had selected subjects different from coal-tar dyes; for example, sewing machines, agricultural implements, typewriters, shoemaking machinery, incandescent lamps and many others, where the sums invested, the high-grade specialists employed, the scientific, systematic and methodical development and merchandizing lose nothing whatever by comparison with what is done in coal-tar dyes in Germany. This was my first conclusion 20 years ago and it has since been confirmed by comparison with conditions on both sides of the Atlantic and has long since become a firm conviction with me, fortified as it is by close and intimate contact with a number of large enterprises at home and ten different trips to Germany, covering a total of 36 months' residence in Germany, where and when I checked up my views. Also, I have met competitively and collaboratively coal-tar dye chemists and researchers, not only of Germany, but of Austria, France, Switzerland and England as well, and have worked side by side with them in three different research laboratories, two in Germany and one in England. Each trip brought me home more convinced than ever that neither Germany nor any of these other countries had anything fundamental to teach us in the way of research even though, as a people, we did have much to learn, particularly from Germany, in determination to know how to make everything count to its utmost profitably realizable capacity, and to make specialists out of university graduates—in other words, national teamwork.

In short, we have as good educational institutions, as good chemical instructors, as good chemical investigators, and as good native ability as has Germany or any other country, but with us these are not as widely diffused.

In the final analysis "Research" is made up of "I want to know" and "I am going to find out,"—two qualities which the American people, inclusive of its chemists, have always had in abundance and to spare, but not always coordinated nor efficient. Desire to know cannot have practical effect unless opportunity to find out be available. To-day's opportunity was generally yesterday's impossibility. If opportunity ever presents itself in this country to find out about coal-tar dyes, I am confident that we will find out all that such opportunity can be made to make available and without going beyond our own borders for the men or the "know-how." What we do not have now, our own educational institutions are fully capable of supplying, if and when called upon. But in this, as in all like things, the time element is one that must be taken into serious account.

Like coal-tar dyes, our sewing machines, incandescent lamps, agricultural, writing and shoemaking machines are not natural products and had to make their own way in the markets of the world; they too had to be created and developed; as in coal-tar dyes every other country had the same initial opportunity to make the same kind of machines that we did, but we created those industries and we have maintained our supremacy against the world. It is nothing unheard of or new for us to create new things, overcome long-standing prejudices and to conquer foreign markets.

Fundamentally then, we have done all the things that made the coal-tar dye industry, but our efforts have been along other specific lines; it merely remains for us to decide definitely to attack that particular problem, it is no harder to solve than many others that we have solved. It is not, and probably never has been, a question of whether we can or cannot make coal-tar dyes or whether we could learn how, but rather a question of when we did do it would it be worth our while; could we not do something else to better advantage?

<sup>1</sup> Address at the Chemistry Conference, 25th Anniversary University of Chicago, June 5, 1916.



## THE COAL-TAR DYES

In the coal tar dyes industry as it is to-day, all but two of those dyes are without counterpart in nature; they are as much man created as is a sewing machine or a typewriter. Two of the dyes now made from coal tar were, prior thereto, secured entirely from vegetable sources and had been used for centuries as dyestuffs: these two are alizarin and indigo. The coal-tar product is identical with the vegetable product in both cases. It was chemical research that pointed the way for the founding and development of this industry in both the above branches.

As applied to chemistry, research may be scientific, empirical or industrial; it is as impossible to draw the dividing line between these three classes as it is to designate the precise instant of time when night ceases and day begins, or the reverse. The scientific research of to-day is the empirical research of to-morrow and the industrial research of the day after.

**INDIGO AND ALIZARIN**—In the case of both indigo and alizarin, scientific research first of all had to determine the chemical constitution of these substances and confirm them by a synthesis; then empirically, and guided by the spirit and method of scientific research, the commercially possible syntheses had to be explored and then industrial research had to adapt one or more of these methods to commercial use—a general procedure fundamentally familiar to Americans in many other lines.

Scientific research attempted to solve the chemical constitution of alizarin as early as 1848; in 1852 a constitution, since recognized as erroneous, was assigned to it but in 1869 its correct constitution was deduced and its synthesis from anthracene accomplished; its commercial introduction was accomplished within 1 year; empirical research, in less than 6 months from the discovery of the first synthesis, developed the method which, with but few nonfundamental changes, is the one used to-day, and shortly after its discovery the annual value of its production was \$8,000,000; that is, 20 years were required to solve the scientific research, and less than 1 year was needed for commercial introduction. Vegetable alizarin was practically conquered in less than 2 years of commercial effort, or a total of 22 years.

Scientific research into the chemical constitution of indigo began in 1841 and was not concluded until 1882; in 1890 empirical research led to the present-day commercial process, but it was not until 1897 that the industrial research was concluded; it required 5 years in addition to conquer vegetable indigo; that is, the scientific research required 41 years to complete its task, empirical research 8 years, industrial research 7 years, and commercial exploitation 5 years, or a total of 61 years. The annual value of vegetable indigo in 1882 was about \$20,000,000.

The contribution of scientific research was not limited to the ascertainment of the constitution of these two substances. In the case of alizarin the use of caustic-alkali melt of sulfoacids for the making of hydroxyl derivatives was discovered in the course of scientific researches in France and in Belgium in 1867, and applied in Germany and in England almost simultaneously in 1869 for making alizarin.

For indigo, liquid chlorine—in 1890 an industrial fact—was the direct offspring of a scientific research (though carried out in an industrial establishment) into the conditions under which chlorine can be liquefied and into the properties of liquid chlorine itself; the conversion of phthalimid into anthranilic acid was accomplished in 1890 in Holland by applying to phthalimid a reaction originally applied in Germany in 1882 to acetamid and thereafter largely developed by chemists in Holland and elsewhere; the use of phenylglycine and of its carboxylic acid as an indigo intermediate was discovered in Switzerland in 1890; the use of mercury in connection with sulfuric acid for oxidizing organic substances controllably, as well as to complete oxidation, was discovered in 1883 and is of Danish origin, but was not

applied to the oxidation of naphthalene until 1896. Therefore, scientific research also blazed the way for the commercial alizarin synthesis and provided the direct fundamentals of four of the necessary things in the first commercially successful indigo synthesis.

Furthermore, before the makers of synthetic alizarin and of synthetic indigo could afford to commit themselves definitely and heavily to the production of these two things, it was necessary to make reasonably sure that the particular method to be operated was as cheap as any as would be likely to be developed by others and above all that there were no "next-door-neighbors" chemically known as isomers, homologues and substitution products, that would be better than these two substances or either of them. Here is where the results of scientific research through its achievements in determining the possible number of isomers, homologues and substitution products enabled the empirical investigators to delimit and circumscribe the field to be investigated with reasonable assurance as to accuracy and certainty that nothing had been overlooked, that nothing was left for those who came after to create unwelcome effective competition—and in these empirical investigations the laboratory, investigational and reasoning methods of scientific research were liberally drawn upon.

**MAGENTA AND ITS CONGENERS**—Passing now to those coal-tar dyes not to be found in nature, *i. e.*, the created dyes of this industry, it may be said that for the great majority of them the chemical constitution is assumed as known, based upon the methods of their production and the rules in relation thereto which scientific research established; to some of these dyes no chemical constitution has been assigned and for some even the chemical composition is not known.

Magenta was first discovered in Russia in 1856; chemists in France and England from 1858 to 1860 developed and patented various methods of manufacture from the commercial anilin of that day; but it was not until 1864 and 1866 that it was discovered that pure anilin or pure para- or orthotoluidin when treated by these methods would not yield magenta but that a mixture of these three is needful; it was not until 1878 that its constitutional formula was determined. Long prior to this the industrial method of to-day had been found by empirical or exploratory research; the constitutional formula, however, gave greater certainty to the conclusion of the industrial men that the limit of successful further investigation had been reached for at least a reasonably long period of time. In this case, knowledge of the constitution did not itself point to any commercially new or useful results; it merely confirmed the conclusions as to temporary finality of the work of others.

Long before the constitution had been determined it was definitely ascertained empirically by men in France and England, and to a lesser extent in Germany, that there were three amido groups in magenta, and long before that, that there were replaceable hydrogens in magenta and the empirical workers had exhausted the then available means of treatment of magenta for its substitution products and had worked out substantially all the commercially useful products which included red, blue, violet and green, both basic and acid, of the present day.

As a direct result of the scientific investigation for the constitution of magenta came the investigation of condensation products of benzaldehyde with tertiary amines and from that the use of benzaldehyde and of substituted benzaldehydes in the making of dyes which have since acquired great commercial importance. Once the direction was given, it was only necessary to prepare the various substituted benzaldehydes and the substitutes for dimethylanilin employed in making the pioneer of this class in 1878 and systematically to exploit the field thus marked out. In 1878 it was recognized that nitration and reduction might yield new dyes but attempts in this direction

then failed only to become commercially successful about 10 years later.

In a scientific investigation into the constitution of rosolic acid in 1878 it was found that dioxybenzophenone combines with phenol to produce aurin. Michler's Ketone, a "next-door-neighbor" of dioxybenzophenone, was discovered in 1876; its production on a commercial scale was realized in Switzerland in 1883, in which year it, like benzaldehyde in 1878, was treated, also in Switzerland, with dimethylanilin and gave a violet. From then on it was only needed to treat Michler's Ketone with all the substitutes for dimethylanilin and to work out the commercially useful dyes in the field thus laid out—a labor not completed in the 33 years that have since elapsed.

**THE PHTHALEINS**—All of these investigations reflect the influence of the scientific researches begun in 1871 on the behavior of phthalic acid with phenols in which the trihydric phenol, pyrogallol, was first examined, then the dihydric phenol, resorcin, and, finally, phenol itself; the commercial introduction of the first did not take place until 7 years later, while the second required 3 years, this delay being due to the difficulties encountered in commercially making the intermediates, namely, phthalic anhydride and the phenols; the bromination products of fluorescein, though discovered in 1873, were not marketed until 1874; these were thereupon followed by iodination, methylation, chlorination and nitration products of fluorescein, but it was not until 13 years later, or in 1887, that alkylated amidophenols were investigated in their behavior towards phthalic acid and yielded most valuable dyes; still, not until 1894 or 7 years later was it discovered that this reaction proceeded in a two-stage manner, combining first in equimolecular proportions and this result then reacting with the second molecule of the amidophenol, although such behavior was foreshadowed in the work done in the scientific investigation of the constitution of magenta and the synthesis of the benzaldehyde dyes and the dyes from Michler's Ketone just considered. While in this particular case, failure to recognize the two-stage character of the reaction did not result in the loss to the art of really valuable dyes, yet our knowledge of the mechanism of this reaction was by that much retarded. In the case of tartrazine, which was discovered in 1884 and marketed in 1885, although its two intermediates were known to scientific investigators wholly as the direct result of abstract scientific work as far back as 1879, the two-stage nature of its synthesis was not observed until 1893, or 9 years later; in this case the two-stage process enables the production of commercial dyes of real value not theretofore available.

Methylene blue, discovered in 1876 and marketed in 1877, was manufactured in three different ways before conclusive answer was obtained as to the mechanism of any of these reactions by scientific examination, in 1889; no method of manufacture, at all new in principle, grew out of this investigation.

**THE AZO DYES**—The reactions underlying the azo dyes were exhaustively treated, scientifically, in researches begun in 1860 and completed in 1870; the reactivity of diazo compounds with amido compounds was discovered in 1864 and with phenolic compounds in 1870. The first of the azo dyes appeared on the market in 1861 and was followed in 1863 and 1875 by two others, but it was not until 1876 that this reaction began to be exploited to any considerable extent and here again the reason was the difficulty of obtaining the intermediates in commercial quantities. All products of this class were direct dyes for wool or mordant dyes for cotton and none of them was a direct dye for cotton until 1884, when benzidine, itself described in scientific literature as early as 1846, was found to be capable of producing direct cotton dyes; but these first benzidine dyes were not very fast to acids, alkalis or light and the chase for phenolic or amido or amidophenolic substances which, when combined with benzidine or benzidine substitutes, would yield fast colors,

was on! In this chase scientific investigators contributed little of effective specific help; they had marked out the field, provided the general implements, intellectual and manipulative, but the magnitude of the problem was too great for any individual and one wholly unsuited to university treatment; its solution called for careful preparation of the individual materials, combining them with benzidine and benzidine substitutes, to yield direct cotton dyes, examining these dyes in their behavior towards cotton and other fabrics under service conditions or their substitutes and, profiting by whatever they showed, forecasting further work with the help of the general scientific rules and laws of structure of these materials and to take up the task anew. A heart-breaking, desolate and uninspiring lot for the isolated worker, not in the confidence of those who know commercial conditions as to the availability, immediate or remote, of the materials needed to make these new intermediates, and of the commercial requirements of the dye markets, but a task full of zest and excitement when carried out in cooperation and collaboration with those who were conversant with all these details—for it was clear that there could be but few victors, the laggards would be beaten. Surely, the university and the individual investigator were hopelessly outclassed in this particular chase for only the worst kind of a fluke could lead to a useful result; true, new results could be obtained, but differing to the uninitiated in such subordinate and seemingly trifling details as to make the work actually sheer monotony. Yet the greatest skill and knowledge was required of the men who actually carried out this work in the industrial establishments.

In the middle of the eighties investigation by individual investigators and by institutions of learning began to cease contributions of pioneer value to this industry and except for the brilliant glycine synthesis of indigo in 1890 the scientific researchers have done nothing since which specifically and directly approaches pioneer work. By that time research in this field had settled down to the humdrum task of sifting out from the hundreds of thousands of millions of possible dye combinations those that could survive in the world's markets. The work theretofore done by the university investigator was now done in industrial establishments and the new types of commercial dyes since then introduced have emanated from these industrial establishments themselves and as a direct result of industrial conditions themselves, and not from any real scientific experimentation, reflection or deduction by university investigators, as such.

#### RETROSPECT

However, looking backward, it does seem that industrial investigators could have developed the industry faster and that university investigators could have pointed out new fields a little more quickly than they did. For example, sulfonating as a means of rendering dyes better adapted for animal fiber, was discovered as early as 1862, yet Martius' Yellow, discovered and marketed in 1856, was not sulfonated until 1879, nor was magenta, also marketed in 1856, sulfonated until 1877; anilin yellow was not sulfonated until 1877, although on the markets in 1859; as early as 1876 it was known that sulfur could be substituted for the imido group to produce new dye-stuffs, but this substitution in the indigo group was not tried until 1905, although all needful materials were known as early as 1890, and the real development of the indigoid dyes did not begin until well after 1900, although most of the materials had then been available for upwards of 10 years. Instances like these could be given in great numbers.

Of course, after things have been done it is not only very easy but most ungracious to say that they should have been done sooner or better, but these comparisons are not here made for any purpose of criticism or fault-finding; they are made in



the hope that calling attention to a few opportunities now easily recognized as having been overlooked in the past, may sharpen our foresight and increase our powers of intellectual penetration and deduction and hearten university investigators so that they may again be the pioneer leaders in a field which is without limit and whose future cannot but be far brighter than its past, however glorious that has been. The opportunities for applying constructive imagination and selective judgment to the logical and systematic development of this field for pioneer work along the lines of types and subtypes are far greater to day than they ever were and the chances of success are certainly no smaller than they were in the days when the university investigator was the guiding spirit in this industry. A comprehensive and useful answer to the question as to the causal relationship between tinctorial properties and chemical constitution has still to be given; no more powerful intellectual instrument than this could be devised and the university investigator has an almost equal chance, so far as materials, facts and facilities go, with his industrial brother, and so far as surroundings in sympathy with such work are concerned the industrial chemist or researcher is very greatly at a disadvantage; an insight of this kind should be as powerful in this branch of chemistry as the calculus is in engineering; the fact that more than 40 years have passed since the first attempts were made in this direction should not discourage—centuries before Newton and Leibnitz the world had many mathematicians of undoubted ability and power.

#### CONCLUSIONS

It would be idle to suppose that in the foregoing anything more than a mere fragmentary outline sketch of the relative contributions of research and its various subdivisions to this industry have been given; nevertheless, the essentials are there, and they justify the following general statements:

I—The coal-tar dye industry had its origin in an accidental occurrence in the course of a purely scientific research.

II—For the first 8 years the development was wholly through empirical research with no scientific or very clear guide to the field.

III—When scientific investigation had established certain fundamental scientific data the development proceeded more rapidly than theretofore and with greater certainty.

IV—The first individual success of real commercial magnitude and permanence owed its conception and execution wholly to scientific research.

V—Empirical investigation, both in institutions of learning and in industrial establishments, profiting by and taking advantage of purely scientific achievements and results, reached its conclusions and completed its labors more speedily and certainly than it otherwise would and made the commercial venture less hazardous than it otherwise would have been.

VI—The industrial research needed for the industrial application, itself, depended for much, and in some cases for all, of their material upon scientific research in no way connected with dyes or anything relating to them.

To return, then, to the beginning and fulfil the avowed purpose of this paper, namely, comparison of researches carried out in institutions of learning and in industrial establishments.

The university and like men for the first 30 or 35 years, by the development of the general and specific laws of chemical constitution, placed in their own and in the hands of industrial researchers means more powerful than ever existed as helps in chemical research; as a result, new methods of manufacture, new dyes and new types of dyes were made foreseeable long before the industrial researcher and chemist could get around to the experimental testing of the material thus laid bare.

The industrial chemist and researcher has not provided his university or scientific brother with any such broad general helps but he has contributed an enormous amount of fact-

material and has discovered a multitude of new manipulative methods but all of them more or less disconnected and not coordinated; the successful methods of industrial research were all borrowed from scientific research; for the past 25 or 30 years the industrial researcher has accomplished all new advances himself but in so doing he has drawn very heavily and without stint upon the results of scientific research not at all connected with the subject of dyes.

Who shall say which is the more important achievement? Both are wholly essential to progress; neither can develop to its fullest extent without the other; the scientific investigator needs access to an amount of fact-material which it is beyond his strength to gather; the industrial researcher needs rules, laws, generalizations, experimental and manipulative methods which his surroundings usually make impossible for him to discover or to devise; the coal-tar dye industry never would have existed without both.

This answer is probably the only one that should have been expected, yet the general and wide-spread opinion was and is otherwise. This answer portrays approximately the conditions existing in whole or in part in our own chemical, mechanical and electrical industries and in every application of science to every-day life, and why should chemistry applied to coal-tar dyes be different? The answer is that it is not.

Since our success as a nation in chemical, mechanical and electrical endeavor is in part, at any rate, based upon essentially the same attitude towards their respective purely scientific branches and their commercial application, is not that a complete warrant for the conviction that we also have the ability to build up a coal-tar dye industry? Our institutions of learning have long been prepared competently to make their contribution should our industrials make the call. Will our industrials send forth the call?

25 BROAD STREET, NEW YORK CITY

#### THE AMERICAN TEXTILE MANUFACTURER: HIS ATTITUDE TOWARD AMERICAN-MADE DYES<sup>1</sup>

By FREDERIC DANNERTH<sup>2</sup>

So much has been said during the past two years regarding the attitude of American textile manufacturers toward American-made dyes that it seems necessary to correct some current impressions.

One of the principal, if not the most important, reason for using German-made dyes in the United States was the fact that nearly all the sunfast and laundryproof dyes available were and are still made in Germany. The dyes used for printing colored stripes on men's cotton shirts are the well-known vat dyes which occur in commerce under the distinctive names of Helindone, Algole, Indanthrene, Cibanone. Then, too, there are a large number of "acid" dyes which are characterized by unusual fastness to light when applied to wool and silk fibers. These acid dyes if applied to silk fabrics can be exposed to direct sunlight for a period of 40 days, in a latitude of 41° North, during July and August, without showing any appreciable "fading." For the benefit of such research chemists as may be interested in developing dyes of this character, I have appended a list of some sunfast dyes together with the index number under which they appear in Schultz' "Farbentabellen" (1914 edition). This might well serve as a basis for advanced dye investigations in our organic chemical laboratories.

#### SUNFAST DYES ON ANIMAL FIBERS

(865) Alizarin cyanin green GX	(853) Anthrachinon violet B
(864) Anthrachinon green GXN	(852) Alizarin Irisol D
(863) Anthrachinon blue-green BXO	(851) Alizarin direct blue B
(862) Alizarin blue-black B	(850) Indanthrene blue WB
(861) Anthrachinon blue SR extra	(639) Gallanil violet RB
(860) Cyananthrol G	(303) Brilliant yellow
(859) Cyananthrol R	(249) Crocein scarlet 3B
(858) Alizarin Saphirol B	

<sup>1</sup> Presented at the One Hundredth Meeting of the National Association of Cotton Manufacturers, Boston, April, 1916.

<sup>2</sup> Head of the Textile Trade Laboratory, Newark, N. J.

These and a score of others including such well-known dyes as Cloth Red and Naphthol Green are dyes which are to-day of importance to the textile manufacturers of the United States. To the list given might be added such dyes as Patent Blue (Hoechst) and Rhodamine (Elberfeld), which stand entirely in a class by themselves in the matter of brilliancy. The dyes mentioned have all been tested out in this laboratory and have been found to possess the properties mentioned.

In view of the extensive discussion of tariff protection for our American dye industry it seems that attention should be called to one of the important factors which has heretofore received no consideration in discussions of this measure. The industry of coal-tar dyes is based on the science of organic chemistry, and this is a branch of chemical research which is at present being taught to only a limited extent at our American colleges. This statement is based on an inspection of the catalogue of five leading universities located in the Atlantic States, and is supported by a personal contact with graduates of these institutions. It therefore seems timely to call attention to this deficiency in our educational system, and if possible provide ways and means for altering these conditions. The points which require emphasis are:

(1)—The supremacy of the German dye-manufacturing industry at the present day is probably due primarily to the advanced instruction in organic chemistry which is offered to students in German universities and technical colleges.

(2)—The manufacture of modern *sunfast* and *laundryproof* dyes in the United States cannot begin until there are in the country a sufficient number of men with an adequate education in the methods of organic chemical research.

(3)—Until this instruction is given in our American colleges,

the extension of our dye factories and the invention of new and useful dyes must of necessity be very limited. Even if our college courses are revised to-day, it will be three or possibly four years before adequately trained men are available. The past twenty-five years of activity in our American dye factories bear abundant witness to the fact that our dye manufacturers are not inclined to spend time or money in the development of dyes of especial "fastness." This, however, is the particular point which European chemists have emphasized in all their dye developments and any rational consideration of tariff protection must take this point into consideration. The mere investment of capital will not insure for us an American dye industry.

(4)—The numberless complaints which have already been made with regard to the "fastness" of American-made dyes, demonstrate conclusively the present state of the industry in the United States, after an unhampered development of forty-six years.

(5)—An investigation will show that European chemical laboratories, in the majority of cases, have their doors open from seven o'clock in the morning until six o'clock in the evening. Which of our American universities can say as much?

The textile manufacturers of the United States have been variously accused by some of our less conservative collegiate professors, of favoring English and German dyes to the exclusion of American-made dyes. The answer to this accusation has already been given. All that the American dyer asks is that he be supplied with *modern dyes* which shall equal in brilliancy and in "fastness" the products which are now made by foreign manufacturers. It is also fair to assume that this will not be possible until students are given the necessary basic instruction in our colleges.

THE TEXTILE TRADE LABORATORY  
325 ACADEMY STREET, NEWARK, NEW JERSEY

## CURRENT INDUSTRIAL NEWS

### BRITISH SUPPLY KIESELGUHR AND TUNGSTEN ORES

It is satisfactory to learn, says the *Times Engineering Supplement*, that the supply of diatomite, more familiarly known as kieselguhr, much of which was formerly obtained from foreign sources, will, in future, be obtained from sources within the British Empire. Diatomite is not only used in the production of dynamite but also in sugar refining and other industries, and it is important to have regular supplies in times of peace as well as in war times. It seems from the results of research carried out at the Imperial Institute, London, that valuable sources of supply have been found in Victoria and New South Wales. Attention has also recently been directed to the question of supplies of another important raw material, tungsten powder. Now that the technical problem in connection with the production of tungsten has been solved, it is necessary that the new industry should be assured of supplies of raw material to keep the new plants in regular operation. It is probable that, as in the case of diatomite, resource will be had to the large supplies of ores which are known to exist in Australia, and it has been suggested that a sound policy would be to erect concentration machinery in close vicinity to the wolfram deposits so that the ore, shipped to home manufacturers, might contain a conveniently high percentage of tungsten.—A. McMILLAN.

### NEW ZEALAND CHINA CLAY

According to a report in the *Chemical Trade Journal*, what will eventually prove to be a valuable industry has been started in New Zealand despite the war. For some months past developments have been proceeding on a large reef of china clay at Ngauruahia in the north island. Analysis made by the government analyst has shown the material to be very similar to the china clay of Cornwall.—M.

### REVISED MINING REGULATIONS IN COREA

H. M. Consul at Seoul has furnished a translation of a Mining Ordinance issued by the Governor-General of Corea, to take the place of the mining law of July 12, 1906. The ordinance, which is to take effect upon a date to be determined by the Governor-General, consists of 64 articles and is based on the Mining Law of Japan. The main feature of importance is that, in future, foreigners, as individuals, will be prohibited from obtaining mining concessions in Corea. The grant of mining interests by the new regulation is to be limited to Japanese subjects or juridical persons established in accordance with Japanese law. Mining rights already in existence and held by foreigners are not to be interfered with but foreign juridical persons in order to succeed to such rights must become juridical persons established in accordance with Japanese law, and must have their head office in Corea. Priority of application will probably no longer ensure the grant of mining rights although this is not expressly stated in the ordinance.—M.

### SIAM BENZOIN

According to a report from Bangkok, one of the staple products of Siam is gum benzoin (the resinous exudation of a tree closely related to the *Styrax benzoin* of Sumatra). Siam benzoin is collected in the northern forest regions of the country and is very highly esteemed for its delicate odor. It is used to some extent locally for the preparation of toilet water, and allied preparations. During the year ending March, 1915, 52,251 lbs. of benzoin were available for export and with a value of \$27,918. Most of the benzoin exported went to the United Kingdom but a large quantity went to Germany before the outbreak of the war.—M.



### PETROLEUM DISCOVERY IN CHILE

According to a report in the *British Board of Trade Journal*, a telegram from Punta Arenas states that splendid samples of petroleum have been extracted from borings at Rio Amarillo and the existence of this oil in considerable quantities can be taken for granted in that district.—M.

### SULFUR PRODUCTION IN RUSSIA

At the foothills of At-Chagyl, alongside the salt lake of Kukurt-Ala, 62 versts (40 miles) from Krosnovodsk, the exploitation of an immense deposit of sulfur has been begun. The deposit is said to consist of 90 per cent pure sulfur.—M.

### POWER TRANSMISSION UNDER WATER

International power transmission, says a contemporary, by submarine cable has now been established between Sweden and Denmark, having been put into use in January. The cables run from Palsjo just north of Elsinore, Denmark, the underwater distance being 3.35 miles, the transmission voltage 25,000, and the energy transmitted 5,000 kilowatts. The two power cables are laid parallel to each other 100 m. apart while a protecting steel cable with a breaking strength of 40 tons is run parallel to the power lines and 100 m. from the nearest. Iron towers 25 m. high on either shore warn vessels against attempting to anchor near the cables. These towers carry green lights at night. A steam station on the Denmark side serves as a reserve in case of interruption on the submarine line.—M.

### EFFICIENCY OF GAS-FIRED FURNACES

A wide range of gas-fired furnaces for melting and annealing metals is described in a list recently published by a Birmingham firm. The crucible melting furnaces are fitted with Wright-Brayshaw burners and use gas at ordinary pressure with an air blast at a pressure of 3 lbs. per sq. in. A comparative test, extending over 4 working days, has been carried out between one of these furnaces and a coke-fired furnace at a brass foundry. The coke-fired furnace was able to melt an average weight daily of 592 lbs., the number of melts being 13, each requiring 53 min., while the total fuel used was 300 lbs. The average weight of brass melted with the gas-fired furnace was 910 lbs., the number of melts 20, each requiring 34.5 min. and the total fuel consumption being 2,076 cu. ft. The gas-fired furnace proved the cheaper as the average cost of the castings produced was 0.3 cent, while for the coke furnace the cost worked out about double that amount. Furthermore, with the coke, the cost for crucibles was more than twice as much as with gas and the gas-fired furnace crucibles are able to stand regularly 90 to 100 melts. The best result obtained during the tests was the melting of 45 lbs. brass in 15 min. with a consumption of 67 cu. ft., or 1.49 cu. ft. of gas per lb. of metal melted. In the annealing furnace, a reducing, neutral of oxidizing atmosphere can be obtained at will. Gas at ordinary pressure is employed with air at 2 to 4 in. water-gauge pressure and a temperature of 1400° F. is readily obtained. Other types of furnaces are referred to, for the heat treatment of high-speed steel tools, for heating and mixing chemicals and for heating rivets.—M.

### MOLYBDENITE AND ZINC IN NEW ZEALAND

H. M. Trade Commissioner in New Zealand has forwarded extracts from the local press relating to reported discoveries of deposits of molybdenum and zinc ores in the Dominion. The deposit containing the molybdenum has been discovered at Takata and the samples assayed were found to contain 50 per cent  $\text{MoO}_3$ . Ore declared to be pure sulfide of zinc has also been discovered at Wangapeka, 53 miles distant from Nelson. The reef is from 4 to 5 ft. wide and the ore is said to run 18 per cent zinc.—M.

### ANNEALING OF ALUMINUM

In a recent report to the Faraday Society, London, on the annealing of aluminum, Messrs. Seligman and Williams describe some interesting anomalies in the behavior of the metal. Hard-worked aluminum seems to be more readily soluble in nitric acid than the annealed metal and, if the hard-worked sample be heated to 125° C., a definite change in the rate of dissolution is brought about. A specimen of hard-worked metal which lost 56 mg. per 100 sq. cm. per 24 hours in nitric acid (sp. gr. 1.42), lost only 39 mg. when similarly exposed after being annealed at 500° C. (a decrease of 30 per cent). On annealing for 10 hours at 125° C. there was a decrease of 5.3 per cent in the rate of dissolution, whereas it had been anticipated that if the heating were prolonged, the decrease in the rate of dissolution might be augmented. If samples were heated for 80 hours at 152° C., the rate of dissolution was very much the same as if no prolonged heating had been used at all. These facts do not seem to tally with the observations of other workers. A release of strain should certainly be accompanied by reduction in the rate of dissolution but this release of strain would not account for the subsequent increase. The behavior of aluminum as described above does not seem to fall in with any theories which have yet been put forward.—M.

### A NIGERIAN COALFIELD

It is possible that the recent discovery of coal at Udi, in Southern Nigeria, may mark a new and important epoch in the history of West Africa, as it may start many industrial developments in that little-known country. The discovery was made in the course of a mineral survey of Southern Nigeria. According to the *Engineer*, 122, No. 3157, steps have been taken by the government to work the field, following a favorable report from the Imperial Institute, London, and 10,000 tons of coal have already been mined and stacked for use. The coal field is in the immediate proximity of the New Nigerian railway from Port Harcourt, whence the distance is only 150 miles; when this line is opened for traffic—some time this year—transport can begin at once and the coal be at the service of the whole of Nigeria. Many specimens of Udi coal have been fully examined and it has been subjected to exhaustive trials on the Nigerian railway, the reports upon it as a locomotive fuel being entirely favorable. The total area of the Udi deposits is, as far as can be at present estimated, not less than 2100 sq. mi. and in places the seams are 5 ft. thick.—M.

### ZINC BRONZE

*Bulletin 59* of the Technological Series of the British Bureau of Standards gives an account of an investigation of standard test specimens of a zinc bronze (Cu 88, Sn 10, Zn 2) by Messrs. C. P. Carr and H. S. Rawdon. The authors draw the following conclusions: (1) The addition of a small percentage of zinc does not affect the theoretical microstructure of the alloy; (2) the method of casting, pouring temperature, etc., affect the structure only indirectly by influencing the rate of cooling, amount and distribution of enclosures; (3) the microstructure offers an explanation for the characteristic appearance of the tensile bars after testing; and (4) of the various microstructural properties affecting the physical properties, oxide films must be considered to exert by far the greatest influence. The best type of test bar where the metal is to be cast in sand is the cast-to-size shape and if the metal is poured at a temperature ranging from 1120 to 1272° C., uniformity of tensile strength and ductility are obtained. The advantage of the cast-to-size shape is that it is easy to mould and inexpensive to machine into the shape and size required for testing. It is recommended as the form which should be adopted as standard for general foundry practice.—M.

## MINING DEVELOPMENT IN PERU

According to a report from the British Vice-Consul at Callao published in the *Mining World*, 91, No. 2362, there seems to be considerable activity towards the development of mining throughout Peru. Work in the gold placer claims of the Peruvian Exploration Co. on the Marañon River has forged ahead rapidly and there is a working staff of 300 men, including experts in hydraulic operations, while new machinery has been obtained. At Cerro de Pasco, investigations have been made and proposals put forward in regard to the possibility of working the ore dumps by the cyanide process. The low-grade silver ore tailings scattered over the pampas amount to something like 15,000,000 tons running 15 oz. of silver to the ton, and it is suggested that this ore might be treated at a total profit of over £6,000,000 (\$30,000,000), which would make Cerro de Pasco a silver producer of considerable magnitude as well as a copper producer. The Morococha Mining Co., a subsidiary of the Cerro de Pasco, although in a preliminary state of development, is producing from 80,000 to 90,000 tons copper a year which is shipped to La Fundicion for smelting. The Morococha region is one of the most actively worked mining zones in Peru. For some time past, satisfactory investigations have been made on properties some 35 miles from Cerro de Pasco and exploration work on a large scale has been determined upon. At present, machinery is in process of erection, but operations have been somewhat checked by the war. At a later date, it is intended that a smelter shall also be erected and, from indications, it is thought that the output from these mines should then rank with that of the biggest copper producers of this region. Practically the only tungsten properties so far discovered in Peru are now being developed in the Conchucos district of the department of Ancachs and that of La Libertad, but owing to lack of funds no great progress has been made.—M.

## BRITISH BOARD OF TRADE

During the month of July, the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles. Firms which may be able to supply information regarding these things are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall St., London, E. C.

American cloth  
Asbestos, A. P. jointing  
Batteries for pocket flash lamps  
Brackets, spring, for cycle lamps  
Bricks, magnesite  
Burners for cycle lamps  
Cardboard containers for office paste  
Celluloid ring cases  
Cerium stones for pocket lighters  
CHEMICALS:  
Alum  
Green coppers  
Manganese dioxide for Leclanché batteries  
Quinoline  
Sodium silico-fluoride  
Combs, horn and nonflammable  
Duplicators, composition  
Dyes, henna powder  
Electrical novelties  
Electrolytic iron  
Fiber, vulcanized, red  
Gelatin, high-class for photographic purposes  
GLASSWARE:  
Arc lamps, inner and outer globes  
Lamp chimneys  
Glass stoppered bottles  
Glass screw cap jars, 1 lb. and 1/2 lb. capacity  
Glue, fish, liquid, genuine  
Glycerine substitutes  
Grasses, artificial  
Honey sections glazed  
Helmets, papier maché  
Hollowware, cheap, enamelled for West African market  
Insulators, steatite

Kettles or pans, brass, as used in West Africa for rubber  
Lamp burners, cheap, for Indian markets  
Locks, small for fancy boxes

MACHINERY FOR:  
Bronzing, vacuum, hand  
Flattening and heading nails  
Knitting gas mantles  
Making dominoes  
Making calcium carbide  
Making metal tubes for tooth paste  
Graduating glassware  
Making spectacle and eye-glass ear-pieces  
Making gramophone needles  
Mactear furnace for making hydrochloric acid  
Magnets, tungsten-steel, permanent magnetite  
Monazite sand  
Metal plates, enamelled for domestic use

ORES AND MINERALS:  
Celestine  
Strontianite  
Razors and safety-razors  
Steel sheet, perforated like grater  
Steel castings, electric  
Syringes, hypodermic 10 per cent and 2 per cent  
Vices, hand  
Vacuum Basks  
WIRE:  
Bismuth, 0.1 mm. diam.  
Silver, 0.0165 mm. diam.  
Wire-netting (rolls) 2 ft. × 50 yds.  
—M.

## CASE HARDENING OF MILD STEEL IN GAS

Such work as is described by Mr. C. M. Walter in a recent paper on this subject, says the *Journal of Gas Lighting and Water Supply*, should be given a wider circulation among steel manufacturers. Little work has seemingly been done on the use of town gas as a carburizing or case hardening agent, but Mr. Walter's experiments show that its use for this purpose in the case of mild steel is highly effective and a good commercial proposition. His results confirm the classical researches of Prof. A. H. White and Mr. H. T. Hood, who were able to show efficiency of quality of product and controllability such as cannot be realized with the solid agents ordinarily employed for the purpose. It is important in this carburizing work that the rate at which the gas is passed through the apparatus should be slow, as this affects the quality of the carburizing.—M.

## NITRATES FROM ATMOSPHERIC NITROGEN

The statement, *Nature*, 97 (1916), 408, that since the war began Germany has succeeded in obtaining her full supply of nitrates by fixation from atmospheric nitrogen, lends additional interest to an account given in *Dagens Nyheter* (June 8) of a Swedish Company formed for the same purpose. The method of obtaining nitrogen from the air by means of an electric arc is relatively expensive and its success as a commercial project depends on the local price of electrical energy. It has further been calculated that, even if all the waterfalls of Europe were to supply energy for this purpose alone, this would be hardly sufficient to cope with the increasing demand for fertilizers throughout the world. The Swedish Company employs a method invented by Th. Thorssell (formerly head of the fertilizer and sulfuric acid works in Malmö), which method depends purely on chemical processes and demands only the special treatment of easily accessible raw material. No details of the process have as yet been given. The chief products of the factory are ammonia, ammonium nitrate and cyanide compounds, saltpetre and sulfuric acid. The process is said to be of such a nature that factories can be installed in most places without requiring any large supply of energy. Experimental work in connection with the process seems to have been started in the autumn of 1911, and during the summer of 1912 the results were approved by outside experts. The company was then set going and is now preparing to deliver its products in large quantities and has decided to raise its capital from 3.7 million to 8 million Kroner.—M.

## OILSEED INVESTIGATIONS

An article in the *Indian Trade Journal* (Feb. 11, 1916) deals with the report of the Imperial Economic Botanist, more particularly with two crops, *Carthamus tinctorius* and "rai," *Brassica juncea*. The former, safflower, is distributed widely in different parts of India and has been under investigation at Pusa for six years. Twenty-four different types have been separated and closely studied. The coloring matter, carthamin, is absent in some types and in others only feebly developed. The plant has been investigated regarding its dyeing properties by an expert who found that the best color varieties are eight times as strong as the weakest. As a rule the percentage of oil in the seeds varied between 22.77 and 30.19 and a high percentage of oil and a high color yield could be found together. Rai or Indian mustard, when studied in the pure culture, gave a large number of varieties. No fewer than 102 pure types were separated and these varied in height from 30 in. to 10 ft. The writer of the report is of the opinion that, in the case of safflower and Indian mustard, by careful selection, any types desired may be produced and, by the distribution of these types, the crops may be greatly improved both with regard to yield of seed and oil content.—M.



### ALLOYS USED FOR ZEPPELINS

A French chemical journal has published analyses of the alloys used in the construction of a Zeppelin brought down recently in France. The angle brackets were found to contain aluminum to the extent of 90.27 per cent, while zinc and copper were present to the extent of 7.8 and 0.73 per cent, respectively, together with small amounts of iron, manganese, silicon and tin. For the channel sections an alloy composed of 88.68 per cent aluminum, 9.1 per cent zinc and about the same quantities of the other elements as for the angle brackets, was used. The braces seemed to be composed of commercial aluminum, as that element was found in their composition to the extent of 99.07 per cent.—M.

### NITRATE OUTPUT

The total nitrate production for the year just ended, *i. e.*, July to June, reached about 57,850,000 quintals (a quintal = 100 lbs.) against 34,000,000 quintals for the previous year, when the total available production, after deducting oficina consumption and merma, proved to be about 33,500,000 quintals and against 62,300,000 and 62,000,000 quintals for the year ending June 30, 1914. Shipments during the past year have been about 55,000,000 quintals against 32,000,000 quintals for the year ending June 30, 1915, and 58,750,000 quintals for the year ending June 30, 1914. Mr. Thomson Aikman, in his annual report on the nitrate position, says that as no figures of European deliveries have been available during the war, it is impossible accurately to ascertain what the world's consumption has been, but it may be estimated that the total which has disappeared throughout the world has been approximately about 48-50,000,000 quintals, which is a figure greater than generally looked for. The principal features have been the continued demand for refined quality for explosive purposes (which has been considerably greater than generally anticipated), and the very large shipments to the United States and other countries outside Europe. As regards the latter, however, the excess over the normal is also probably due to the demand for explosives. The demand for agricultural purposes is understood to have been somewhat disappointing due to a variety of causes but, probably, principally on account of the difficulty of getting supplies when required and the necessary high price through excessive freights. The International Institute of Agriculture has published an extensive table showing the world's production of fertilizers, but the figures are carried down only to 1913. The following, however, are the figures for the production of sulfate of ammonia in the different countries for the years 1914 and 1915:

	1914 Tons	1915 Tons
France.....	91,500	42,000
Italy.....	14,323	15,000
Sweden.....	1,510	.....
United Kingdom.....	433,235	429,768
United States.....	166,015	192,323
Germany.....	413,837	.....

Italy and Norway produced 2,500 and 14,670 tons cyanamide, respectively, in 1914.—M.

### ELECTRICAL TREATMENT OF TIMBER

The *Builder*, 110 (1916), 405, quoting from a Swiss contemporary, refers to methods of treating timber electrically. When a current is passed through freshly cut timber a chemical change is stated to occur which renders it more able to withstand attacks of fungi. By using the "Nodon" process, it is claimed that the effect in a few hours is equivalent to months of ordinary drying in free air. Since moisture assists the flow of the electric current, the process is best applied after the tree is felled and in this way the transit weight is reduced. The electric power required is 3 kilowatts to 6 kilowatts per cubic meter.—M.

### MANUFACTURE OF VISCOSE

Two French inventions of recent date deal with the manufacture of viscose. The first concerns the precipitating bath for the preparation of the thread, and the use of a saturated solution of a double sulfate of ammonium and sodium has been patented. The solution is used as the precipitating liquor at a temperature of 30 to 40° C. and, if it is made slightly acid by means of an excess of bisulfite of soda, the ammonia is not lost, but if the liquor be raised to a temperature of 80 to 90° C. the xanthate of cellulose becomes transformed in half an hour to the hydrate and the sulfur and alkaline polysulfides retained by the threads are eliminated. The second patent is somewhat different and refers to the preparation of a saturated solution by dissolving xanthate of cellulose in aqueous solutions of acid salts. The acid salts recommended for use are bisulfite of soda in proportion 10 to 15 per 100 parts of cellulose, bicarbonate of soda and diphosphate of soda. Under these conditions a solution of viscose is obtained in a state like that of the neutral xanthate not containing free alkali but only a certain proportion of alkaline salts derived from the acid salts employed.—M.

### MOTOR CAR CONSTRUCTION

To introduce anything approaching a right-angled bend in the immediate vicinity of the exhaust part of motor car engines, says the *Autocar*, is obviously an erroneous practice. Yet, this is exactly what is done in the case of internally exhaust manifolds where the deflection of the gases from their transverse direction of emergence into a longitudinal direction can be effected only within the limited dimensions of a *monobloc* casting by what almost amounts to a right-angled bend. In the case of a new and clean engine with a fairly free exhaust and carburetor conditions to suit, fair results may, for a little while, be achieved, but there generally comes a time when a permanent carburetor blow-back sets in and defies the majority of experts.—M.

### RAPID DRYING PAINT

In the March-April number of the *Bulletin de la Société d'Encouragement*, a report is given of a rapid drying paint. As many as three coats can be given in one day. The rapid drying is obtained by using, instead of refined linseed oil, linoline or linseed oil solidified by oxidation such as is obtained in linoline manufacture. This is dissolved in a small quantity of slightly acid amyl alcohol and then a considerable quantity of turpentine added. When this solvent evaporates, the paint is completely dry since the oil has been oxidized in advance. What the lasting qualities are time alone can tell, but, in one case, walls coated with the paint show no signs of deterioration after five years. The price in normal times would be a little higher than that for ordinary zinc paint, but the advantages in quick drying would more than make up for the extra cost in many cases where quick drying is an important factor.—M.

### USE OF REFUSE

In a paper recently published by the Bureau of Mines it is reported that within the last five or six years marked progress has been made in Europe in the utilization of various waste material not ordinarily thought of value. The manufacturers of producer gas report the successful use of a large variety of fuels including wood-shavings, wood-blocks, sawdust, excelsior, coffee-husks, rice-husks, coconut shells, straw and spent tan bark. The figures in fuel consumption reported by the main factories are as follows: With reasonably dry wood (say, mixed oak, ash and elm) the consumption has been as low as 2 lbs. per brake horse-power hour; with sawdust the average consumption is 3½ lbs. per brake horse-power hour, and with spent bark containing 50 per cent moisture, it is about 4½ lbs.—M.

### FUSEL OIL FROM CANE MOLASSES

It is opportune, says the *Int. Sugar Journ.*, to remind readers who have the control of cane molasses distilleries that fusel oil is a material very much in demand at the present time and that high prices for it are now ruling. Previous to the war the cost of raw fusel oil seldom fell below about \$1 per gal., and \$1.80 could perhaps be taken as a normal figure. At the moment, however, that product cannot be obtained for less than \$.52 to \$.3 per gallon, according to quality and it would seem that the price may be yet increased. Although the amount obtained from fermented cane molasses is less than in cases of sources such as grain, potatoes or the "inarc" of grapes and in pre-war days its recovery may have been unfavorably considered in cane-growing countries, present conditions make the question worthy of consideration particularly where patent stills are in operation. Those interested may be reminded that fusel oil enters the British Isles free of duty provided it contains less than 15 per cent of proof spirit.—M.

### CANADIAN WOOD-PULP INDUSTRY

According to information received in London, the consumption of wood in Canada for the manufacture of pulp has increased threefold during the past eight years and, in the same period, the value of wood consumed for this purpose has increased from slightly under \$3,000,000 to nearly \$9,500,000. Fifty mills reporting to the government show a consumption in 1915 of 1,405,000 cords of wood valued at \$9,426,000 with an average value of \$6.71 per cord. Canada produced pulp-wood in 1915 valued at \$15,590,000, of which \$6,164,000 worth was exported. The province of Quebec leads in the number of mills and in the value of pulp-wood exported, possessing 24 out of the 50 mills in the Dominion and exporting \$4,000,000 worth of wood-pulp.—M.

### REMOVAL OF RESIN FROM SULFITE PULP

The *Paper-Maker*, 52 (1916), 53, quoting from a German contemporary, states that the removal of resin from sulfite wood-pulp is best effected by washing with hot water, not in the digester but in the stuff-chest outside the digester. The

usual method of sprinkling has not much cleansing effect because the rinsing water tends to take the shortest path from the inlet to the outlet so that large masses of stuff escape the washing altogether. It is recommended that the stuff be diluted largely with hot water and stirred up and washed by blowing in large quantities of air. The inlet tube for the hot water is situated underneath the false bottom and filtered air at a pressure of 6 to 8 atmospheres is forced through a system of hard lead pipes to the false bottom. A charge of 15 tons of pulp can be washed in 37 minutes and the bleaching qualities of the pulp are improved by the treatment.—M.

### PORTUGAL OLIVE OIL PRODUCTION

The *Diário de Governo* (Lisbon), of June 6, publishes an official statement giving the total production of olive oil for 1915 as 27,965,078 liters. The stock of oil on March 20, 1916, amounted to 33,904,475 liters. The above mentioned issue of the *Diário* contains detailed statistics of the production and stocks in each of the oil-producing districts of the Republic.—M.

### TRADE OPENING IN BOLIVIA

The British Consul at Oruro (Bolivia) reports that there is a shortage of many goods, especially of those required by the mining industries. The greater part of the machinery and electrical fittings was in the hands of German importers up to the outbreak of war, and there is now an opening in Bolivia for manufacturers and exporters who wish to secure a good and profitable market for mining requirements. There has been a great boom in mining recently in the state.—M.

### GREENLAND CRYOLITE

Cryolite, says the *Chemical Trade Journal*, 59 (1916), 45, has been found in commercial quantities at Ivigtut, an Eskimo hamlet on the southern coast of Greenland. The cryolite deposit is said to be a solid mass having surface dimensions of about 200 ft.  $\times$  600 ft.; it has been worked as an open cut to a depth of about 150 ft. The deposit widens with depth and the depth is unknown.—M.

## NOTES AND CORRESPONDENCE

### ON THE EFFICIENCY OF AIR DRYERS

*Editor of the Journal of Industrial and Engineering Chemistry:*

With reference to the letter of Mr. W. E. Wadman<sup>1</sup> relative to the efficiency of air dryers, Mr. Wadman states that the "consumption of heat in an 'air dryer' for evaporating purposes is a perfectly definite thing and just as definite as in the case of the steam boiler." In this Mr. Wadman is mistaken. Mr. Wadman states that it requires practically 1120 B. t. u. to evaporate 1 lb. of water in such a dryer under even the most ideal conditions, but to convince him of his error I propose to describe an air dryer so designed as to evaporate water at a much lower heat consumption than this, and if any inherent impossibility attaches to the proposed method it will clear up the matter to have it pointed out.

Assume a material which may be dried at a temperature of 160° F. without injury, but which can be dried successfully at a temperature even as low as 90°. Assume that the air supply is at 50° with a dew point of 40°, carrying 0.0052 lb. of water per lb. of dry air,<sup>2</sup> that the material to be dried enters at 60°, and that the specific heat of this material is negligible.

<sup>1</sup> THIS JOURNAL, 8 (1916), 755.

<sup>2</sup> These calculations are made with the use of Grosvenor's curves, Supplement to Transactions of American Institute of Chemical Engineers, 1 (1908).

Let the air leaving this dryer have a temperature of 160° and a dew point of 140°, carrying 0.1514 lb. of water per lb. of dry air. Instead of throwing this air away, let us use it as the heating element in another air dryer immediately beside the first, cooling the air to 100° and operating the dryer at 90°, thus having available a temperature difference between heating element and air in the dryer of 10° at the least, and with an average of much more than this. The air cooling to 100° will deposit 0.1090 lb. of water and give up 132.3 B. t. u. It is theoretically possible to reduce the heat consumption of the first dryer to 1102 B. t. u. per lb. of water evaporated (the heat of vaporization at 160° plus the heat necessary to heat up the water from 60°). The water evaporation per pound of dry air entering the first dryer is 0.1462, and the minimum heat consumption in this dryer is therefore 161.2 B. t. u. per lb. of dry air. The theoretical consumption in the second dryer is 1081 B. t. u., and it is therefore possible in this dryer to evaporate 132.3/1081 or 0.1223 lb. of water per lb. of dry air without the use of any additional heat. In the two dryers we have therefore evaporated 0.2685 lb. on a heat consumption of 161.2 B. t. u. or 600 B. t. u. per lb. This of course assumes perfection in each of the units employed, but we can sacrifice 50 per cent efficiency and still be far below the limit specified by Mr. Wadman.



It must be pointed out that to secure a higher efficiency than corresponds to the figure quoted by Mr. Wadman, requires the condensation of the water evaporated and the recovery of the heat given up thereby. This amounts to an application of the principle of multiple-effect evaporation, but this principle can in theory at least be applied just as effectively in air drying as in ordinary evaporation. Furthermore, the only industrial obstacle to a realization of these conditions is the low heat conductivity from gas through solid separating wall to gas, a fact which necessitates an enormous heating surface.

In the discussion of several years ago a heat consumption resulting from a commercial test of a Ruggles-Coles dryer was quoted as below the figures stated by Mr. Wadman to be the theoretical minimum possible, and it was stated that such a result was impossible. Unlikely such a result may be, but it is not impossible, in the type of dryer employed. That dryer cools the gases to a remarkable extent, and under certain conditions the gases leaving the dryer coming in contact with the cold, wet material entering it are cooled below their dew point. This results in separation of moisture in the form of fog, which is carried along by the gases. It is easily possible for the heat given up upon condensation of this moisture to more than compensate for the fact that the gases are still higher in temperature than the air supply. Under such conditions the Ruggles-Coles dryer is effectively utilizing a part of the heat of condensation of the water once evaporated, and in this way is making use to a degree of the multiple-effect principle. While such conditions can arise only under unusual circumstances in that dryer, there is no inherent absurdity in the low heat quotation referred to, and it is readily conceivable that in the future that particular type of dryer may be perfected to the point where such re-utilization of the heat may become industrially practicable.

Just because it is possible to lay out a dryer using air under atmospheric pressure which will evaporate water at practically any heat consumption demanded, it must be admitted that there is no theoretical consumption for such an apparatus and therefore no meaning to the term "efficiency" as applied to air dryers. The writer feels very strongly that it is unfortunate to consider evaporation and air drying as unrelated, and that it is *not* true "that the two things are quite distinct;" on the contrary, the fundamental factors involved are identical while the differences are scarcely more than superficial, and appreciation of this is necessary to progress in the development of both types of processes.

Regarding Mr. Wadman's misunderstanding of the statement concerning the evaporation of solutions, I evidently failed to make the point clear in my first communication. As a specific illustration, assume a 34 per cent solution of caustic soda, boiling under atmospheric pressure at 120° C. Mr. Wadman evidently understands that the vapor coming from such a solution is at 100° C., but such is not the case. The vapor coming from a solution cannot possibly be at a temperature other than that of the solution itself. It is true that in this case the vapor must cool to 100° before condensation will take place. Furthermore, if a thermometer be inserted into the vapor space, its cooling action will cause condensation of vapor upon it, and it will therefore register 100° until that condensation has been re-evaporated. The vapor rising from the solution, being at 120°, must be compressed *isothermally* to 14 lbs. gauge in order to condense at slightly above 120°, its heat of condensation then being available for evaporation of more water from the original solution. The work consumption necessary to remove 1 lb. of water from the 34 per cent solution of caustic soda is therefore

$$W = nRT \ln p/p_0 = \frac{1}{18} (1545)(460 + 248) \ln(14.7 + 14)/14.7 = 40,600 \text{ foot-pounds of energy per pound of water}$$

evaporated. The process involved is truly isothermal throughout—solution, vapor, and condensed steam being at all times at 120°.

W. K. LEWIS

MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
CAMBRIDGE, August 17, 1916

### SIR WILLIAM RAMSAY

*Editor of the Journal of Industrial and Engineering Chemistry:*

In the death notice of Sir William Ramsay, in your August issue, the fact is omitted that he studied for some time under Prof. Rudolph Fittig, in Tuebingen, where he also acquired his degree of Dr. Sci. Nat. He came to Tuebingen while Ira Remsen was there and he told me that he tried to enter the laboratory through a door seldom used, which was locked; after considerable knocking Remsen opened the door and promptly answered Ramsay's question in broken German, in English.

PITTSBURGH, PA.  
August 23, 1916

K. F. STAHL

### ANILINE OIL POISONING

*Editor of the Journal of Industrial and Engineering Chemistry:*

A letter in THIS JOURNAL, 8 (1916), 573, written by Messrs. Fiske and Green on the subject of aniline poisoning, has come to my notice and I commend it to the careful consideration of all manufacturers and users of aniline oil. It is with the hope that I may add a few details thereto, that I am writing this.

Soon after the outbreak of hostilities, this company realized that it could no longer depend upon overseas sources for its aniline and by November 1, 1914, we were manufacturing aniline in large quantities; since that date the plant under the writer's supervision has produced approximately 1500 tons without a single fatality due to aniline poisoning; our good fortune has not been a matter of pure luck but is the result of a persistent campaign to eliminate every possible source of danger and to care promptly for such cases of poisoning as have actually resulted.

The premonitory symptoms of aniline poisoning are as described by Fiske and Green, the severe cases showing dizziness, unsteadiness on the feet and finally unconsciousness; however, men who are working constantly in the plant and who have, in a measure, become immune to the effect of aniline vapor, show bluish lips and skin; the poisoning does not seem to go beyond that stage and the men are not inconvenienced in any way; it has been our experience that the severest cases, those most prompt in making themselves manifest, have resulted from the spilling of aniline, nitrobenzol, or aniline hydrochloride liquor directly upon the skin and on this point we seem to be at variance with Fiske and Green.

Realizing that poisoning may be caused either by inhalation of vapor or direct contact with liquid, our manufacturing precautions have been based upon these two points; the building is provided with suction ventilating fans in the roof; several 24-in. fans located in the exterior sidewall of the building play streams of air directly upon the men while they are at their operating positions; in clement weather the windows are removed, at other times satisfactory floor ventilation is provided; suction ventilating ducts are led directly to stuffing boxes and iron-boring feeders where there is always more or less escape vapor; the manufacturing system is closed so that at no point is it necessary for a man to handle open aniline; drinking men are excluded from the operating force; regular rations of milk are issued and their consumption insisted upon; showers are provided and a daily bath is compulsory; the company provides two clean working uniforms weekly per man; rubber boots are supplied; pumps, valves, stuffing boxes, etc., are inspected frequently and all leaks taken care of at once.

The necessity of replacing the stirring paddles in the aniline reducers has been the cause of many of the aniline poisoning cases in our plant; these repairs have been made by our general repair crew, composed of men not familiar with the handling of aniline and not inclined to observe the precautions dictated by experience; in spite of continued washing and steaming-out, there is sufficient aniline saturating the residual iron borings in the reducer bottom to make it inadvisable for men to remain in the reducer for more than a half hour.

Dr. Hamilton, in *Bulletin* 179, U. S. Bureau of Labor Statistics, "Industrial Poisons Used in the Rubber Industry," has written fully on the use of aniline in rubber manufacturing, while Drs. Hamilton and Luce, *Journal American Medical Association*, 66, 1441-1445, have written of "Industrial Aniline Poisoning in the United States" from a purely medical standpoint.

THE GOODYEAR TIRE & RUBBER COMPANY  
AKRON, OHIO, August 8, 1916

W. W. SANDERS

### THE LIEBERMANN-STORCH COLOR TEST FOR ROSIN— A CORRECTION

The peculiar fugitive violet color formed by the action of sulfuric acid on a solution of rosin (or rosin oil) in acetic anhydride is usually said to be produced by only one other substance, the alcohol *cholesterol*, which is found in all animal glycerides. This substance, however, contrary to the usual statements found in textbooks, gives a deep blue color with the L.-S. reagents, quickly changing to a permanent green, and in addition usually occurs in such small amounts in animal oils that it is practically negligible.

There is, however, a resin which gives a color almost exactly like that of rosin, although the intensity is not the same in all varieties. This is the fossil resin known as "Kauri," which is obtained from New Zealand, and forms one of the most common "gums" used in varnish making. The varieties showing the color best are those having a milky core surrounded by a nearly transparent shell, while in the varieties known as "Swamp" or "Brown Kauri," where the resin has undergone oxidation through contact with air and water, the color is to a great extent masked by impurities. Kauri resin, like common rosin or colophony, was originally produced by a coniferous tree, hence we can see why this color-producing substance is common to both resins. It does not appear to be altered much on fusing the resin as is usually conducted in the varnish industry.

Below are given the color reactions of some of the principal resins used in varnish making. These specimens were all authentic and in unbroken pieces so that contamination with rosin was entirely out of the question. The test was conducted by treating about 0.25 g. of the finely powdered resin with about 10 cc. C. P. acetic anhydride on the hot plate until the mixture just began to boil. After cooling, a portion of the clear liquid was removed to a watch glass and a few drops of C. P. sulfuric acid (sp. gr. 1.53) allowed to run down the side of the glass, and the color noted.

ROSIN	Deep violet-red color quickly changing to brown
KAURI RESIN (Fossil)	Deep wine-red, then brown
AMBER (SUCCINITE) (Fossil)	
MANILA, PONTIANAK, and BORNEO RESINS (Fossil) (g)	Dark brown color
BATAVIA and SINGAPORE DAMAR RESINS (Recent)	Deep wine-red color which does not change on standing
EAST INDIA and BLACK DAMAR RESINS (Fossil)	Deep wine-red color which gradually turns brown on standing
CHOLESTEROL (Merck's C. P.)	Deep blue color which quickly changes to a permanent green

(g) Some specimens of Manila have been observed to respond to the L.-S. test.

In the routine testing of oil-resin varnishes for rosin it is easy to see why we sometimes get a positive reaction with the L.-S. test, although the samples had been guaranteed by the manufacturer to be free from rosin.

7606 LA GRANGE AVE., N. E.,  
CLEVELAND, OHIO

P. E. JAMESON

### THE OLD GUARD

The American Chemical Society complete forty years of existence this autumn; on June 1st it had 8,057 members. Of those still living who became members during the first ten years—which includes 1886, as all those in the list joined during the ten-year period—there are now but 37. They were about one-seventh of the membership then; they are one-two hundred and fiftieth now. The list is as follows:

1876	1880
Baumgarten, F. M.	Booraem, J. V. V.
Chandler, C. F.	Hale, A. C.
Doremus, C. A.	1881
Goldschmidt, S. A.	Colby, A. L.
Herreshoff, J. B. F.	Dunham, E. K.
Krause, O. H.	Hallock, A. P.
Munroe, C. E.	1882
Niese, H. E.	Pitkin, Lucius
Parker, T. J.	1883
Ricketts, P. de P.	Breneman, A. A.
Sharples, S. P.	Krause, G.
Terne, Bruno	McKenna, C. F.
Waller, Elwyn	Tucker, W. G.
1877	1885
Geyer, W. E.	Morgan, T. M.
Hindley, R. C.	Williams, J. T.
Prochazka, G. A.	1886
Sturberg, J. A.	Cawley, John
1878	Drummond, I. W.
Prentice, W. P.	Geisler, J. F.
1879	Sabin, A. H.
Doscher, Henry	Schupphaus, R. C.
Eimer, August	

111 BROADWAY, NEW YORK CITY  
August 14, 1916

A. H. SABIN

### ILLUMINATING ENGINEERING LECTURE COURSE

A notice of the Illuminating Engineering Lecture Course to be held in Philadelphia, September 21-28, under the joint auspices of the Illuminating Engineering Society and the University of Pennsylvania, appeared in the Personal Notes of our August issue. The preliminary list of lecture subjects of this Course with the names of the lecturers is given below:

#### A—GENERAL

Illumination Units and Calculations. A. S. McALLISTER.  
Modern Photometry. CLAYTON H. SHARP.  
The Principles of Interior Illumination (Two Lectures). COMMITTEE:  
J. R. CRAVATH, Chairman, WARD HARRISON and ROBERT PIERCE.  
The Principles of Exterior Illumination. LOUIS BELL.  
Color in Lighting. M. LUCKIESH.  
Architectural and Decorative Aspects of Lighting. GUY LOWELL.  
Recent Developments in Electric Lighting Appliances. G. H. STICKNEY.  
Recent Developments in Gas Lighting Appliances. R. PIERCE.  
Modern Lighting Accessories. W. F. LITTLE.

#### B—SPECIAL LECTURES ON INTERIOR ILLUMINATION

The Lighting of Factories, Mills and Workshops. C. E. CLEWELL.  
The Lighting of Offices, Stores and Shopwindows. NORMAN MACBETH.  
The Lighting of Schools, Auditoriums and Libraries. F. A. VAUGHN.  
The Lighting of Churches. E. G. PERROT.  
The Lighting of the Home. W. H. JORDAN.  
Railway Car Lighting. G. E. HULSE.

#### C—SPECIAL LECTURES ON EXTERIOR ILLUMINATION

Street Lighting (Two Lectures). P. S. MILLAR and C. F. LACOMBE.  
The Lighting of Yards, Docks and Other Outside Works. J. L. MINCK.  
Headlights, Searchlights and Projectors. E. J. EDWARDS.  
Sign Lighting. L. G. SHEPARD.  
Building Exterior, Exposition and Pageant Lighting. W. D'A. RYAN.

Subscription tickets for the Course and further information covering the same may be obtained by communicating with Clarence L. Law, Irving Place and 15th Street, New York City.

### COOKING OF SODA PULP—CORRECTION

Editor of the Journal of Industrial and Engineering Chemistry:

In reference to my article in THIS JOURNAL, 8 (1916), 601, I find that the curves shown in Fig. IV were mislabelled. They should be changed as follows: Cook 1 to Cook 5; Cook 2 to Cook 4; Cook 4 to Cook 2; and Cook 5 to Cook 1.

MADISON, WISCONSIN  
August 3, 1916

S. D. WELLS



# SCIENTIFIC SOCIETIES

## MEETING OF THE AMERICAN CHEMICAL SOCIETY AND THE SECOND NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES

The Fifty-third Meeting of the American Chemical Society will be held in New York City, September 25 to 30, inclusive, in conjunction with the Second National Exposition of Chemical Industries. The American Electrochemical Society and the Technical Association of the Pulp and Paper Industry will also hold meetings in New York City during the same week. It is expected that 2000 to 2500 chemists will be in attendance during the week's exercises, and that this meeting of the American Chemical Society will be the banner chemical meeting of the world. The registration office will be open at the Chemists' Club, 52 East 41st Street, throughout the week. Society headquarters will be at the Chemists' Club; hotel headquarters at Hotel Astor, 43rd Street and Broadway.

### CHAIRMAN OF LOCAL COMMITTEES

*Executive:* J. M. Matthews, 50 East 41st Street, New York City.  
*Finance:* L. H. Baekeland, Snug Rock, N. Broadway, Yonkers, N. Y.  
*Registration:* H. R. Moody, College of the City of New York  
*Reception:* To be announced.  
*Entertainment:* E. G. Love, 124 East 15th Street, New York City.  
*Hotels:* T. J. Parker, 92 William Street, New York City.  
*Press and Publicity:* Allen Rogers, Pratt Institute, Brooklyn, N. Y.  
*Ladies' Committee:* Mrs. L. H. Baekeland, Snug Rock, N. Broadway, Yonkers, N. Y.

### GENERAL PROGRAM

Dr. Charles H. Herty, president of the American Chemical Society and chairman of the Exposition Advisory Committee, will open the Second National Exposition of Chemical Industries, at the Grand Central Palace, on Monday, September 25, at 2 o'clock in the afternoon, with an address reviewing the history of chemistry and the chemical industries in this country and outlining developments since the outbreak of the war in Europe. Dr. Francis A. Fitzgerald, president of the American Electrochemical Society, and Dr. Arthur B. Daniels, president of the American Pulp and Paper Association, will also make addresses, after which the assembled guests will visit the exhibits.

The Second National Exposition of Chemical Industries is already an assured success. The managers report that there are but a few spaces still remaining on the second floor for exhibits and that a third floor is being seriously considered and a diagram being prepared. The greatest part of the Exposition will be devoted to things that are made from coal, ranging all the way from phonograph records and aniline dyes to road building materials. Of intense and recent interest, there will be exhibits showing porcelains made in America from American clays as fine as any produced by the Royal Berlin Works and also American glass the equal of the celebrated Jena glass. By way of surprise, Mr. Arthur D. Little will exhibit some silken purses made from sows' ears, thereby disproving the old, proverbial saying that silken purses could not be made from sows' ears. Practically all the large chemical industries of America will have exhibits which will offer unexcelled opportunity for study to American chemists. There will be no entrance fee charged to members of the American Chemical Society and the American Electrochemical Society. The member's badge obtained at the registration desk will admit him at all times.

The American Chemical Society, the Chemists' Club, The American Institute of Mining Engineers, the American Electrochemical Society, and the Technical Association of the Pulp and Paper Industry will all have booths at the Exposition.

The Bureau of Mines is preparing an elaborate working exhibit. The Bureau of Commercial Economics is collaborating in arrangements for a motion picture program.

Two other features of the Exposition that have been added this year are a large "Southern Opportunity Section," showing the opportunities that await the chemist in our South, and a section for the "Paper and Pulp Industry" composed of materials and machinery used in the manufacture of paper and other related products.

The American Electrochemical Society have planned a very interesting program and will open their meeting on Thursday, September 28, with a "Made in America" technical session devoted to a review of American progress in the electrochemical industry.

The official opening of the American Chemical Society Meeting will take place at the Horace Mann Auditorium, Columbia University, on Tuesday morning, September 26. The provisional program of the A. C. S. Meeting is as follows:

### MONDAY, SEPTEMBER 25

*Afternoon:* Official Opening of Exposition; Addresses by Dr. C. H. Herty, Dr. F. A. J. Fitzgerald and Dr. A. B. Daniels. Council Meeting, Chemists' Club.  
*Evening:* Council Dinner, Chemists' Club. Council Meeting, Chemists' Club.

### TUESDAY, SEPTEMBER 26

*Morning:* General Meeting of the Society at Horace Mann Auditorium, Columbia University. Addresses of Welcome by Health Commissioner Emerson of the City of New York and President Butler of Columbia University. Response by President Herty, followed by General Papers.  
*Afternoon:* Public Meeting, Horace Mann Auditorium, Columbia University. Addresses (*speakers to be announced*). Presidential address by Dr. Herty.  
*Evening:* Reception at Hotel Astor. Members American Electrochemical Society invited.

### WEDNESDAY, SEPTEMBER 27

*Morning:* Divisional Meetings, Columbia University, Symposium on Colloids (Theoretical).  
*Afternoon:* Industrial Conference, Chemists' Club, "American Dye-stuffs Manufacture." Industrial Conference, Grand Central Palace, "Steel Alloy Metals: Electric Steel."

### THURSDAY, SEPTEMBER 28

*Morning:* Divisional Meetings, Columbia University. Symposium on Colloids (Applied).  
*Afternoon:* Industrial Conference, Chemists' Club, "Industrial Alcohol, Acetone and Formic Acid." Industrial Conference, Grand Central Palace, "American-Made Glassware and Porcelain."  
*Evening:* Invitation Smoker of American Electrochemical Society.

### FRIDAY, SEPTEMBER 29

*Morning:* Divisional Meetings, Columbia University, Symposium on Occupational Diseases in Chemical Trades. Industrial Conference, Grand Central Palace, "American Pulp and Paper Manufacture."  
*Afternoon:* Joint Industrial Conference with American Pulp and Paper Association, Grand Central Palace, "American Pulp and Paper Manufacture." Industrial Conference, Chemists' Club, "Medicinal Chemicals."  
*Evening:* Subscription Banquet at Waldorf-Astoria, members and wives \$3.50. Guests at cost (about \$7.00). Members American Electrochemical Society and Technical Association American Pulp and Paper Industry invited, with cost same as to members American Chemical Society.

### SATURDAY, SEPTEMBER 30

*Morning:* Meetings of Divisions. Industrial Conference, Chemists' Club, "Oils and Motor Fuels." Industrial Conference, Grand Central Palace, "Miscellaneous Chemical Industries; Convertibility of Plant."  
*Evening:* Exposition closes at Grand Central Palace at 11 P.M.

## DIVISIONAL AND SECTIONAL PROGRAMS

The usual meetings will be held by all of the Divisions with the following special program:

Joint Symposium on Colloids by the Biochemical, Physical and Inorganic, and Industrial Divisions—two mornings.

Symposium on Occupational Diseases in the Chemical Trades by the Division of Industrial Chemists and Chemical Engineers. Prof. Charles Baskerville, head of the department of chemistry in the College of the City of New York, will preside. The symposium will consider the chemical trades, prophylaxis in chemical industry, diseases incidental to work in aniline and other coal-tar products, cedar lumber, mines and explosives, and will be followed with a general discussion by the leading authorities of the country: These will include Drs. W. Gilman Thompson, F. L. Hofman, J. W. Schereschewsky, G. P. Adamson, H. K. Benson, W. A. Lynott, Alice Hamilton and Mr. J. B. Andrews.

The Section of Rubber Chemistry, which has held no meeting since the meeting at Cincinnati, will gather for papers and a general conference on the progress of the Chemistry of India Rubber. The Section will be under the chairmanship of Mr. L. E. Weber, with Mr. J. B. Tuttle as secretary.

## PAPERS FOR THE MEETING

All titles for papers should be in the Secretary's hands on or before September 11; or in the hands of the secretaries of divisions on or before September 9, with the exception of the Physical and Inorganic Division, for which titles of papers should have reached the divisional secretary by September 1, and the Secretary of the Division of Industrial Chemists and Chemical Engineers on or before September 5.

The Division of Industrial Chemists and Chemical Engineers have voted that the titles of all papers shall be sent to the Secretary of the Division, which title should be accompanied by an abstract; that any title sent without an abstract shall not be printed in the program, and that the time limit for the presentation shall be 5 minutes, unless special arrangements are made with the Secretary of the Division.

The Division of Physical and Inorganic Chemistry have voted that a committee of three, consisting of James Kendall, Belgrade Lakes, Maine, Secretary of the Division, W. D. Bancroft, 7 East Avenue, Ithaca, N. Y., and Colin G. Fink, 33 Carleton Street, East Orange, N. J., be appointed to arrange the program of the Division for the September meeting; that no paper exceeding 5 minutes in length shall be read before the Division, unless an abstract is received by the Committee and approved by them, and that no member shall present more than one paper before the Division unless an abstract of each paper be received and approved by the Committee.

*By vote of the Council no papers may be presented at the meeting, titles for which are not printed on the final program.*

If any member sending in a paper does not expect to attend the meeting, he should put the words "By Title" on his announcement, so that members may understand in advance that the paper will not be read.

## ADDRESSES OF DIVISIONAL AND SECTIONAL SECRETARIES

*Agricultural and Food Chemistry:* G. F. Mason, H. J. Heinz Company, Pittsburgh, Pa.

*Biological Chemistry:* I. K. Phelps, Bureau of Chemistry, Washington, D. C.

*Fertilizer Chemistry:* F. B. Carpenter, Virginia-Carolina Chemical Company, Richmond, Va.

*Industrial Chemists and Chemical Engineers:* S. H. Salisbury, Jr., Lehigh University, South Bethlehem, Pa.

*Organic Chemistry:* H. L. Fisher, Landing, N. J.

*Pharmaceutical Chemistry:* G. D. Beal, Univ. of Illinois, Urbana, Ill.  
*Physical and Inorganic Chemistry:* James Kendall, Belgrade Lakes, Maine.

*Rubber Chemistry Section:* J. B. Tuttle, Bureau of Standards, Washington, D. C.

*Water Sewage and Sanitation:* H. P. Corson, U. S. Public Health Service, Grove City, Pa.

## ABSTRACTS OF PAPERS

In order that the meeting may receive due and correct notice by the New York Press, every member sending a paper is re-

quested to send an abstract not exceeding 200 words to Mr. Allen Rogers, Pratt Institute, Brooklyn, N. Y. It is hoped that all members will aid the Society by so doing. A copy of the abstract should be retained by the member and handed to the Secretary of the special division before which the paper is to be presented in New York. Such abstracts will be printed in *Science*.

Members will especially note that by vote of the Division of Physical and Inorganic Chemistry and the Division of Industrial Chemists and Chemical Engineers, papers cannot be presented before these divisions unless abstracts are in the hands of the secretary of the division as before stated, in time to have the abstract passed upon before the paper is put on the program.

## ENTERTAINMENT OF THE LADIES

The Committee headed by Mrs. L. H. Baekeland is actively at work arranging the program for the pleasure of visiting ladies at the time of the meeting. Ladies may come with the assurance that everything will be done for their comfort and pleasure. Details will be found in the final program.

## RAILROAD RATES

No special reduced fares have been granted for the meeting. No special cars will be provided from any points by the general secretary. Special cars may, however, be arranged for by the secretaries of local sections, if desired.

## HOTELS

The following list of hotels, with rates, was taken from a recent publication. There are, however, plenty of hotels in New York City—really first-class hotels that you never heard of—where you can be very comfortable at reasonable rates. If you wish special information, write to the Chairman of the Hotel Committee.

NAME	LOCATION	ROOMS WITH BATH		ROOMS WITHOUT BATH	
		DOUBLE	SINGLE	DOUBLE	SINGLE
Algonquin	59 West 44th St.	\$3.50	\$2.50		
Astor	43rd St. & B'way	4.00 up	3.00 up	\$3.00	\$2.00 up
Belmont	42nd St. & Park Ave.	4.00 up	3.50 up	3.50 up	2.50 up
Biltmore	43rd St. & Madison Ave.		5.50 up	4.00	
Breslin	29th St. & B'way	4.00	2.00	3.00	1.50
Grand	31st St. & B'way	4.00 up	2.00 up	2.00 up	1.00 up
Hermitage	42nd St. & B'way	3.00 up	2.00 up	2.00 up	1.50 up
Imperial	32nd St. & B'way	4.00 up	2.00 up	3.00 up	1.50 up
Knickerbocker	42nd St. & B'way	5.50 up	3.00 up	4.50 up	2.00 up
McAlpin	34th St. & B'way	4.00 up	2.50 up	3.00 up	2.00 up
Manhattan	42nd St. & Madison Ave.		5.00 up	3.50	2.50
Martiniere	32nd St. & B'way	3.50 up	2.50 up	2.50 up	1.50 up
Monticello	35 W. 64th St.		2.00 up	1.25 up	
Park Avenue	32nd St. & Park Ave.	4.00	3.00	2.00 up	1.50 up
Plaza	58th St. & Fifth Ave.	5.00 up	3.50 up		
Prince George	28th St. & Fifth Ave.	4.00 up			2.00 up
Seville	29th St. & Madison Ave.		3.00 up	2.50	1.50
Waldorf-Astoria	34th St. & Fifth Ave.	5.00 up	3.50 up	4.00 up	2.50 up
Wolcott	4 West 31st St.	5.00	2.50		2.00 up

## FINAL PROGRAM

The final and complete program will be sent on or about September 18 to all members signifying their intention of attending the meeting, to the secretaries of sections, to the Council, and to all members making special request therefore to the Secretary's office.

## 8100 MEMBERS

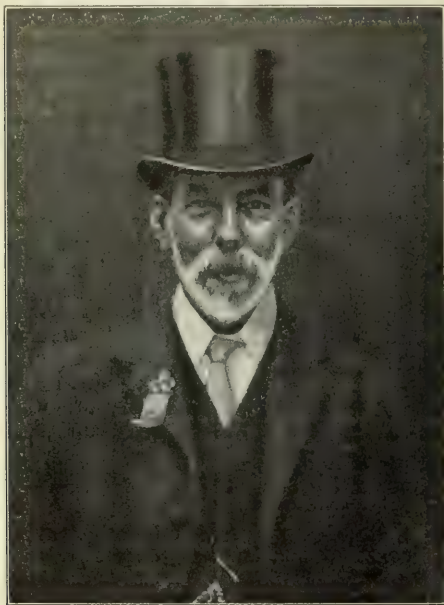
At the time of the Urbana Meeting, the Secretary started a campaign to obtain a membership of 8,000 this year. The Secretary already has 8,100 members. Owing to this great increase, journals for the early part of the year can no longer be sent to new members, but the Secretary has been authorized to begin membership for the present year with July 1 on the basis of payment of \$5.00 to January 1, 1917, with journals from July up to that time and regular yearly dues beginning thereafter.



## OBITUARIES

## SIR WILLIAM RAMSAY

In considering the life of a man, we are apt, I think, to lay stress on what he has accomplished concretely, rather than on what he was abstractly. With the man of affairs it interests people in general to know what he has, rather than what he is, although we know that character is greater than accomplishment. With the scientists we reason the same, and look in the publications for a record of the man. Great as Sir William Ramsay was as a scientist, if we confine ourselves to that side of him we miss, I think, a great lesson of his life. He was not a one-sided man, but rather, a four-square, complete man, which is very different. It is not my purpose in this brief article to review his work. That has been done, and will be done, by far abler pens.



SIR WILLIAM RAMSAY

It was my good fortune to know him intimately, and it is to some of his less known qualities that I would draw attention, as his real greatness cannot be appreciated if that point of view be neglected.

Everybody knows he loved the truth. No man can be a great investigator otherwise. While his investigations carried him far afield, he differentiated strongly between hopes and facts, although well-grounded hopes were not easily set aside.

He realized, as few men I have met have realized, that chemistry is in its infancy, and it would be a long time before it would even reach the age of manhood. Hence anything, not ridiculous on its face, was worth thought, and probably deep thought. Apropos of something said, I asked him once if he really believed in transmutation. His answer, "Why not?" was characteristic. It implied the possibility, while not assenting to the proposition. Dr. John W. Draper, my old preceptor, had progressed that far, without a tithe of the reasons of the modern chemist. Of course he did not teach it.

One of Ramsay's most charming qualities was his simplicity. He was full of fun and jollity. Years ago, he was at my St. Lawrence home when there was a house-party of girls, and he was the life of the party: full of pranks and schemes to amuse. You would lose sight of him a moment, and, behold, he would be quietly sketching the sunset, or some other feature of that beautiful region which filled his simple soul with delight. He was never idle. He was always doing something, generally with the idea of giving others pleasure. Those girls, I am sure, will remember him, not as a great man who overawed them, but rather as a jolly companion.

He was loyal to his friends. No one could be more so. He would go to any amount of trouble to do them a good turn. He was a royal guest, which is a great and rare virtue. He was a charming host, which is more common. His mind was clean and pure, and jealousy and unworthy thoughts could find no lodgment there. There was not a mean streak in him anywhere, that I could ever discover.

He had a great appreciation of humor. I sometimes think no man can be truly great who has not. He could even understand our American jokes, which is not always true of his countrymen. He was interested in everything that was going on about him, and could converse delightfully with anyone, no matter how humble might be his walk in life.

All the fine qualities which went to make up the man came to clearest view when he was stricken with a disease which leaves so little room for hope, and which requires such great patience. Suffering could not dim his courage, or deter him from the endeavor to make his last experience of value to others. To quote from Lady Ramsay's last letter to me: "The courage is not new; but the patience is almost heart-breaking." Writing in bed his last letter to me, he described the various experiments which he was trying on himself—not with any hope of the saving of his life, but with the yearning to arrive at some new knowledge which would help others, if taken in time.

Such, in brief, was the man. Endowed with a splendid constitution, and a wonderful mind, his whole life was spent in endeavoring to do all he could for the benefit of his fellows and the science which he loved so well. To those who knew him intimately, his memory will always be cherished; not so much for what he did, but because of what he was.

WM. H. NICHOLS

## PERSONAL NOTES

Dr. Charles H. Herty, professor of chemistry and dean of the School of Applied Science, University of North Carolina; Dr. W. R. Whitney, director of the research laboratory of the General Electric Company, Schenectady, N. Y.; Dr. Leo H. Baekeland, of Yonkers, N. Y.; and Mr. Warren K. Lewis, of Newton, Mass., have been appointed by the American Chemical Society to cooperate with the Committee of the National Academy of Sciences on the nitrate supply for the U. S. Government.

The Brown Instrument Company, Philadelphia, announce that they will occupy Section No. 306 in the Second National Exposition of Chemical Industries, and will exhibit a complete line of indicating and recording pyrometers, and also their new recording thermometers. They will be represented by Mr. John P. Goheen, sales manager, Mr. William Printz, assistant sales manager, and Mr. J. D. Andrews, New York representative.

The United States Civil Service Commission announces the following open competitive examinations: *Junior Fuels Chemist* (male), salary \$1200 to \$1500 a year, on September 20-21, 1916; *Junior Computer* (male), salary \$1020 a year, September 20-21, 1916; *Assistant Examiner, Patent Office* (male and female), salary \$1500 a year, September 13-15, 1916. Further information may be had from the U. S. Civil Service Commission, Washington, D. C.

The J. P. Devine Company have just received from the press and have ready for distribution copies of the following bulletins: Bulletin 101, covering the Devine line of vacuum chamber dryers, units adapted for the handling of materials that can be dried on trays or pans. Bulletin 102, covering the Devine line of vacuum drum dryers best adapted for all liquid solutions containing solids, drying same to a powder. Bulletin 103, covering Devine rotary vacuum dryers, used in connection with drying materials that can be mixed or tumbled in the drying. They have now on the press additional bulletins covering their entire line of equipment. The Devine Company maintain a laboratory fitted with every type of vacuum and nonvacuum dryer that they build, and where they will, without cost or obligation to the prospective customer, run such experiments as will put them in a better position to definitely determine the type and size of apparatus best adapted for the problem in hand.

R. Martens & Company have extended their export operations in Russia to non-mechanical lines, by creating a subsidiary company under the name of "Russia Trade Corporation of America," with general offices in the Maritime Building, 8-10 Bridge Street, New York City. The new concern will specialize on all kinds of general merchandise, and manufacturers are invited to write concerning the possibilities for selling their products in the Russian market. Mr. Frank G. Bolles, former manager of the export trade publication, *International Trade*, of Chicago, has been made vice-president and will be in immediate charge of the affairs of the Russia Trade Corporation of America. Offices have already been opened in several of the largest commercial centers of Russia and other branches will follow covering every field of importance in the Russian Empire.

The National Paint, Oil and Varnish Association will hold a convention at the Hotel Traymore, Atlantic City, October 9-12. Special information as to any detail can be obtained of D. W. Figgis, chairman of the Entertainment Committee, 447 West 14th Street, New York City.

The Society of Chemical Industry will hold their next annual meeting in Birmingham, England.

Dr. J. P. Longstaff, of Edinburgh University, has been appointed Secretary of the Society of Chemical Industry, and will take up his duties in September. Mr. C. G. Cresswell, who had been Secretary of the Society since 1884, having resigned, the Council has awarded him a superannuation allowance of £300 per annum.

M. C. Whitaker, professor of chemical engineering, Columbia University, has been granted leave of absence for the first term of the academic year 1916-1917.

Mr. L. P. Kyriakides, of the Detroit Organic Chemicals Company, Wyandotte, Mich., announces that he has changed his surname to Kyrides.

Mr. W. R. Hulbert, sales manager of the Goldschmidt Thermit Company, of New York, delivered an illustrated lecture on the theory and practicability of making thermit welds, supplemented with many practical demonstrations, to the members of the Clinchfield Railway Club, Erwin, Tenn., on July 25, 1916.

A. H. Ney, Inc., will continue the business of consulting chemists and chemical engineers, heretofore conducted under the name of A. H. Ney, Ph.D.

Mr. Wallace P. Cohoe, consulting chemist, announces that he has moved his office from the Chemists' Building, 50 E. 41st Street, to Trinity Building, 111 Broadway, New York City, and his laboratory to Bertrand Avenue, Perth Amboy, N. J.

The Oklahoma Producing and Refining Company, a Delaware Corporation, has certified that it has increased its capital from \$2,000,000 to \$5,000,000.

Frank L. May & Co., Perth Amboy, N. J., chemists and druggists, have been incorporated with \$50,000 capital, by E. A. Reinhardt, F. L. May and O. Larsen.

The Ninth Annual Meeting of the American Institute of Chemical Engineers will be held in New York City, January 10-13, 1917.

Mr. Newton D. Arnold, secretary-treasurer and general manager of the Rumford Chemical Company, and the oldest thirty-third degree Mason in the Northern Jurisdiction, died at Keekshaug, R. I., on August 13, 1916, in his seventy-third year.

George Anthony Hill, formerly assistant professor of physics at Harvard University, and author of a number of text books on mathematics and physics, died suddenly on August 18, in Cambridge, Mass., following a stroke of paralysis. Mr. Hill was born in Sherborn, Mass., August 25, 1842. He was a tutor of chemistry in Harvard, 1865-71; assistant professor of physics, 1871-76; and director of the Nolen Laboratory for college preparation in physics and chemistry, 1898-1914. Mr. Hill's last book, "Essentials of Physics," appeared in 1912.

Mr. H. A. Plusch, for the past seven years chief ceramic chemist for the Atlantic Terra Cotta Company, has resigned to take up the practice of consulting engineering. His office will be at Perth Amboy, N. J.

The Block Chemical Laboratories of Chicago were incorporated under the laws of Illinois on June 16, 1916, with the following officers: Dr. D. Julian Block, *president*, Prof. Robert M. Cole, *vice-president*, and Mr. H. B. Keeler, *secretary*.

The Elyria Enamelled Products Company, Elyria, Ohio, has erected a new chemical laboratory equipped to carry on analytical and research work. Any problems relative to the use of glass enamelled apparatus will receive careful attention.

Mr. R. H. Fash, formerly chief chemist and refiner of the Chickasha Cotton Oil Company, became the active vice-president of the Fort Worth Laboratories on September 1st.

The following promotions have been made in the chemistry faculty of the Johns Hopkins University: Joseph C. Frazer, professor of analytical chemistry; E. Emmet Reid, professor of organic chemistry; Paul B. Davis, associate in chemistry.

Electric welding of iron and steel will be one of the feature exhibits of the New York Electrical Exposition which will be held in Grand Central Palace, New York City, October 11 to 21, 1916. The exhibit is being arranged by the Arc Welding Machine Company, 220 West 42nd St., New York City, and Mr. O. A. Kenyon will be in charge. The public will have an opportunity of seeing all grades of welding accomplished in iron and steel, including structural pieces, plates and castings.

The United States Government is cooperating in the Electrical Exposition through the War, Navy and Commerce Departments, all of which will have comprehensive exhibits.

The Association of British Chemical Manufacturers, which had been under consideration for some time, was definitely formed at a recent meeting held in the rooms of the Chemical Society, London.

Prof. Alfred Stenzel has been placed in charge of a clinic at the hospital of the University of Pennsylvania for the exclusive study of industrial and occupational diseases.



# GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

## BUREAU OF STANDARDS

**Effect of Certain Pigments on Linseed Oil.** E. W. BOUGHTON. Technologic Paper 71. 16 pp. "Since white lead, as supplied to painters and paint dealers, is almost always ground to a paste with raw linseed oil, it seemed desirable to determine whether or not the constants of the oil in the paste are materially changed during storage. Furthermore, it seemed desirable to obtain some numerical data regarding the extent to which certain pigments combine with linseed oil during the drying process, and also to make some experiments with drying paint films to determine the relative effect of different pigments on the rate of oxidation of the oil.

"The results as a whole indicate that white zinc combines with the free fatty acids of linseed oil more readily than does white lead. Of the three pigments, white lead, white zinc, and china clay, the former showed the greatest accelerative effect on the oxidation of raw linseed oil in films composed of pigment and oil, while china clay had the least accelerative effect.

"It is obviously unjustifiable to draw from the experimental part of this paper any conclusions regarding the relative values of the different pigments as paint materials. Such conclusions can be properly drawn only from the data afforded by exposure tests with painted panels and from general painting experience."

**An Interlaboratory Photometric Comparison of Glass Screens and of Tungsten Lamps, Involving Color Differences.** G. W. MIDDLEKAUFF AND J. F. SKOGLAND. Scientific Paper 277. 23 pp. Interlaboratory comparison of photometric measurements involving color differences is discussed. It shows how close an agreement may be expected with experienced observers.

**An Investigation of Laws of Plastic Flow.** EUGENE C. BINGHAM. Scientific Paper 278. 47 pp. The nature of plastic flow is described and theory involved is developed, showing that plasticity of a material depends upon its fineness of grain.

**Distribution of Energy in Visible Spectrum of an Acetylene Flame.** W. W. COBLENTZ AND W. B. EMERSON. Scientific Paper 279. 10 pp. This paper gives distribution of energy in visible spectrum of acetylene flame, based upon measurements made with three spectroradiometers. Results supersede data published in previous paper on this subject (Scientific Paper 191).

**A Study of the Inductance of Four-Terminal Resistance Standards.** FRANCIS B. SILSBEE. Scientific Paper 281. 46 pp. This paper deals with the inductance of electrical resistances of less than one ohm, suitable for use in new methods of measuring alternate current that require small resistances for the laboratory tests.

**Sensitivity and Magnetic Shielding Tests of a Thomson Galvanometer for Use in Radiometry.** W. W. COBLENTZ, Scientific Paper 282. 23 pp. This paper describes an investigation made to improve the sensitivity and design of a specialized galvanometer for use in radiometry. By using a lighter sus-

pension in a vacuum, the sensitivity has increased tenfold. The results will be of great value in the study of stellar radiation since the recent advances in this field called for the increased sensitivity which has been now obtained. The paper gives details as to construction and results of tests.

**Volume Effect in the Silver Voltmeter.** E. B. ROSA AND G. W. VINAL. Scientific Paper 283. 11 pp. This paper is a continuation of the Bureau's researches on the silver voltmeter which is the primary standard for the measurement of the international ampere. It has been found that when the electrolyte for the voltmeter is not sufficiently pure that the deposits in the large voltmeters are in excess of those in the small voltmeters in series with them. This phenomenon has been called the "volume effect." The present paper shows that this effect is due to the impurities of the electrolyte and not to other causes as was thought by several previous observers. It is also shown that the effect is the same in all forms of the silver voltmeter which the Bureau has tested. A theory to account for the effect is given. This phenomenon affords a valuable criterion of the purity of the electrolyte used in the voltmeter.

**Constants of Spectral Radiation of a Uniformly Heated Inclosure or So-called Black Body—II.** W. W. COBLENTZ. Scientific Paper 284. 19 pp.

**Strength and Other Properties of Concretes as Affected by Materials and Methods of Preparation.** R. J. WIGG, G. M. WILLIAMS AND E. R. GATES. Technologic Paper 58. 172 pp. This paper describes the effect of variation in composition, proportions, methods of handling, etc., upon compressive strength of these materials. Conclusions are drawn from 20,000 tests of about 300 different mixtures.

**Data on Oxidation of Automobile Cylinder Oils.** C. E. WATERS. Technologic Paper 73. 20 pp. This gives a study of carbonization when heated for different lengths of time at given temperatures and for equal periods at different temperatures. Significance of data for oil testing is pointed out.

**Determination of Volatile Thinner in Oil Varnish.** E. W. BOUGHTON. Technologic Paper 76. 7 pp. Describes method satisfactory for practical purposes, though only approximate for precise values. Methods tried were based on steam distillation, evaporation at 100° C. and from thin film at room temperature.

**Standard Methods of Gas Testing.** Circular 48, 2nd Ed. 202 pp. This circular contains suggestions as to location and equipment of gas-testing laboratories, description of accepted forms of apparatus, directions for making tests, and recommendations as to interpretation of experimental results. For this second edition a thorough revision has been made to correct minor errors, to incorporate suggestions of value, and to take account of recent investigations at the Bureau and elsewhere.

**Further Experiments on Volatilization of Platinum.** G. K. BURGESS AND R. G. WALTENBERG. Scientific Paper 280. 10 pp. This is a continuation of the report on experimental results showing the loss of weight on heating platinum crucibles and the conditions under which this loss may be reduced to a minimum. It is shown that the loss of weight increases rapidly with rise of temperature.

## BUREAU OF MINES

**Effects of Temperature and Pressure on the Explosibility of Methane-Air Mixtures.** G. A. BURRELL AND I. W. ROBERTSON. Technical Paper 121, 13 pp. "The results are important in

that they show that pressure and temperature conditions may vary over rather a wide range without affecting the explosibility of methane-air mixtures. Inconsistent results that have been obtained in the laboratory by different investigators on the limits of inflammation of methane-air mixtures cannot be explained on the basis of slight variations in temperatures and pressures. They depend rather on the nature of the source of ignition, method of ignition, size and shape of the containing vessel, and in some cases inaccuracies in mixing and analyzing the gases."

**Sensitiveness to Detonation of Trinitrotoluene and Tetranitromethylanilin.** GUY B. TAYLOR and WILLARD C. COPE. Technical Paper 145. 9 pp. Paper, 5 cents. "TNT (trinitrotoluene) is much less sensitive to detonation than tetryl (trinitromethylnitramine, or tetranitromethylanilin). The sensitiveness of the former is increased by admixture of the latter."

**Quantity of Gasoline Necessary to Produce Explosive Conditions in Sewers.** G. A. BURRELL and H. T. BOYD. Technical Paper 117. 13 pp. Paper, 5 cents. "In this report are shown the quantities of gasoline that must be introduced into sewers in order to produce explosive mixtures of gasoline vapor and air under certain conditions. Many different factors govern explosibility, such as size of the sewer, velocity of the sewage, temperature of the sewer air, volatility and rate of inflow of the gasoline, so that only under identical conditions of tests would duplicate results be obtained." (See THIS JOURNAL, 5 (1915), 750.)

**Production of Explosives in the United States during the Calendar Year 1915.** With Notes on Coal-Mine Accidents Due to Explosives and List of Permissible Explosives, Lamps, and Motors Tested Prior to May 1, 1916. ALBERT H. FAY. Technical Paper 159. 18 pp. Paper, 5 cents. "The total production of explosives, excluding exports, in the United States during the calendar year 1915, according to figures that the Bureau of Mines has received from manufacturers, was 460,900,796 lbs. (230,450 short tons), as compared with 450,251,489 lbs. (225,126 short tons) in 1914.

"The production for 1915 is segregated as follows: Black powder, 197,722,300 lbs.; "high" explosives other than permissible explosives, 235,828,587 lbs.; and permissible explosives, 27,349,909 lbs. These figures represent a decrease of 8,377,400 lbs. of black powder, an increase of 17,374,616 lbs. of high explosives and 1,652,091 lbs. of permissible explosives, as compared with figures for 1914."

#### BUREAU OF THE CENSUS

**Cotton Production in the United States in 1915.** Unnumbered pamphlet. 28 pp. This reports on the statistics of cotton ginned from the crop of 1915 and is a preliminary statement which will be incorporated with the full annual report which is published about October 1.

#### GEOLOGICAL SURVEY

**Some Paleozoic Sections in Arizona and their Correlation.** FREDERICK LESLIE RANSOME. Professional Paper 98-K, from Shorter Contributions to General Geology. pp. 133-166. Published July 15, 1916.

**Possibilities of Oil and Gas in North-Central Montana.** EUGENE STEBINGER. Bulletin 641-C, from Contributions to Economic Geology, 1916, Part II, pp. 49-91. Published July 17, 1916. "The purpose of the report here presented is to summarize all the available data concerning the possible occurrence of oil and gas in a considerable area in the north-central part of Montana, extending from the latitude of Great Falls northward to the international boundary.

"The facts observed seem to warrant the statement that considerable gas territory, on a scale comparable with the Alberta fields, may be found, and also that the area shows some probability of yielding oil. It cannot be too strongly emphasized,

however, that a rational search for oil and gas in the State should begin with operations in the areas where the rocks are most strongly arched."

**Asphalt, Related Bitumens, and Bituminous Rock in 1915.** JOHN D. NORTHROP. Mineral Resources of the United States, 1915, Part II, pp. 135-150. Published July 18, 1916. "The natural asphalt of all varieties sold at the sources of production in the United States in 1915 aggregated 75,751 short tons, valued at \$526,490, a decrease of 4,137 tons, or 5 per cent, in quantity and of \$15,633, or 2 per cent, in value from the corresponding totals in 1914.

"The statistics of output of the native bitumens, gilsonite and grahamite, in 1915, record slight increases over the output in 1914 and indicate a sufficient expansion of the home markets to compensate largely for the loss of foreign customers as a consequence of the European war.

"The sales in 1915 of manufactured asphalt obtained from petroleum of domestic origin amounted, at the sources of production, to 664,503 short tons, valued at \$4,715,583, an average of \$7.10 a ton, an increase of 303,820 tons, or 84 per cent in quantity, and of \$1,698,614, or 56 per cent, in market value, but a decrease of \$1.26, or 15 per cent, in average price per ton, as compared with the output in 1914."

The asphalt imported for consumption in the United States in 1915 was:

	Quantity (short tons)	Value
Crude.....	135,276	\$661,356
Bituminous limestone.....	2,976	19,001
Total.....	138,252	\$680,357

The occurrence and distribution of asphalt, details of various sources, and the activity of the market in various districts, is discussed together with sections on ozokerite and ichthyol.

#### PUBLIC HEALTH REPORTS

**Artificial Purification of Oysters.** WILLIAM F. WELLS. Public Health Reports 31, 1848-52. This is a report on experiments upon purification of polluted oysters by placing them in water to which calcium hypochlorite has been added. It is concluded that a remarkable degree of purification occurs within a period of 24 hrs. and the character of the results suggests the commercial applicability of this procedure for the purification of oysters otherwise entirely unsuitable for food purposes.

**Court Decisions Pertaining to Public Health.** JASON WATERMAN. Public Health Reports, 31, 1834-48. This is a digest of judicial decisions which were published by title in the Public Health Reports previous to January 1.

#### COMMERCE REPORTS—JULY, 1916

A company is being organized in Japan to manufacture soda electrically from the surplus salt which has accumulated from lack of transportation. (P. 6.)

The price of soap in Germany is now 2 to 10 times that of two years ago. (P. 10.)

Arrangements are being made to develop the oil-bearing lands of Bolivia. (P. 50.)

The prices of drugs in Germany for the last three years are given. Advances are in some cases over tenfold. (P. 36.)

Study of the iron ore deposits near Kuznetsk, Siberia, indicate the presence of over 27,000,000 tons of ore, much of which contains 54 to 58 per cent iron. (P. 61.)

Large manganese deposits are reported from Thunder Bay, Ontario. (P. 68.)

The Census figures for the United States fertilizer industry are given in detail. (P. 70.)

A new iodine factory is to be erected in Vladivostok, to secure iodine from seaweed, which is to be harvested in such a way as not to destroy the roots. (P. 87.)

The principal tanning materials used in the Philippines are



mangrove and camanchili bark. Modern methods are being gradually introduced. (P. 88.)

The deposits of **bauxite** in both British and Dutch Guiana are very promising. (P. 92.)

The fruit of the "vijao" plant is used in Porto Rico as a source of a valuable **red dye** and **red ink**. (P. 110.)

"Humogen" or bacterized peat is not on the market in England. (P. 111.)

Efforts are being made to develop the cultivation of **sisal** in the Philippines. (P. 132.)

Steps are being taken to start a **beet-sugar** industry in Siberia. (P. 147.)

A United States **paper** company is to erect a 200 tons news print paper mill in Canada. (P. 148.)

The output of **tungsten** ores in Argentina consists chiefly of wolframite with some scheelite. (P. 163.)

Experiments in Germany upon the use of alcohol-benzene mixtures instead of **gasoline** as automobile fuels, showed that a mixture of equal parts of alcohol and benzene gives best results. An ordinary carburetor was used, but it was found necessary to install a supplementary reservoir containing gasoline or ether, to be used in starting the car. (P. 171.)

Owing to the scarcity of **manganese** in Germany, iron ores rich in manganese are being shipped from Brunswick to other parts of Germany. (P. 183.)

The **petroleum** industry of Ecuador is very promising. While at present the small output is secured by seepage into shallow excavations, it is believed that deep drilling will prove profitable. At present little refining is done, most of the product being used for asphalt. (P. 186.)

In spite of the high prices, **potassium carbonate**, and **potash soft soap** are still preferred in England for wood scouring. (P. 190.)

Efforts being made in Canada to substitute **pepsin** for rennet in cheese making appear promising. (P. 201.)

Extensive **coal** deposits have been found in Iceland. (P. 205.)

The output of **tungsten** and **iron ores** from Chosen (Korea) is increasing. (P. 206.)

In an effort to solve the **iron** and **steel** problem of Spain, orders have been published prohibiting the exportation of iron or steel until domestic needs are met. Efforts will be made to increase the manufacture of iron and steel instead of as at present, exporting over 90 per cent of the ores mined.

The United States continues to be the largest importer of **rubber** from Java with Great Britain second, and Netherlands third. (P. 241.)

An English report on **oil-producing nuts and seeds**, shows that palm kernel cake is a valuable cattle and hog food. (P. 246.)

**Raffia wax**, obtained in Madagascar from the leaves of the raffia palm, is proposed as a substitute for carnauba wax, to which it is very similar. (P. 259.)

**Hemlock bark** is again being used in and exported from Canada as a source of **tannin**. (P. 260.)

**Iron** mines in China, containing 60,000,000 tons of 65 per cent ore, are to be operated by Japanese interests. (P. 282.)

The Chinese methods of salt production are all primitive. Much of the salt is obtained from gypsum quarries which are allowed to lie idle intermittently. Large quantities of sea salt are also obtained principally by solar evaporation. (P. 313.)

The extract of "babul" pods, the fruit of the tree that produce gum arabic, can be used for **tanning** in India only if a small amount of carboic acid be added to prevent fermentation. (P. 315.)

The wild Philippine plant "datura alba" is a promising source of **atropine** and **hyoscyanine**. (P. 317.)

Switzerland has only one **sugar** factory, and is now almost

entirely dependent upon the United States for sugar, which they have difficulty in importing. (P. 324.)

The **sand-lime brick** industry of Germany has fallen off during the war. (P. 329.)

An extended British report on the **palm-kernel** industry advocates its entire British control. Formerly over three-fourths of the palm kernels, grown on English or French soil, were sent to Germany for extraction. An export duty on palm kernels from West Africa, to countries other than British, is urged. (P. 330.)

Scarcity of **coal** has caused a great shortage of **gas** in Venice, thus crippling the **glass** industry. (P. 335.)

In an investigation of the **waterproofing of concrete**, the Bureau of Standards plans to erect a number of concrete tanks along the Potomac. (P. 339.)

The principal supply of **asbestos** from Russia is of the serpentine variety, found principally in the Ural Mountains. (P. 342.)

Arrangements are being made to supply **cyanide** for South Africa from Glasgow and other British plants. (P. 373.)

A plant for making **nitrates** and **nitric acid** from the atmosphere, under hydroelectric power, is being constructed in Spain. Supplement 15b. (P. 14.)

#### SPECIAL SUPPLEMENTS ISSUED DURING AUGUST ARE AS FOLLOWS:

DOMINICAN REPUBLIC—26a	IRELAND—19b
ARGENTINA—38a and 38b	BRAZIL—40b
GERMANY—6a and 6b	CANADA—23d
SPAIN—15b and 15c	CUBA—25a
NETHERLANDS—9a	HAITI—30a

#### STATISTICS OF EXPORTS TO THE UNITED STATES

QUEBEC DISTRICT— Sup. 23d	GERMANY—Sup. 6a and 6b	LONDON—161
Aluminum	Aluminum	Rubber
Antimony	Carbon electrodes	Tin
Asbestos	Lactic acid	Hides
Balsam gum	Dextrin	Indigo
Bones	Glycerin	Creosote oil
Bronze powder	Lanolin	Platinum
Are lamp carbons	Thorium nitrate	Copper
Calcium acetate	Earthenware	AMSTERDAM—Sup. 9a
Asparin	Glassware	Quinchona bark
Carboic acid	Enameled ware	Quinine
Nitric acid	Glue	Cocoa butter
Oxalic acid	Hides	Copal gum
Tartaric acid	Rubber	Drugs
Wood alcohol	Tungsten	Earthenware
Ammonium sulfate	Paints	Hides
Anilin	Paper	Kapok
Barium chloride	Artificial silk	Magnesite
Bone-black	Tin	Milk sugar
Calcium carbide	Epsom salts	Paraffin
Creosote oil	Ergot	Paint
Glycerine	Ichthyol	Paper
Gum arabic	Thymol	Rags
Gum camphor	Magnesite	Rubber
Gum gambier	Vienna lime	Tin
Gum kauri	Gum	SPAIN—Sup. 15a and 15b
Chloride of lime	Fusel oil	Antimony
Magnesite	Palm-kernel oil	Beet pulp
Menthol	Sesame oil	Cork
Potassium chlorate	Copper ore	Argols
Sodium nitrate	Manganese ore	Fusel oil
Soda ash	Beeswax	Glycerin
Chromic ore	Dyestuffs	Licorice
Coal	Bleaching powder	Calcium tartrate
Copper ore	Quinine	Potassium carbonate
Ammonium nitrate	Sodium cyanide	Hides
Potassium chloride	Zinc dust	Paper stock
Glue	Beet seed	Soap stock
Vegetable tallow	Potash	Essential oils
Hides	FERROMANGANESE	Iron ore
Ferromanganese	BRAZIL—Sup. 40b	Pyrites
Lead	Cottonseed	Copal gum
Mercury fulminate	Carnauba wax	Rubber
Cod oil	Gold	Copper
Castor oil	Hides	Copper ore
Cottonseed oil	Manganese ore	Manganese ore
Palm oil	Monazite	Saffron
Paints	Rubber	Beeswax
Paper	Sugar	Gayuba leaves
Paper stock	CHINA—Sup. 23a	URUGUAY—Sup. 38a and 38b
Silver	Hides	Bones
Sulfur ore	Sugar	Quebracho extract
Tar	Molasses	Glycerine
Tin	Asphalt	Hides
Zinc ore	Copper ore	Rubber
DOMINICAN REPUBLIC— Sup. 26a	Iron ore	Casein
Hides	Manganese ore	Crude tartar
Sugar	Beeswax	Tankage
Molasses	Bone	Glue stock
Copper ore	Fustic	Linseed
Rosin	Guano	(Oleo and stearin oil
Wax	Hides	Tungsten ore
Fustic	Logwood	Tallow

## BOOK REVIEWS

**Outlines of Industrial Chemistry.** By FRANK HALL THORP, with Assistance in Revision from WARREN K. LEWIS. Third Revised and Enlarged Edition. xxv + 665 pp., 137 figures. The Macmillan Company, New York, 1916. Price, \$3.25.

"The great progress which has been made in chemical industry since the publication of the second edition of this work in 1905 has necessitated entire rewriting of many sections of the book, with elimination of much obsolete matter and the introduction of much new material."

A careful examination of this third edition of "Thorp" has convinced the reviewer that in general it presents a clear and concise, yet comprehensive, view of the domain of chemical technology, and that it will serve its purpose of imparting to students "some knowledge of the plant and methods employed in the more important manufacturing operations based upon chemical changes." It will be found to be a useful textbook, but the opportunity for decided improvement is still apparent.

In the first place, a criticism of a work of this size which attempts to cover so large and progressive a field, is that certain of the sections are likely to be so indefinite that they are misinforming. An illustration in point in the present case is the account of the petroleum industry, wherein the author endeavors to describe the refining of crude petroleum without enlightening the student regarding the varieties of crudes and the several distinct processes used for each. Foreign texts do not supply the desired information on present-day American practice in refinery technology, and it is unfortunate that the author did not avail himself of recent literature of the type of F. C. Robinson's paper in *Proc. Eng. Club Phila.*, April, 1913. Moreover, the work could be improved by the inclusion of brief accounts of the technology of hydrogen and the important rarer metals (tungsten, vanadium, thorium, etc.) and by presenting available statistics of production. The importance of chemical economics is not adequately appreciated by teachers of industrial chemistry. Then, too, one is disappointed to observe that the author gives no space to the turpentine industry of the United States and that he has omitted consideration of carbon dioxide, sulfur dioxide, sulfur chloride, sodium silicate, natural gas gasoline, ethyl ether, formaldehyde, and oxalic acid.

In general, the descriptive matter is accurate, although the following oversights have been noted by the reviewer: No mention is made of the important Koppers oven (p. 36); the account of gas producer practice (p. 42) requires modernization; the author states (p. 206) that "in some cases window glass

\* \* \* is machine-blown," while, as a matter of fact, at least 80 per cent of the sheet glass now produced in this country is mechanically blown; providing care is exercised, hydrochloric acid gives just as stable a hydrogen dioxide as phosphoric acid (p. 273); the Smith process for making carbon chlorides is not mentioned (p. 298); "326" on p. 518 should read 362; petroleum (p. 343) is also made from "B. S." and rod-wax; the continuous system of distillation is used not only in Russia (p. 343), but largely in our own country; the oil-shales of Scotland are not "permeated with bitumen" (p. 345), but contain a bituminous substance, kerogen; in connection with asphalt (p. 347), mention should have been made of byerlyte and Dubbs' asphalt; the use of silicate of soda in refining cottonseed oil is not referred to (p. 360); "musk, Baur" is a nitro-derivative of tertiary butyl-xylene (p. 395); and bauxite is not a "hydrated oxide of alumina" (p. 639). The lists of references do not include many recent contributions of importance, which could have replaced a number of the old citations; and then the author has been careless in his bibliographic notes. It is unfortunate that American writers on chemical subjects have not more

generally adopted the logical journal abbreviations of *Chemical Abstracts*.

Owing to the fact that Dr. Thorp's book has demonstrated its general excellence by appearing in a third revised edition, the reviewer has been inclined to refrain from critical comment thereon. However, the desire to be helpful and coöperative has induced him to indicate whereby its established usefulness might be further augmented.

W. A. HAMOR

**Organic Agricultural Chemistry.** (The Chemistry of Plants and Animals.) By JOSEPH SCUDDER CHAMBERLAIN, Ph.D., Professor of Organic and Agricultural Chemistry in the Massachusetts Agricultural College. 319 pp. The Macmillan Company, New York, 1916. Price, \$1.60.

The present volume, as stated by the author in his preface, was written as an elementary textbook with the aim of giving "students of practical agriculture enough general scientific instruction in chemistry to enable them to understand and correlate the broad problems of agricultural practice."

In the first, or systematic, section of the book seven chapters are devoted to a presentation of the simpler facts of organic chemistry in their relationship to the problems of plant and animal life. The second, or physiological, section (seven chapters) discusses the subject of enzymes, composition of plants and animals, the living cell and its food, animal food and nutrition, and plant physiology. In the third section upon crops, foods and feeding, two chapters are devoted to the occurrence and uses of important constituents of agricultural plants and a concluding chapter to animal foods and feeding.

The author's presentation of his subject, which is in the lecture style, is clear and direct. A series of interesting experimental studies are included at intervals in the text. These laboratory exercises, which are carefully selected, advance the student towards obtaining a practical first-hand knowledge of the chemistry of plant and animal life.

In the physiological section of his book the author makes a unique departure from usual custom in presenting the chemistry of animal life before that of plants. This innovation will no doubt come as a shock to those who believe that the subject of agricultural chemistry must be unfolded in the supposedly logical sequence of mineral, plant and animal. Dr. Chamberlain's belief that a previous acquaintance with animal chemistry will help the student to gain a more correct view of the laws of plant life has much to recommend it. To work back from the higher to the lower is sometimes the more rational method. Liebig in his "Natural Laws of Husbandry" discussed the plant before he took up the soil.

The reviewer, after a careful perusal of this new work, has found but little to criticize. While a few statements—as that polarized light is light which has passed through a double crystal of quartz (p. 70), or that the one carbohydrate which does not contain the elements hydrogen and oxygen in the proportion  $H_2:O$  is a pentose sugar, known as rhamnose (p. 110), or that cellulose is hydrolyzed by enzymes to maltose (p. 164)—are incorrect or incomplete, such minor defects in a book not written for specialists are unnoticeable amid the many excellent qualities which Dr. Chamberlain's "Organic Agricultural Chemistry" possesses.

The book contains a good index and is well printed. It is cordially recommended to all who are interested in the subject.

C. A. BROWNE



**Organic Chemistry or Chemistry of the Carbon Compounds.**

By VICTOR VON RICHTER. Edited by PROF. R. ANSCHÜTZ and PROF. G. SCHROETER. Newly translated and revised from the German original (after Prof. Edgar F. Smith's 3rd American Edition) by DR. PERCY E. SPIELMANN. Vol. I (Aliphatic Series), xvi + 677 pp. P. Blakiston's Son & Company, Philadelphia. Price, \$5.00 net.

The advent of this new translation of this standard work will be welcomed by the chemical profession, since it is highly desirable that a reference book of this character should be up to date. Unfortunately, the second volume, dealing with the aromatic series, has not appeared as yet, but is promised for the near future. The original plan of the former editions has been followed. Some minor changes from the original German edition have been made, such as arrangement of some of the formulae to emphasize more clearly certain points under discussion. Only a few errors were noticed by the reviewer and the workmanship is very good.

J. M. NELSON

**Steam Boilers and Combustion.** By JOHN BATEY. Vol. XV, The Broadway Series. 211 pp., 18 diagrams. Scott, Greenwood & Son, London. Price, 4 s. 6 d.

In the preface of this book the author explains his addition to the literature on a branch of engineering which has already been the subject of many treatises by the statement that "most of the books published are highly technical works dealing with what has been done and not with the possibilities of future development." He emphasizes the necessity of improvement in steam boiler operation and implies that in this volume he has laid the way for such improvement by making clear the theory involved. About one-third of the book is given up to the description of different types of boilers and the remainder to the explanation of the phenomena of combustion, heat transfer and steam generation. A careful study of this work has convinced the reviewer that it can be of no possible value to American engineers because most of the boilers described are of types no longer used in this country, and the theories advanced concerning combustion and steam generation are absolutely opposed to those accepted by the engineering profession. The technically trained engineer can but disagree with the author upon almost every subject considered, and the man without a technical education may be led very far astray.

HARRY L. PARR

**The American Fertilizer Handbook.** Ninth Annual Edition, 1916. 400 pp. Ware Bros. Company, Philadelphia. Price, \$1.00.

The ninth annual edition of this Handbook follows the form of the previous editions and contains the standard reference statistics and directories of the fertilizer industry and allied trades. The directories of fertilizer manufacturers, allied fertilizer trades, cottonseed oil mills, and packers and renderers have been carefully revised up to date. The subject list of this edition is as follows:

National Fertilizer Association and Southern Fertilizer Association (Officers, Committees and Members); Agricultural Experiment Stations; State Fertilizer Officials; Fertilizer Materials Statistics, covering the production, imports, consumption and prices of Sulfate of Ammonia, Atmospheric Nitrogen, Blood, Guano, Potassium Salts, Bones, Pyrites, Sulfuric Acid, Fish Scrap, and Nitrate of Soda; State Fertilizer Tonnage; Soil Improvement Committees of the National and Southern Fertilizer Associations; Potash Salts; Cottonseed Oil and Meal; Rank of States in Crop Values; Reference Library—an index of the important articles in the previous editions of the Handbook; Reference Index—a list of the important articles in *The*

*American Fertilizer* from January 1, 1915, to May 15, 1916; Directory of Fertilizer Manufacturers; Directory of Allied Fertilizer Trades; Phosphate Rock Section; Fertilizer Machinery, Factory Construction Equipment and Supplies Section; Fertilizer Materials Section; Brokers, Exporters, Importers, Commission Merchants and Forwarding Agents Section; Chemists, Assayers, Engineers, Contractors, Leadburners, Samplers and Laboratory Equipment Section; Cottonseed Oil Mill Directory and Machinery Section; Packers and Renderers Directory and Machinery Section.

In addition the following special contributions are included: "Fertilizers: What They Are—How to Apply Them," by H. G. Bell, J. W. Henceroth and C. A. Waugh; "The Sulfuric Acid Industry," by A. M. Fairlie; "Possible Sources of Potash in America," by F. K. Cameron; "Potash Salts—1914," by W. C. Phalen; "Preventable Losses in Fertilizer Plants," by S. J. Martenet; "Sulfur and Pyrite in 1914," by W. C. Phalen; "The Cyanamid Industry—World Status," by E. J. Pranke; "The Production of Phosphate Rock in 1914," by W. C. Phalen; "The Cottonseed Oil Industry," by T. C. Law; "The Western Animal Ammoniate Market," by J. H. Schmaltz.

**The British Coal-Tar Industry.** A series of papers edited by WALTER M. GARDNER, Bradford Technical College. 437 pages. Williams and Norgate, London. Price, \$2.25.

This volume is a collection of the more important papers and addresses on the coal-tar industry of England which have appeared from time to time during the past forty odd years. The first paper in the collection is naturally the original Cantor Lecture of Sir William H. Perkins given in 1868, and entitled "The Aniline or Coal-Tar Colors." Other important papers marking the progress of this branch of chemistry are "The Artificial Production of Alizarine" by Prof. H. E. Roscoe (1870); "The Synthesis of Indigo" by Prof. R. Meldola (1901). These earlier articles dealing with the chemical development of the coal-tar colors are really quite interesting reading even at the present date. The later articles in the book, however, appearing from 1908 on to 1915, are chiefly of a polemical or retrospective character, and their keynote is one of mournful self-recrimination for allowing Germany to run away with all the dyestuff business which should have by right belonged to England. The chief reason from the English point of view as to why England should have controlled the manufacture of coal-tar products appears to be the fact that Perkin discovered and manufactured the first real coal-tar dyestuff. The English chemists also acknowledge that they are equal, if not superior, to their German confrères, and consequently the industry should have remained in England. But sad to relate it did not. There are many reasons, or rather excuses given for this circumstance. The manufacturers of England were not alive to the advantages of painstaking chemical research, they did not sufficiently encourage the chemist in his pioneer work; the Government did not lend it its power and influence to the proper development of the industry; and the Universities maintained a supercilious disregard of the technical sciences, and in so far as chemistry was concerned, seemed to have no interest beyond laboratory experiments.

Some of the authors in this volume also are very insistent in putting forth the argument that the character of the British patent laws worked an unfair advantage in favor of the German competitor. While this makes a good hook on which to hang an argument, I doubt if it has much real weight of reason behind it. As a matter of fact the English, both as manufacturers and chemists, were more interested in other things than the making of dyestuffs, and neglected this branch to follow others which they considered more profitable.

J. MERRITT MATTHEWS

# NEW PUBLICATIONS

By IRENE DeMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

- Batteries: Starting and Lighting Batteries; Upkeep, Care and Repair of Storage Batteries.** 8vo. 47 pp. Price, \$1.00. American Bureau of Engineering, Chicago.
- Bridge Engineering.** J. A. L. WADDELL. 8vo. 2177 pp. Price, \$10.00. John Wiley & Sons, Inc., New York.
- Chemistry of Familiar Things.** S. S. SADTLER. 2nd Ed. 8vo. 320 pp. Price, \$1.75. J. B. Lippincott Co., Philadelphia.
- Coal-Tar and Ammonia.** GEORG LUNGE. 3 vol. 1718 pp. Price, 63 s. Gurney & Jackson, London.
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Aluminum Sulfate, high grade.....	Ton	65.00	@	100.00
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Ammonium Phosphate, commercial, 98-100%.....	Lb.	—	@	—
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Soda Ash, 48 per cent.....	100 Lbs.	3	@	—
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Sodium Bicarbonate, domestic.....	100 Lbs.	1.80	@	2.00
Sodium Bicarbonate, English.....	Lb.	3 1/2	@	3 3/4
Sodium Bichromate.....	Lb.	30	@	32
Sodium Chlorate.....	Lb.	23	@	25
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**ORGANIC CHEMICALS**

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Acetic Acid, glacial, 99 1/2%, in carboys.....	Lb.	30	@	32
Acetone, drums.....	Lb.	40	@	—
Alcohol, denatured, 180 proof.....	Gal.	47	@	48

Alcohol, grain, 188 proof.....	Gal.	2.64	@	2.66
Alcohol, wood, 95 per cent, refined.....	Gal.	61	@	66
Amyl Acetate.....	Gal.	5.25	@	5.50
Aniline Oil.....	Lb.	30	@	32
Benzoic Acid, ex-toluol.....	Lb.	7.50	@	8.00
Benzol, 90 per cent.....	Gal.	63	@	65
Camphor, refined in bulk, bbls.....	Lb.	60	@	61
Carbolic Acid, U. S. P., crystals, drums.....	Lb.	50	@	55
Carbou Bisulfide.....	Lb.	6	@	6 1/2
Carbon Tetrachloride, drums, 100 gals.....	Lb.	17 1/2	@	18
Chloroform.....	Lb.	48	@	50
Citric Acid, domestic, crystals.....	Lb.	64	@	67
Cresol, U. S. P.....	Gal.	70	@	75
Dextrine, corn (carloads, bags).....	100 Lbs.	3.50	@	3.55
Dextrine, imported potato.....	Lb.	12	@	13
Ether, U. S. P., 1900.....	Lb.	15	@	15
Formaldehyde, 40 per cent.....	Lb.	11	@	11 1/2
Glycerine, dynamite, drums included.....	Lb.	35	@	36
Oxalic Acid, in casks.....	Lb.	59	@	61
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Starch, corn (carloads, bags) pearl.....	100 Lbs.	2.55	@	2.61
Starch, potato.....	Lb.	6	@	6 1/2
Starch, rice.....	Lb.	8	@	10
Starch, sago.....	Lb.	3 1/2	@	4
Starch, wheat.....	Lb.	5	@	6
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Cottonseed Oil, p. s. y.....	Lb.	10 3/4	@	—
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Menhaden Oil, crude (southern).....	Gal.	49	@	50
Naphtha, 68 @ 72%.....	Gal.	36 3/4	@	37 1/2
Neat's-foot Oil, 20%.....	Gal.	1.08	@	1.10
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Paraffine Oil, high viscosity.....	Gal.	29 1/2	@	30
Rosin, "F" Grade, 280 lbs.....	Bbl.	6.75	@	—
Rosin Oil, first run.....	Gal.	29	@	31
Shellac, T. N.....	Lb.	30	@	31
Spermaceit, cake.....	Lb.	25	@	26
Sperm Oil, bleached winter, 38%.....	Gal.	80	@	82
Spindle Oil, No. 200.....	Gal.	24	@	25
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Copper, lake.....	Lb.	27	@	—
Lead, N. Y.....	100 Lbs.	6.50	@	6.75
Nickel, electrolytic.....	Lb.	45	@	—
Nickel, shot and ingots.....	Lb.	50	@	—
Platinum, refined.....	Oz.	60.00	@	65.00
Silver.....	Oz.	66 1/4	@	—
Tin.....	Lb.	38 1/4	@	38 3/4
Zinc, N. Y.....	Lb.	10	@	—

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Calcium Nitrate, Norwegian.....	100 Lbs.	—	@	—
Castor Meal.....	Unit	—	@	—
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Tennessee, 78-80 per cent.....	Ton	5.00	@	5.50
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## ANNUAL MEETING AMERICAN CHEMICAL SOCIETY

The Fifty-Third Meeting of the American Chemical Society convened in New York City, Monday, September 25th, to Saturday, September 30th, with headquarters at the Chemists' Club and Hotel Astor. Division Meetings took place at Columbia University, the Chemists' Club, New York College of Pharmacy and the Grand Central Palace. The special Industrial Conferences are reported elsewhere in this issue.

The Council met at 4:00 P.M. on Monday at the Chemists' Club and were the guests of the New York Section at dinner, continuing their deliberations throughout the evening. The following officers were elected for the coming year: Charles L. Parsons, *Secretary*; Dr. Charles H. Herty was chosen *Editor* of the JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY, with authority to revise his Board of Associate Editors; this action was later confirmed by the directors. Dr. Herty succeeds Prof. M. C. Whitaker who declined reelection. The Council deferred the election of the Treasurer to the directors, who elected Dr. E. G. Love *Treasurer*. The next annual meeting of the Society will be held September 1 to 10, 1917, in Boston.

The registration took place at the Chemists' Club under the direction of Mr. H. R. Moody. The total registration was 1905, including 1438 members and 467 guests of which 194 were ladies. A special room was provided on the mezzanine floor for the Ladies' Committee headed by Mrs. Leo H. Baekeland. Mrs. Frank Hemingway and her associates assisted the visitors in arranging for the various functions provided for their special entertainment. On Wednesday morning, a special automobile tour, in charge of Mrs. J. Merritt Mathews and Mrs. J. M. Muir, started from the Chemists' Club, went through the various large parks, and reached Longview at Hastings-on-Hudson in time for luncheon. On Thursday, the ladies visited Altman's and Tiffany's stores, where special arrangements had been made by Mrs. R. N. Shreve and Mrs. Morris Loeb for exhibits not ordinarily seen. Later, luncheon was served at the Woman's City Club and at the Woman's University Club. Choice seats were reserved for Thursday evening at the Criterion and for Friday afternoon at the Strand, where the ladies were entertained under the leadership of Mrs. Maximilian Toch and Mrs. Chas. Baskerville. The Chemical Show was open to the ladies with Mrs. Bernhard C. Hesse directing the guides who conducted the strangers through the exhibits.

The official opening meeting was held at the Horace Mann Auditorium, Columbia University, with J. Merritt Mathews, Chairman of the New York Section of the Society, in the chair. The Address of Welcome on the part of New York City, delivered by Health Commissioner Dr. Haden Emerson, appears in full on p. 870. In welcoming the Society on behalf of Columbia University, President Nicholas Murray Butler stated that he considered the assembly of the American Chemical Society as the mobilization of a

very large part of the civilized fighting army. He emphasized especially the necessity for proper sanitation and protection of the health of the employees in connection with manufacturing operations in order that they may be commercially successful. The audience was interested to hear that Dr. Mitchell, who occupied the Chair of Chemistry in the old Kings College, 100 years ago, was the first, and has been the only, chemist to have a seat in the Senate. Later on, his successor, Dr. Chandler, organized the work of the Department of Health of New York City on a scientific basis and thus carried the chemistry of that day into public service. Dr. Butler expressed his appreciation of the intelligent and unselfish devotion of the unusual group of young men scientists and experts who are giving their services to the general public in New York City, making possible the results reported in Dr. Emerson's address.

In turning over the meeting to Dr. Herty, Dr. Mathews took occasion to express the appreciation of the New York Section for his vigorous and unstinted labor in Washington in connection with the bill recently passed, protecting the chemical industries, particularly those relating to coal-tar products.

Dr. Herty responded for the American Chemical Society to the Addresses of Welcome. He said that he was glad to be present and called attention to the many factors which had worked against the American Chemical Society meeting in New York. He was particularly struck by the coincidence that there was no better indication of the rapid strides in the chemical industry during the last few years than the fact that only four years ago in the room in which the opening meeting was held, Dr. Berntsen demonstrated publicly for the first time in America the synthesis of ammonia from nitrogen and hydrogen gases, and that now this synthesis is practically the mainstay of Germany's strength.

At the business meeting held Tuesday afternoon, in the Horace Mann Auditorium, in addition to the Presidential Address by Dr. Herty, addresses were made by General William Crozier, Chief of Ordnance, War Department, and Mr. John E. Gardin, Vice-President of the National City Bank. These addresses appear in full below.

On Tuesday evening a reception was held at the Astor Hotel. Members, guests and members of the American Electrochemical Society and the Technical Association of Pulp and Paper Industry were invited. About 400 guests were present. After the guests had gathered, the dancing hall was opened and at a late hour delightful refreshments were served.

Wednesday evening was left open for visiting the Second National Exposition of Chemical Industries at the Grand Central Palace. Further discussion of this Exposition can be found elsewhere in THIS JOURNAL.

On Thursday evening the members of the American



AMERICAN CHEMICAL SOCIETY BANQUET AT THE WALDORF-ASTORIA, SEPTEMBER 29TH

Chemical Society were the guests of the American Electrochemical Society at a Smoker, held in the ballroom of the Astor Hotel. Mr. Wallace P. Cohoe had charge of the exercises of the evening. The meeting was opened by songs of the American Electrochemical Society, words of which were printed on pamphlets and in which the company joined at various times during the evening. A masque entitled "The Odyssey of Science" was presented. The principal part was taken by "Chemistry" in the rôle of Cinderella. The lover and rescuer of "Chemistry" from "Despair" was "Research," and the arch enemy was "Capital," who read a paper entitled "On the Evil of the Theorist." "Common Sense" played the part of the Great Reconciler. Prof. Ambrose Jeffries, brother of Jim Jeffries, and a ventriloquist, furnished considerable entertainment during the evening. Mr. Saunders appeared in the rôle of a dashing golfer with such bravado that no one took up his bet. During the evening a female dummy "Maid in America" was abducted by some member of the audience and her subsequent fate is unknown. Mr. Winter gave a humorous monologue, "Bureau of Mine," "to disclose many scientific secrets, but not to talk about radium." About 800 people were present, and cigarettes, beer, sandwiches, cheese, crackers and sour pickles were the refreshments served in abundance. The American Chemical Society is greatly indebted to the American Electrochemical Society for a highly enjoyable evening.

On Friday evening the Subscription Banquet was held in the handsomely decorated ballroom of the

Waldorf-Astoria, jointly with the members of the American Electrochemical Society and the Technical Association of Pulp and Paper Industry: 341 persons were present. Dr. W. J. Schieffelin acted as toastmaster. Mr. Ellwood Hendrick read a poem entitled "Rollo and His Uncle," which appears below. President Herty spoke briefly of his pride in the rapid growth of the Society. Mr. Charles H. Sherrill, for years the representative of the United States in Argentina, gave an interesting and convincing plea for closer relations between the United States and South America. Dr. Arthur D. Little spoke briefly of the relations of the chemical engineer to industrial progress, and Mr. Frank S. Washburn told of the present-day opportunities and achievements of the chemist. After the serving of the delicious nine-course banquet, members and guests indulged in dancing.

On Saturday 200 members joined an all-day excursion up the Hudson River on a boat specially chartered by the American Electrochemical Society. The weather was delightful. A negro orchestra of four went with the party and furnished music for dancing. The crowd sang, ate good things and had a jolly good time. The courtesy of the American Electrochemical Society was greatly appreciated by all.

The American Chemical Society was well cared for in New York and Mr. J. Merritt Mathews, Chairman of the Local Section, is to be complimented on the excellence of his plans and the cordial manner in which his various committees took up their duties. The visitors and guests will long remember the Annual Meeting in New York City.



## ROLLO AND HIS UNCLE

"Dear Uncle, I would like to be  
A man of circumstance,"  
Said Rollo, having just been kissed  
By several different aunts.

"I want to be a man of might,  
Want to be left alone,  
I do not want, when I grow up  
To hear the sugary tone  
Of praise, because I am so sweet  
I do not want to be  
So kissable." Quoth Uncle, "Then  
Just study chemistry."

Address yourself to mercaptans,  
Butyric acid, or  
Naphthylamine, and other things  
Of which there plenty more

I once was young myself, my child  
And understand your pain;  
Those blandishments are hard to bear;  
They leave a psychic stain.

"Then Uncle dear," said Rollo, "How  
Shall I begin my work?

I want to be a chemist and  
I do not want to shirk  
The preparation for the task,  
The study, the career,  
That promises immunity  
Which is to me so dear."

"Ah, times have changed," his uncle said.

"But nowadays, at first  
For physics and for calculus  
You'd better show a thirst.  
It makes a good impression, and  
If you would be in style,  
Show off your mathematics, but  
At mere reactions, smile.

You'll find professors do not care

About The Ways of Stuff;  
"Free Energy's" their ruling thought  
And that is most enough  
To satisfy the questing minds  
That give you your degree  
So bear in mind you must be glib  
About free energy.

In elementary inorganic

You may learn a few  
Reactions, but time presses and  
You'll have to hurry through  
The work in hand, because to-day  
But few professors care

For all that old-time, text-book stuff  
Of this you should beware

Soon you begin in earnest and  
Proceed, for instance, with  
A standard work in chemistry  
By Alexander Smith.

Read carefully, my boy, because  
Your teacher may not want  
Even to think of half the text  
He'll tell you that he can't  
Spare all the time to bother with  
The personality  
And ways of stuff. Then he will talk  
About free energy.

Ionization is a theme that  
Rules him like a lion,  
He'll break all rules of chemistry  
To satisfy an ion

'Tis better, cast all doubt aside  
When he begins on this;  
If you should raise a question he  
Will scowl at you and hiss.

I used to think theology  
Was rather rough on doubt,  
But chemistry, with ions, beats  
Theology all out

You'd better join the church before  
This course is well begun  
Because you'll need to exercise  
The art of faith, my son  
Solutions he'll discuss at length  
Provided always they  
Contain solute to solvent as  
The needle in the hay.

So, while he talks and wanders on  
Read carefully your book,  
If he says 'Physical Chemistry,'  
Put on a pleasant look.

When you begin analysis  
You'll start qual-i-ta-tive,  
And get in loose and messy ways  
As surely as you live.

Why teachers do not change and give  
The quantitative first  
Is something I can't understand  
Except that no one durst

In other walks of life we learn  
First to be neat and clean;  
In chemistry on t'other hand  
The opposite has been

The modish operandi which  
Is after all like life  
We learn to virtue in old age,  
In youth to sin and strife.

Then you'll have physical chemistry,  
The darling of the gods,  
The measurement of things in dreams,  
Philosophy of sauls,  
Mass action where there is no mass,  
The phase rule and the law  
Of whatsoever might occur,  
Or what you ever saw.

And now forget what you have learned,  
Most everything you know,  
Organic chemistry's your task  
And other things are not so  
Which you have pinned your faith upon,  
The things are turned about.  
Though once your greatest need was faith,  
Your present need is doubt

The harmony of nature has  
Not entered in between  
The two domains of chemistry,  
Alas! there is a screen  
That has been made, the light of truth  
To sunder, to divide  
Which makes those universal laws  
Fit one or t'other side.

Now, let us say, you've turned the trick  
And taken your degree  
And all the kissing aunts have gone  
Beyond, along with me.

It may be that you'll wonder as  
You rub your bearded face  
Just what it was that started you  
As chemist in the race.

It may be that your tastes will change  
And you will want to be  
In favor with the ladies, and  
Want their society.

But even then, do not lose hope, for  
Chemists, somehow, find  
As mates the most delectable  
Of all womankind."

"Oh, Uncle, dear!" cried Rollo, then,  
"I beg of you desist;  
I am resolved, when I grow up,  
That I shall not be kissed."

—Ellwood Hendrick

## ADDRESS OF WELCOME

By DR. HADEN EMERSON

In acting on behalf of His Honor, the Mayor, to welcome you to New York, it is a privilege of no small degree to greet those who have accomplished a more direct assimilation of the products of theory and research into the body of industry and practical production, than any other representatives of science and commerce. As the present administration of New York City has devoted itself to the application of personal standards and business practice in public affairs, so the Department, which I have the honor to represent, has devoted itself to an increasing degree, to placing preventive medicine as applied to public health administration, among the exact sciences.

New York City is not unlike the human body in the complexity of its functions and the differentiation among its units. Just as the study of human physiology made scant progress until functions, organs, and even individual specialized cells were subjected to close scrutiny, so in analyzing the city from the point of view of the Health Department, we have passed from a study of boroughs and wards, to the survey of census units, the investigation of hazardous trades, and still further, to the medical examination of the men and women individually, whom we know will suffer in a certain proportion from pre-

ventable diseases and incapacity, even when, to their own minds and senses, they are in perfect health. It is worth as long a search to find the unrecognized typhoid carrier, the origin of most city epidemics of typhoid fever, as to search for the uncompleted synthetic in a hydrocarbon series.

Advancing from the general principles of the sanitation of environment, to the precise control of the particular infectious individual, from policies to persons, we are continuously reducing the number of deaths and the cases of preventable disease, not before the rates prevailing in many smaller communities, where the distribution of population per acre is more naturally favorable to healthy living, but below the rate of other large cities in the world. New York is surpassed in certain particulars by various cities, but in our general death-rate, and in our infant mortality rate, the most accurate and the most sensitive indices of a city's health, New York City has a better record than London, Paris or Berlin. In the first year of the organization of the Board of Health (1866), there were 3000 deaths recorded to every 100,000 population—in 1915, 1400 deaths; or to put it in other words, if the death-rate of fifty years ago had prevailed in 1915, there would have been recorded 166,000 deaths or 88,000 more than actually occurred.

The death-rate from typhoid fever decreased 80 per cent.

The deaths from small-pox during the first decade of health administration numbered 6260—in the last decade, 7.

In 1915, there were relatively 2,600 fewer deaths from diphtheria than in 1866. Scarlet fever showed a decrease in mortality of 95 per cent—measles decreased 50 per cent.

The greatest achievement of the administration was the reduction in the mortality from diarrheal diseases among children under 5 years of age—in 1915 a little over 3900 children died from this disease, whereas if the rate of 50 years ago prevailed, 13,000 children would have succumbed—a yearly saving of over 9000 lives.

Fifty years ago, 4 out of every 10 children born, died before completing the first year of life—to-day, only 1 out of every 10 born, dies before the end of the first year.

And now, what is the next step in the endless controversy with ignorance, prejudice, inertia, and the pressure of commercial competition, the four great obstacles to health protection.

Unhesitatingly I say, it is a forward march upon occupational disease, the health hazards of industries. Two great groups vie with each other for the unenviable distinction of producing per thousand employees more cases of industrial disease, accidents and deaths, than any others. Opinions differ as to which holds the palm, but whether we put the metal industries first, because they dominate with their great numbers of employees, or choose the chemical industries, because the variety of hazards is greater, there is no doubt as to the joint burden of these two groups for a vast amount of preventable disease.

It is not enough that we see and admit the necessity of removal of fumes, gases and dust, and provide a better general ventilation of shops and furnaces, we must enroll ourselves now, and for all time, among the teachers for self-protection.

If a fraction of the thought and money had been spent on the protection of the worker, that has been lavished on the protection of the product against foreign competition, no cry of preparedness would be heard in the land. A healthy nation with a spirit of regard for its most priceless and most wasted resources, its human lives, will always keep out of touch of its nearest competitor in vital, as in financial resources.

In one new factory, in this city, devoted to the production of aniline dyes, not a week passes without at least one serious case of aniline poisoning. No insurance company would, knowingly, take as a risk, the workman in the autoclave room.

See the ever lengthening list of specific and incapacitating volatile poisons handled recklessly and with utter disregard of human wastage, in the cause of the manufacture of explosives, rubber articles and aniline derivatives or compounds.

The chemical industry employs upwards of 50,000 workers now, exclusive of all those working in the petroleum industry, the paint industry and the processes of manufacture which require the use of chemicals, such as dry cleaning, felt hat making, etc.

In Germany, Weyl has shown that out of 165,820 employees in the chemical industry, in 1905, there were sicknesses of 8 days duration in 88 per cent of all employees—there were 11,000 accidents, gases, hot vapors and explosions causing most of them.

Leyman showed that laborers and mechanics contributed 27 and 45 per cent, respectively, of the sickness rate from internal diseases and 37 and 43 per cent, respectively, for sickness from external affections.

The manufacture of hydrochloric acids, sulfates, chromates, caustic potash, chloride of lime and trinitrophenol are especially prone to cause respiratory diseases.

Next to the workers in lead products and compounds, those who work in aniline manufacture suffer most commonly from poisoning.

Curschman's recent statistics show that the sick rate in

chemical works with improved sanitary conditions is still 54.9 per cent per annum of the entire force, with an average duration of sickness of 17.8 days.

Gentlemen of the American Chemical Society, I appeal to you, as the brains and hearts of the greatest present, and most rapidly growing industries of our time, to consecrate a part, at least, of your deliberations to a constructive policy of education of the workmen in the factories.

Technical improvements in method, automatic devices, painstaking supervision, will play a part, but the great hope and opportunity, the foundation stone of permanent remedy, is in education of the workmen.

Health officers owe it to you to include among the preventable diseases that they are engaged by the public to prevent the diseases of occupation.

For every 1000 men employed in industry in the United States, 3.39 are killed and but 0.91 in France, with Prussia, Great Britain and Belgium in between, with rates of 2.06, 1.28 and 1.10, respectively.

Before giving you my message of invitation, I wish to indicate briefly, the character and extent of the chemical activities of the Health Department of this city.

The Department of Health produces curative and preventive sera, and bacterial products, and carries out a variety of diagnostic tests of chemical and biological character. It maintains, also, analytical laboratories to assist in the regulation of food and drug products. It carried out in the last year 358,406 diagnostic tests, of which there were 96,585 bacterial examinations for milk, water and other foods. The Department produced 3,762,100 cc. of serum products and 201,000 cc. of vaccine products and in the past year, 56,000 Wassermann reactions, 11,000 complement fixation tests for gonococcus infection have been made in our diagnostic laboratories.

Any who are free and interested, will be welcomed at our research laboratory, at the foot of East 16th St., where representatives of the Department will be available to play the part of hosts. Furthermore, if there are phases of our activities in the direction of inspection of the manufacture and distribution of foodstuffs, which you wish to study while in the city, Mr. Lucius P. Brown, a member of your Society and the Director of the Bureau of Food and Drugs of the Department of Health, will be responsible for your guidance and so far as possible, your conveyance, to points of special interest.

## CHEMISTRY AND THE NATIONAL WELFARE

By GENERAL WILLIAM CROZIER

The published title of the very short address which I have been honored by a request to make to you is "Chemistry and the National Welfare;" but as there is very little which I can tell you about chemistry, even in connection with the national welfare, which you do not know better than I, it seems that a better title would be "Chemists and the National Welfare," for I think it is likely that there are some aspects of your relations to the military element of the national welfare to which I have given more contemplation than you have. It is not difficult to admit the general need of the military service for the class of knowledge which you represent, and the wide publicity which the European war has given to the indisputable importance of the chemistry of explosives has enabled not only the educated layman, but even the superficially informed man in the street, to appreciate that war cannot be carried on in these days without a great draft upon the services of chemists and chemical engineers. It has also been made apparent that for a proper utilization of the chemical as well as other professional and technical knowledge of its citizens, for military purposes, the Government cannot rely alone, nor even very largely, upon the services of the professional men in its own employ, but that it must receive the benefit to be had from drafts upon the national resources



in this kind of knowledge, as well as upon industrial establishments and other civic organizations and societies, as well as individuals.

It would in all probability be admitted in any discussion between reasonably well informed men, that the affairs of the Government should be so conducted in time of peace by those charged with their administration as to prepare for the utilization in an emergency of the country as resources in capacity of all kinds which contribute towards military success, so that it would be necessary only to follow plans already made in order to set going the machinery of utilization with a promptness and smoothness which would depend only upon the intelligence and industry with which the plans had been laid. This preparation is not always such an easy matter. Although there is powerful sanction for it, and evidence that men of intelligence in responsible positions have intended to provide means for it, there is also evidence that there are persons in positions of influence, and of some power and responsibility, who do not share the view that the Government should in ordinary times place such reliance upon the private resources of the country as would require co-operation with those resources in the production and improvement of war material during those times of peace which constitute the periods of preparation for war. There is in recent legislation some evidence of this conflict of view which necessarily operates to a certain extent to the embarrassment of those governmental agencies whose duty it is to prepare the country for war, in accordance with the wishes of the people as expressed through their Representative in Congress.

In the National Defense Act, approved June 3, last, there is found the following wise provision:

"The Secretary of War be, and he is hereby, authorized to prepare or cause to be prepared, to purchase or otherwise procure, such gauges, dies, jigs, tools, fixtures, and other special aids and appliances, including specifications and detailed drawings, as may be necessary for the immediate manufacture, by the Government and by private manufacturers, of arms, ammunition, and special equipment necessary to arm and equip the land forces likely to be required by the United States in time of war: PROVIDED, That in the expenditure of any sums appropriated to carry out the purposes of this section the existing laws prescribing competition in the procurement of supplies by purchase shall not govern whenever in the opinion of the Secretary of War such action will be for the best interest of the public service." (Sec. 123.)

The object of this legislation is apparent. You will know the length of time which is required for fitting even a going manufacturing concern with the special tools, fixtures, and other appliances necessary to turn out in large quantities such articles as small-arms cartridges, for instance, or fuses for field-artillery ammunition. It is conservatively estimated that a plant well equipped for the manufacture of a military rifle of a given model would require something like 8 or 9 months to supply itself with these special fixtures, etc., for use with its already installed machinery, in sufficient quantity to enable it to turn out a rifle of a different model in some such reasonable number as 1000 per day. The value of advance preparation in the matter of these special appliances is, therefore, recognized in this legislation; and there is further latitude given to the Government in the proviso that in the expenditure of appropriations for carrying out this legislation such selection may be exercised, irrespective of competition, as, in the opinion of the Secretary of War, will be for the best interest of the public service. The spirit of the legislation is most helpful. It will be observed that no appropriation is made, but that funds are to be provided in other acts.

One of these Acts is the one known as the "Fortifications Act," approved July 6th last. In it we find, among other items, the following:

"For the procurement of such gauges, dies, jigs, tools, fixtures, and other special aids and appliances, including such plans, specifications, and detailed drawings as may be necessary for the immediate manufacture of arms, ammunition, and other material necessary for the defense of the country, and for plans

for and the installation of such material in private plants in the United States under such contract and agreement as may be made by the Secretary of War, \$1,000,000: PROVIDED, That not exceeding twenty-five per centum of said sum may be used in obtaining from plants so equipped such war material as may be desired: PROVIDED FURTHER, That not exceeding \$50,000 worth of such material may be purchased from any one person or company, and in making such expenditures the laws prescribing competition in the procurement of supplies by purchase shall not govern."

Here is a generous provision for carrying out the object of preparing for the utilization of private industries. It is apparent that in the legislation quoted the spirit of such utilization was in the ascendant.

Other legislation, however, is not quite so encouraging. In the same Act—the Fortifications Act—are found the following:

"That except as expressly otherwise authorized herein no part of the sums appropriated by this Act shall be expended in the purchase from private manufacturers of any material at a price in excess of twenty-five per centum more than the cost of manufacturing such material by the Government, or, where much material is not or has not been manufactured by the Government, at a price in excess of twenty-five per centum more than the estimated cost of manufacture by the Government: PROVIDED, HOWEVER, That whenever in the opinion of the President, an emergency exists affecting the general welfare of the United States, he may waive the limitations contained in this section."

\* \* \* \* \*

"That expenditures for carrying out the provisions of this Act shall not be made in such manner to prevent the operation of the Government arsenals at their most economical rate of production, except when a special exigency requires the operation of a portion of an arsenal's equipment at a different rate."

The Ordnance Department has taken some pride, and believes it has met with some success, in cheapening the cost of government manufacture. If its own estimate of its success has not been overdrawn it may not be easy to find private manufacturers willing to accept as small an order as might be permitted under the limitation cited above if their prices shall be limited to 25 per cent in excess of the cost to the Government. And there is some possibility that acceptance in such cases may have to be induced by appealing to the patriotism of the manufacturer in co-operating with the Government, without profit, in preparing himself to meet the Government's needs in time of emergency. The requirement for operating the government arsenals at their most economical rate before giving orders to private manufacturers will probably call for their operation at double shift; we will, therefore, be limited in the orders which we can give for keeping private manufacturers in that knowledge of the methods of making war material which comes only from practice, to the extent of the excess of the sums appropriated over and above the amounts which will be necessary to keep the arsenals going at double shift. I am glad to state that the appropriations have been sufficiently generous to provide this excess in most cases; but the extent to which private establishments can be employed in the manufacture of war material, to the advantage of the Government, will be less than it would have been if we had been authorized to operate the arsenals at a single shift only, which is the rate which, in my testimony before Committees of Congress, I have advocated as being of most advantage to the Government.

In another Act, the Army Appropriation Act of August 29, 1916, there is an appropriation of \$10,000,000 principally for small-arms ammunition, which is accompanied by the proviso that not more than \$5,000,000 of this appropriation may be used in the purchase of ammunition. Here again the authority for making purchases is sufficient to permit a good deal of encouragement of private manufacturers, and, in addition, it is further provided that \$25,000 of the appropriation may be used in equipping private manufactories with special tools, fixtures, etc., and that \$50,000 worth of orders may be given to individual private manufacturers, in furtherance of their preparation to

meet the Government's emergency needs, by War Department selection, instead of by competition. Most of the items of appropriation for munitions, in the Army Appropriation Act, are accompanied by similar restrictions, and in some instances they are likely to be less encouraging than those just mentioned to the preparation for utilizing the national resources. For example, an appropriation of \$3,000,000 for ammunition and other articles for small-arms target practice is accompanied by the proviso that not more than \$1,500,000 of this appropriation may be used for the purchase of articles not manufactured by the Government and necessary for small-arms target practice, from which it appears that under this item of appropriation the only articles that can be purchased from private manufacturers are those for the manufacture of which the government arsenals are not fitted.

In previous years the restrictions placed upon purchases have been more severe. In the Fortifications Act of March 3, 1915, it is provided that of the sums available "not more than 10 per cent may be used to purchase not to exceed 10 per centum in quantity or value of any article or material herein appropriated for that can be manufactured at the arsenals of the Ordnance Department, except when contract costs are less than the arsenal manufacturing cost," and in the Army Appropriation Act of March 4, 1915, under an appropriation of \$100,000 for ammunition, it was provided that not more than \$5,000 of the appropriation might be used in the purchase of ammunition.

These illustrations show that in the matter of preparing to utilize the private resources of the country in case of emergency the legislation under which the executive departments must operate looks both ways. It is apparent that there is a sentiment in Congress reflecting a sentiment among the people in favor of such advance preparation, and willing to provide effectually and generously for its promotion, and that there is also a sentiment, which might perhaps be illustrated by the demand for taking the profit out of war, in favor of the greatest possible utilization of government manufacture, to the exclusion of the utilization of private resources, which sentiment has made itself felt in the preparation and passage of the supply bills and other military legislation.

Now, these examples illustrate also something else, and that is the necessity for the interest and support of public opinion for carrying out any governmental plan, whether for the military utilization of private resources or anything else. I am not complaining of the action of Congress, or criticizing that body. I know something of the difficulty of framing legislation and putting it through, when there is conflicting sentiment in the country in regard to a policy; but the greatest difficulty we have to encounter is when there is no sentiment at all, that is when there is public indifference, which is our normal condition in times when the stimulus of a great war in some part of the world is lacking. In such times I have, in a number of years of attendance upon its committees, usually found Members of Congress in advance of their constituencies, in thoughtful consideration of the military necessities of the country. And that thought brings me to your relations to those needs.

The Government has, and will continue to have, a great need for your professional knowledge and professional labors, and in ordinary times there is no great prospect of reward for either. We have just now an illustration in a call upon your membership for assistance in a very important matter. I refer to the nitric acid factory for the erection of which, with the necessary preliminary investigation, and appropriation of \$20,000,000 was made by Congress at its last session. The War Department has called upon the National Academy of Sciences for a report which will assist it in reaching a conclusion as to which one of the various known processes for the manufacture of nitric acid, by a method not requiring dependence upon a foreign source of supply, would be most to the advantage of the Government

for adoption, in the erection of its plant, taking into consideration all of the legislation in the Appropriation Act concerning the use of the excess capacity of the plant over that which would be required for the Government's military needs in peace time. The National Academy has associated with it the American Chemical Society, and has appointed a committee for the consideration of this subject from the membership of both bodies. These gentlemen will receive no pecuniary compensation for their services. They do not desire any. Their reward will be the consciousness of public duty performed, which in this instance, I am glad to say, will be accompanied by a certain prominence of the subject in which they are working, which has attracted a good deal of attention. But this prominence cannot always or often be had. In ordinary times of peace our people do not think much of military matters. In such times one might almost say that the stomach takes precedence of the chest, and under the title of the business interests of the country absorbs all of the best energies of the people themselves and of the statesmen to whom they entrust the provision of the means and the formulation of the rules for equipping and guiding the ship of state.

I once heard a very prominent and very useful statesman say that what he did not know about military matters would fill a very large book, with the same self-deprecating mock modesty which might have accompanied the statement that he had never learned to play the fiddle, or had time to devote to any other unimportant matter. He was a good man, too, a man of high order, and particularly skilled in feeling the public pulse. Such a man, similarly placed in Europe, would not have made that kind of a statement. I do not think that this situation indicates blameworthiness upon the part of any one. I think that in a country happily situated as ours is, with little direct threat of aggression against it, and with the great underlying causes of wars in which it might become engaged even more obscure than in the case of countries situated otherwise, it is inevitable; but this makes it all the more necessary that the educated and thoughtful men who constitute the membership of bodies such as yours shall think about military matters in a way in which the general public does not think about them, and remember that most of the support of military preparation must come from the topmost intellectual layer, which must make its most valuable contributions, not only without pecuniary reward, but also without the kind of satisfaction which comes from useful public service rendered in a matter which is prominent in the minds of one's countrymen, and, therefore, to be justly and generally appreciated. The labor of providing for military preparation, both in special personal services and in the direction of public opinion towards that object, although essentially to the average man's interest, is the high-class man's burden and it is upon his clear vision and personal devotion that the reliance of the nation must be for appreciation of the necessity for thoughtfulness as to war in time of peace, for intelligent contribution towards preparation for it. For both of these classes of service your membership will be called upon in the future, as it has been in the past, and is now. Your service is indispensable, and in rendering it you will, of course, be guided, as are the gentlemen who are now being specially called upon, by the sense of duty which works without reward.

WAR DEPARTMENT, WASHINGTON

## CHEMISTRY AND BANKING

By JOHN E. GARDIN

The present struggle at arms sooner or later will be followed by a struggle, possibly just as fierce, for the supremacy of commercial interests, and in this the chemist will play no small part. At one time England held the whip hand and had absolute control over the chemical industry of the world. But



this position has been wrested from her by the plodding and thrifty industrial methods of Germany, and the future necessity of each country standing on its own merits has been brought to the world's attention in a most forceful manner by the present conflict prevailing in Europe.

The familiar economic theory that things should be purchased where they can be produced the cheapest, while fundamentally sound, has, from the practical standpoint, disadvantages that become apparent only in times of stress and trouble. The people of the United States of America, never before have realized how dependent they were upon the German chemist, not alone in the matter of dyes but also of other chemicals, and the sudden collapse of the commercial relationships between the two countries is a calamity. The lesson has been taught us, and it now remains for the people of this country to profit by it. That they will do so, there is not the slightest doubt in my mind. But the great fear is that the attempt will be only a sporadic one and that, just as soon as the European equilibrium has been re-established, matters will again run along the lines of least resistance and, before we know it, we shall again be the vassals of some European power so far as certain industrial products are concerned.

Theoretically I never was a believer in tariffs, having been educated in a school where free trade was considered the acme of scientific government. Practice, however, teaches us a different lesson, and the cost of any other policy must be put to book in our national system, just as the cost of the upkeep of our military and naval service—and that is the protection of our natural resources. It is through the intervention of tariffs that the inequalities of methods of production are equalized, and while to some it may not seem wise statesmanship to have imposed an especially high duty on dyestuffs to take effect after the war, still our legislators are perhaps to be congratulated that they have used foresight in this respect.

The capital invested in the chemical industry in this country, not alone directly but indirectly, is something enormous, and unless we enter upon a campaign of preparedness now, we are likely to receive some very rude shocks when the other war—that is, the economic war of nations—is launched upon us.

Theorizing is all very well, but it does not take a very astute mind to determine that if the flood gates are open for the influx of the world's products later on, a great deal of this capital will be absolutely wiped out, and it, therefore, behooves the banker, the merchant, and the professional man to put his best efforts behind the one thought at the present time, and that is, to create a stability in our production that will resist all attempts of the outsider to overcome.

The chemical industry of the United States is making wonderful strides. It has quadrupled its output since 1880, and doubled it since 1905.

The capital invested is over six times as much as in 1880, and more than double that of 1905. This relates to the group of products classed by the census, from which the above figures are quoted, as "general chemicals." The capital in 1880 was 29 million dollars, in 1910, 155 million and in 1915 approximately 220 million, this estimate of capital for 1915 being based upon official figures of product of that year. The value of products turned out in 1880 was 39 million dollars and in 1915 approximately 158 million.

In addition to this there is a large group of products, many of them very important, classified by the census as "allied industries," including fertilizers, dyestuffs, explosives, essential oils, wood distillation, sulfuric and nitric acids, bone, carbon and lampblack, and paints and varnishes. The value of the output of these "allied industries" is much greater than that of the group classed distinctly as chemicals, having been in 1880 approximately 72 million and in 1915, 400 million; the capital employed in 1880, 57 million, and in 1915 approximately 480 million.

This makes the grand total of output of the groups of manufactures classed by the census as "general chemicals" and "allied industries" about \$550,000,000 in 1914 (census of 1915), and the capital invested approximately 700 million dollars, the 1915 figures of capital being estimates based upon known figures of output in that year and also known figures of capital in 1910.

All of the foregoing statements regarding the figures of the 1915 census, and those which follow, are necessarily based upon preliminary returns thus far received from the census of 1915, and must, therefore, be regarded as subject to revision, and in some cases, especially as to capital employed in 1914, merely estimates, based upon stated value of output in 1914 and capital shown by the 1910 census.

Moreover, the figures of the various census years are not absolutely comparable. The first special report on the manufacture of chemicals and allied products issued by the Census Bureau was presented in 1880, covering the manufactures of 1879. This report, like those of succeeding censuses, covered the operation of establishments engaged in the manufacture of acids, sodas, potashes, alums, glycerin, dyestuffs, tanning materials, explosives, fertilizers, pigments, wood distillation, salts and certain elementary substances. In addition, the census of 1880 included in its figures of "chemicals and allied products" soap, candles, glucose and sulfur, while all of these were omitted in the subsequent censuses. In 1890, however, paint and varnish were added to the group of "chemicals and allied industries," and in 1900 essential oils and lampblack were also added. Thus the figures of total output and total capital for the various censuses are not absolutely comparable, though the fact that paints and varnishes were substituted in 1890 for the groups, soap, candles, castor oil, glucose and sulfur, suggest that the changes are not sufficient to affect seriously the grand totals of products and capital employed running through the census records beginning with 1880. The capital figures for 1915 are in all cases estimates, but based upon census figures of production for that year, and the comparison of figures of capital with production in 1910 and earlier censuses.

Attention is especially called to the relation of capital employed to the value of output. The figures quoted are in all cases those of the census, except, as above indicated, that the 1915 figures are my own estimates based upon the census figures of output for that year. It will be noted that a comparison of the figures of capital employed and product turned out shows a steady growth in the amount of capital utilized in the production of a given value of output. In the group "general chemicals," the census figures show, for 1880, 29 million dollars of capital and over 38 millions worth of products turned out. The 1910 census shows 155 million dollars of capital and only 118 million dollars worth of products turned out. This increase in the amount of capital utilized in producing a dollar's worth of chemicals has been steady and consistent, as will be noted by comparing figures of capital and output for each as given by each census. In the allied industries, conditions are similar. In fact, this general rule applied in most of the manufacturing industries, the capital employed in all manufacturing being, according to the census figures in 1910, thirty-five times as much as in 1850, the value of manufactures only twenty-three times as much as in 1850.

It is, however, proper to add that the Census Bureau itself states frankly that its figures of capital employed in the manufacturing industries are far less reliable than those of the value of the output, but as approximately uniform practice has been followed in the collection of the figures of capital from census to census they are presumably worthy of attention in considering the relative growths of capital and output.

The production of chemicals and allied products is quite widely distributed, though occurring chiefly in the section east of the Mississippi.

Chemicals form an important factor in the foreign trade of the United States, both as to imports and exports. Prior to the war, imports of chemicals were largely in excess of exports, but the war has greatly increased the exportation of articles included in the general group "chemicals, drugs and dyes." The total imports of chemicals, drugs and dyes has grown from 48 million dollars in 1896 to 70 million in 1906, and 109 million in 1916. The exports of chemicals, drugs and dyes were in 1896 9 million dollars, in 1906 19 million, in 1914, the year preceding the war, 27 million, in 1915 46 million, and in 1916 124 million, all of the above figures of imports and exports being for the fiscal years ending June 30th.

The United States is apparently the world's largest importer of chemicals, the imports of Germany in 1913, the year prior to the war, being about 75 million dollars, Great Britain 70 million and France 50 million. The exports of Germany for 1913 were 140 million, Great Britain 60 million and France 25 million. It is proper to add, however, that these figures are only approximations, because of the uncertainty as to the grouping of many articles which by certain countries are classed under the general head of chemicals, drugs and dyes, and by other countries otherwise classified.

#### PRODUCTION OF GENERAL CHEMICALS IN THE UNITED STATES AND CAPITAL EMPLOYED

U. S. Census Figures

Census of	Capital	Product	Employees	Wages and Salaries
1880.....	\$29,000,000	\$38,600,000	11,000	\$6,200,000
1890.....	55,000,000	59,400,000	17,100	10,100,000
1900.....	89,100,000	62,700,000	21,200	12,100,000
1905.....	96,600,000	75,200,000	22,600	14,800,000
1910.....	155,100,000	117,700,000	27,600	20,300,000
1915(a).....	220,000,000(a)	158,000,000	No data	No data

(a) Estimate based on stated value of product in 1915 and stated value of capital and product in 1910.

#### PRODUCTION OF GENERAL CHEMICALS AND ALLIED PRODUCTS AND CAPITAL EMPLOYED, 1880 TO 1915

Allied products include fertilizers, explosives, dyestuffs, essential oils, wood distillates, sulfuric and nitric acids, carbon, bone and lampblack, and paints and varnishes

	Capital	Product
1880.....	\$86,000,000	\$99,000,000
1890.....	180,000,000	125,000,000
1900.....	238,500,000	202,500,000
1905.....	324,100,000	281,000,000
1910.....	483,700,000	425,100,000
1915.....	700,000,000(a)	550,000,000

(a) Estimate based on stated value of production in 1915 census and census figures of capital and product in 1910.

#### PRODUCTION OF FERTILIZERS, EXPLOSIVES AND PAINTS AND VARNISHES, AND CAPITAL EMPLOYED, 1880 TO 1915

Year	Fertilizers Capital	Fertilizers Product	Explosives Capital	Explosives Product	Paints and Varnishes Capital	Paints and Varnishes Product
1880	\$17,913,000	\$23,651,000	\$6,585,000	\$5,802,000	\$17,333,000	\$29,113,000
1890	40,594,000	39,181,000	13,539,000	11,353,000	45,318,000	54,234,000
1900	60,686,000	44,657,000	19,466,000	17,125,000	60,053,000	69,582,000
1905	68,917,000	56,541,000	22,307,000	29,602,000	75,486,000	90,840,000
1910	121,537,000	103,960,000	50,168,000	40,140,000	103,995,000	124,889,000
1915	No data	168,388,000	No data	42,160,000	No data	149,049,000

Unfortunately the American banks have not the wide powers in connection with this particular industry, or in fact any other industrial undertaking, that the European banks have. The law forces the banks here to pursue merely a commercial business, and it is perhaps well that it is so. The relationships between the banks and the public in this country are quite different from what they are abroad. In America the banks are supposed to be the custodians of their clients' money, whereas in Europe the general idea is that the banks are the investors of the public's money and oftentimes the public is not quite so fortunate in the choice of fiduciary. Therefore, in view of this known circumstance, when failure overcomes a bank, owing to bad investments, it is taken as a natural consequence and unless absolute fraud can be shown no particular odium attaches to the bank's officers. In this country, however, surrounded as we are with legal technicalities, the banks are not in a position to employ customers' money in founding industries of any kind. In fact the law prohibits specifically national banks from owning stock of any character whatsoever.

This does not, however, mean that capital is not available for

industrial purposes. No meritorious undertaking is ever allowed to suffer for want of the necessary means to develop it. Capital is a greedy monster and seizes upon every opportunity whereby an increase can be expected and the attention of the investor of the United States to-day is directed in a great measure toward the development of the chemical industry and its allied branches.

Under the protection of the Government through its tariffs, numerous projects will be brought forward for the exploitation of this, that, or the other enterprise, some of them meritorious, others of no value whatsoever. It must be borne in mind that the investor will not trust his money to anything that is not absolutely certain and, this being the case, it is futile to endeavor to attract his attention to anything that does not possess absolute perfection.

Chemistry is out of its swaddling clothes, and while it has a great future in most lines, the experimental stage in a great measure has been past.

Chemistry goes into practically every feature of the world's industrial activity, no matter how lowly it may be, and to be able to command such enormous power in the control of the human requirements, it seems to me the chemist should be a proud individual. In the olden days the alchemists sought the easy means of the transmutation of metals. The modern chemist, through his skill, his industry, and his research, turns the basest product into glittering gold.

NATIONAL CITY BANK  
NEW YORK CITY

#### PRESIDENTIAL ADDRESS

#### THE EXPANDING RELATIONS OF CHEMISTRY IN AMERICA

By CHARLES H. HERTY

After a year of such strenuous service as characterized that through which we have just passed, it is well that we are again assembled for report on the work of our laboratories and for helpful conference concerning future growth and broader service. A large part of the past year's work has, through the suddenness of the call, been necessarily individualistic; the assemblage of this week furnishes the means for planning more coordinated effort, for mutual counsel and for deepening that spirit of coöperation which is so essential if we are to meet worthily our full responsibilities.

It is again incumbent upon me to address you. In seeking a subject I have put aside the temptation to lay before you statistics illustrative of marvelous growth during the past year, and, in spite of our belief in specialization, it has not seemed suitable to select any one line of development for tracing in thorough detail. This period is still too formative and the demands upon you too many-sided for such restricted discussion. I have, therefore, selected the broader topic "The Expanding Relations of Chemistry in America," using the present participle advisedly as indicative of growth and as mandatory of greater effort if the widening circles of chemical influence are to reach the broad shores of full-fledged accomplishment.

The dynamic center of this movement is the American Chemical Society which now consists of 8136 members, a net growth of more than 1000 during the year just ended. This splendid growth is not only a tribute to the energetic activities of our efficient secretary, but is an evidence of increased activity in chemistry and of a quickened realization of the need of the strongest possible national organization. The strength of this organization, however, is not measured so much by numbers as by the loyal and unselfish response of its members to every call made in its name. To this I can abundantly testify.

In considering the expanding relations of Chemistry in America let me group these under four heads—the relations to university administrations, to the national government, to our daily needs and to national thought.



## RELATIONS TO UNIVERSITY ADMINISTRATION

Without doubt university executives have gained during the past year a clearer conception of the fundamental value of chemistry to the nation. Aside from our own exhortations, this conception has been easy of attainment through the increased publicity given by the daily press and by periodicals to matters chemical, through the difficulty to purchase certain needed supplies, through the feverish activity to meet these unexpected demands, and through the call for young chemists from university laboratories. Has the conception, however, been translated by the makers of university budgets into deeds which will insure an adequate response by the universities to the increased demand which is to be made upon them for chemists possessing the best possible training? I have neither purpose nor desire to criticize, nor even to attempt answer, but I do not hesitate to suggest that in these abnormal times the demands upon chemistry departments are unusually great and should be generously met if we are to view the future with equanimity. The bounds of the service of chemistry to the nation are prescribed by the character and extent of the training given in our universities. Physical equipment must be increased and bettered and staffs must be maintained adequate in number to allow full opportunity for research along with teaching duties.

The stimulus of these remarkable times upon the minds of the students is plainly evident, but here lies a danger. The expansion of existing industrial plants and the creation of new lines of endeavor in chemical industry call for many young men to serve in control work, and the call is often very alluring. It would be a great misfortune if the filling of these new positions should be at the expense of the graduate students of the future. We cannot afford an abridgment of the number of young men thoroughly trained in our universities in the methods of research. Graduate fellowships in largely increased number should be provided, for without such aid the door of opportunity will be closed to many whose full mental potentialities will be needed in the future.

The danger of losses from university ranks, however, is not confined to graduate students; already there are strong indications of a considerable raid by the industries upon the staffs of universities, and the question of professorial emolument is, therefore, not one for leisurely future consideration, but belongs to the immediate present.

To sum up, the university budget for chemistry needs prompt and decided expansion.

In the matter of coöperation between universities and industries definite progress has been made. Four important matters typify this progress.

The New York Section has conducted throughout its winter meetings a symposium on this subject, and these discussions resulted in a request of the Society that a permanent committee be appointed to carry forward vigorously such coöperation.

The General Chemical Company announced the formulation of a new policy in the creation of an advisory staff of university professors.

The Massachusetts Institute of Technology announced a Master's Course in Chemical Engineering, including a School of Chemical Engineering Practice. Through the coöperation of industrial plants a half year of systematic plant experience and training is added to the curriculum without sacrifice of thorough foundation work or training in research. In return for the privileges offered by the plants, the research facilities and the faculty of the Institute will be available for the study of special problems connected with each plant.

A joint meeting of the Puget Sound Section and the Seattle Chamber of Commerce aroused great enthusiasm and resulted immediately in the creation of industrial fellowships in the University of Washington for the study of the problems of the Northwest.

Such illustrations furnish proof that earnest thought is being given to this phase of coöperation and it is inspiring to note how quickly such thoughts are being translated into definite action.

## RELATIONS TO THE NATIONAL GOVERNMENT

Forty-nine members of the Society, representing the several states and Alaska, on appointment, responded to the request of the President of the United States that the chemical industries be mobilized under the program of the organization for industrial preparedness. Publication of the correspondence in connection with these appointments would furnish lasting testimony to the loyal and unselfish patriotism of the membership of our organization.

In response to the invitation of the National Academy of Science our representatives are now coöperating in the organization of the research facilities of the nation and in questions connected with the establishment of the government nitrate plant.

If we are to proceed promptly and intelligently with the development of a diversified and comprehensive chemical industry we must know the detailed character and amounts of chemical importations. The statistics now published by the government are inadequate in their itemization. The formulation of the character of the information needed is our responsibility. This is the work of the committee on Government Statistics, of which Committee Dr. B. C. Hesse is chairman. The inauguration of the work has unfortunately but necessarily been delayed. It is now well under way, and for its full consummation I beg to urge the thoughtful aid of every member of the Society, and the coöperation of each of the Local Sections. We have never undertaken any more important or fundamental work than this. If, as a result of this inventory, we are able to state in exact terms the specific character of the information needed by the chemical industries, in order to render this country independent of foreign sources of supply, we shall then have a right to expect with confidence the sympathetic coöperation of the federal authorities.

May I, under this heading, make two suggestions to the National authorities:

*First*, Provision should be made in the immediate future for the storage of large quantities of government-owned toluene. With the cessation of European war orders for explosives, and with the rapid increase of by-product retort ovens for coke manufacture, we shall eventually have a large over-production of toluene, with consequent lowering of price. The potential value of this hydrocarbon in munitions is too great to allow its sacrifice as a fuel or as an illuminant, and its storage involves no unusual difficulties. The moral effect alone of its known presence in our midst would in itself fully justify the investment as a preparedness measure.

*Second*, Modern warfare is largely dependent upon the successful work of chemists, not alone in the direct production of munitions, but, through research, in husbanding the resources of the country, and in increasing knowledge which in times of stress may be vital to the nation. In view of the now well recognized fundamental character of such work the military authorities should formulate a definite policy in regard to the chemist, whereby in times of war his services may best be applied to the advantage of his country. The lack of such a policy during the recent enlistment of the National Guard has in several cases interrupted lines of research whose successful outcome would prove much more vital to the power of the army than the presence of the individuals bearing arms. England somewhat tardily recognized that her chemists were more needed at home than at the front, and, therefore, recalled them.

## RELATIONS TO OUR DAILY NEEDS

The economic developments of the past two years have emphasized the close relation between normal daily needs and

the activity of chemists, particularly through certain shortages which have brought economic distress. Among these shortages three stand out preëminent—motor fuel, potash for fertilizer and coal-tar products, particularly synthetic dyestuffs. Let me discuss the first and second of these briefly and the third somewhat more at length.

**MOTOR FUEL.** The enormous annual increase of motors using gasoline as fuel, together with the largely increased export of this material, has resulted in greatly increased price of this product. To meet the situation chemists have naturally turned their attention to the "cracking" of the residues of crude petroleum, furnishing thus some relief. In view, however, of the uncertainty of petroleum supply such efforts cannot prove the ultimate solution of the problem. With the cessation of the war further aid may be expected from the benzol recovered in the by-product coke oven plants. With this at its maximum, however, it is estimated that it would equal only 10 per cent of the motor fuel now consumed. Plainly we must look further for the permanent supply, and that seems to me to be alcohol. I am fully aware that there is nothing original in this suggestion. It is mentioned rather for the purpose of urging greater consideration of the problem by chemists, who must solve the problem, by manufacturers of motors who have such great interests at stake, and by lumbermen who, in their mill waste alone, possess the raw material from which, by processes in operation to-day, alcohol could be produced equal in volume to 40 per cent of our present gasoline consumption.

What striking advance in this line could be confidently expected if the automobile manufacturers and lumbermen of the nation would join forces with chemists in the creation of a great research laboratory where the problems of motor fuel could be vigorously attacked, not by the "green powder" method of recent notoriety, but by common sense, scientific investigation, conducted by the ablest of chemists and chemical engineers, unfettered by tradition and filled with the conviction that the day of genuine new things will never end.

**POTASH.**—To meet our present shortage of this valuable fertilizer constituent we have sought relief feverishly through the kelp fields of the Pacific coast, the alunite deposits of Utah, the feldspars, blast furnace and cement works waste, and have as yet obtained but slight relief. Something noteworthy may yet result from these earnest efforts, especially through the aid of the appropriation of \$175,000 by Congress for further investigation of kelp, but at present we seem to have adopted the general policy of waiting until the war is ended.

Let me, in this connection, remind you of the old problem: namely, the rendering available *in situ* of the potash now in the fields in the form of silicates. The records of the U. S. Bureau of Soils show that the average weight of a foot acre of the sandy soil of the cotton belt weighs 1,750 tons, and contains an average of 0.1 of 1 per cent potash, or  $1\frac{3}{4}$  tons  $K_2O$  per acre, while the clay soils average in weight 2000 tons per foot acre and show an average potash content of 1.68 per cent or 33.6 tons  $K_2O$  per acre. From this material nature slowly supplies available potash for plant food through the action of the soil solution upon the potash bearing silicates, but the process is too slow. Many lines of research are in daily progress in our laboratories whose object is the discovery of "accelerants" for certain chemical reactions. Does not the importance of this problem and its altogether normal character demand of us greater effort to find a suitable accelerant for this world wide process. The problem is easy to state; its solution has as yet proved impracticable. May we not hope that the activities of physical chemists through studies of the soil solution and its action upon the mineral constituents of the soil will be ultimately successful?

**COAL-TAR DYESTUFFS.**—It is unnecessary for me to remind you at this time of the great disturbance of our industrial life

which resulted from the cessation of imports of German dye-stuffs, nor of the rapid extension of the by-product coke oven whereby we are now assured of a far more than adequate supply of raw material for an American dyestuff industry sufficient for American needs. It is a pleasure to testify to the energy and resourcefulness of our dyestuff manufacturers, who, in spite of competition with the munitions industry for coal-tar crudes and for necessary acids, and with uncertainty as to the future constantly dogging their steps, nevertheless have notably contributed to the relief of the dyestuff famine.

It is my purpose, however, to trace, for the sake of the record, the efforts made during the past two years to obtain legislative assurance of a fair start in the upbuilding of a well rounded, permanent industry, and to point out the character of the legislation which on the last day of the present session of Congress became a law of the land. It is a distressing story, humiliating to all who wish for our country freedom in every possible form. Here is the story.

Immediately after the outbreak of the war the New York Section of this Society, foreseeing economic distress from possible shortage of dyestuffs, appointed a representative and politically non-partisan committee to report on the prerequisites of an adequate self-contained American dyestuff industry. The report, unanimously adopted by this the largest of our local sections, recommended congressional enactment of protective duties amounting to 30 per cent *ad valorem* and  $7\frac{1}{2}$  cents per lb. specific on finished dyestuffs, one-half these amounts on intermediates and an effective anti-dumping clause. The protective rates of this report formed the basis of the Hill bill, introduced in the House on the opening day of Congress by Representative Ebenezer J. Hill, of Connecticut. In January, 1915, hearings were held on this bill and there was presented the unusual sight of both producers and consumers urging the Ways and Means Committee to report the bill favorably. In spite of this unanimity the report was not forthcoming. Public demand for such legislation, however, increased, and finally, after a conference between leading members of the controlling party in both the Senate and the House with representatives of a large number of producers and consumers, a form of legislation was proposed by the congressional representatives which embodied the *ad valorem* rates of the New York Section but reduced the specific duties by one-third, such specific duties to continue in full force for a period of only five years, after which time they were to decrease 20 per cent annually. Another feature was the proviso that if at the expiration of five years American dyestuff factories were not producing 60 per cent of the values (note this carefully) of American consumption, the specific duties were to be immediately and completely repealed by Presidential proclamation.

In spite of the lowered specific duties, this agreement, confirmed by authorized interviews from Washington, led to increased activity by many producers. It is not difficult to imagine, therefore, the amazed surprise which greeted the appearance of the dyestuff section of the General Revenue Bill, which, while it contained all of the above, showed one other totally unexpected feature, *viz.*, the exclusion of indigo and alizarin and their derivatives from the benefit of the special duty of 5 cents per lb. Such an exception was fatal to the purposes of the bill. The *ad valorem* duty alone would not suffice to promote and encourage the manufacture of synthetic indigo and alizarin. No scientific or technical justification existed for discrimination against these two coal-tar dyes, which constitute 29 per cent of the values of our consumption. Furthermore, the manufacture of at least 10 per cent of dyestuffs could not for the present be attempted in this country because of existing foreign patents. Such considerations show that the possibility of expansion of the home industry within the five-year period to 60 per cent of the values of consumption would be precluded by the terms of



the bill itself. Consequently the duration of the special duty for any dyestuff would be restricted to the initial five year period. Evidently our lawmakers had surpassed the skill of the alchemist, in that they had demonstrated their ability to transform at least dyes into gold.

Pressed for a justification of the exclusion of indigo and alizarin, the Chairman of the Ways and Means Committee made explanation on the floor of the House in a speech which by previous agreement was to conclude the debate. In this speech reference was made to the satisfactory character of the conference with the representatives of the industries; individual manufacturers were referred to as not desiring full protection for indigo and alizarin; and no justification on scientific or technical grounds was attempted. Then the dyestuff section of the bill was adopted by a party vote. Immediately briefs were filed with the subcommittee of the Senate Committee on Finance in charge of this section of the House Bill. These briefs included letters and telegrams from the individuals referred to in the House debate refuting the statements made by the Chairman of the Ways and Means Committee. Moreover they pointed out clearly that the exception of indigo and alizarin was not in accordance with the original conference agreement and would prove disastrous to the entire industry. The Senate subcommittee was convinced and accordingly struck from the bill the objectionable exceptions, and in addition included natural indigo and coal-tar medicinals and flavors, additions in every sense logical, and giving to the classifications of the bill a thoroughly comprehensive character.

With the appearance of the printed hearings and briefs an interesting exhibit was made by the plea of a large consumer of indigo located at Greensboro, North Carolina. Not content with the discrimination given indigo in the measure as passed by the House, he urged its complete removal to the free list. No other consumer of indigo joined in this request. The subcommittee rejected his plea.

The completed section of the Revenue Bill was then endorsed by the full committee and by the majority-party conference, and was adopted by the Senate. In the last hours of the session the section emerged from the joint conference of the majority-party conferees from both Senate and House with indigo and alizarin excluded from the special duty, and carrying along with them, as a sort of legislative by-product, medicinals and flavors. As no record is published of the proceedings of conference committees we are left to assumptions as to the influence which prevailed to give the section its final form; but in the light of the history of the legislation and the personnel of the conferees, as published in the Congressional Record, it is not difficult to imagine whose influence was determinative in maintaining the discriminatory feature of the original House legislation, against which united protest has been made, save for the voice of one consumer. The section in this disastrous form was then adopted by both Senate and House and is now the law of the land.

Such is the answer of the present Congress to the nation-wide (with one exception) call for adequate protective duties for the encouragement and upbuilding of this much-needed industry. The claims of this industry, upon non-partisan legislative aid, are reasonable, because of initial difficulties in manufacture and the character of the competition to be met after the war. These claims are also commanding, through the intimate connection of the industry with adequate munitions for our army and navy. Nevertheless, the measure, professedly enacted for its upbuilding, stands to-day stamped with the evidence either of the most specialized form of legislation for special interests, or of stupidity, as a tax placed upon the consumer without the benefit of an assured home industry, or of stubbornness in maintaining a wrong position rather than admit an error in judgment. I do not believe the citizens of this nation will set the seal of their approval upon such legislation.

#### RELATIONS TO NATIONAL THOUGHT

In the light of the activities of the past year let us ask ourselves frankly, "What is the position of chemistry to-day in the thought of the nation?" No one can doubt that it occupies a much more prominent place. This is due in part to the superb response American chemists have given to the sudden call upon their resources and ingenuity, in part to the advertisement through the press of the important rôle of the German chemist in the industrial upbuilding of that nation, and to the constant repetition of the phrase that modern war is largely a matter of chemistry and engineering.

Concrete evidence of increased appreciation of chemistry is furnished by the Second National Exposition of Chemical Industries now in progress. Its exhibitors are more than double those of last year; its exhibits show many new products, born of the exigencies of the year; its underlying thought has been broadened to include a more systematic showing of the importance of chemistry to the wise use of natural resources; and its purposes have gained a far wider and more appreciative understanding by our people as a whole.

Again we find evidence in the recent issuance of a special chemistry edition by a prominent trade journal, *The Manufacturers' Record*. The purpose of that unusual issue was not merely to emphasize the advantages of a great section of the country for the upbuilding of chemical industries, but, of far greater importance, it sought to vitalize the thought of the people of that section as to the fundamental character of chemistry among the factors of industrial development.

Furthermore, it must be noticeable to all that slowly but surely an educational campaign is getting under way in the daily press and in periodical literature which will eventually result in the arousal of our people to a full comprehension of the value of chemistry as a national asset.

These are simply signs of the times. We cannot, however, feel that the national thought has as yet grasped in its entirety the all-pervading influence of chemistry so long as Cornell University, with its strong chemistry staff, must delay the replacement of its burned laboratory through lack of funds; so long as Johns Hopkins University, the cradle of American chemical research, must undergo such struggle for the means to erect a new laboratory on the beautiful new site of that institution; so long as members of Congress view chemists and chemical manufacturers as fit subjects for hard bargaining; so long as railway presidents feel that chemistry has no part in the development of the natural resources of the sections traversed by their lines; and so long as waste in any form is allowed to continue unheeded.

Further expansion of the relations of chemistry to the national thought involves:

*First*—Continued educational effort through the press. Plans for such are being evolved, and these plans are meeting the quickened sympathy of the leaders of the press. Each of us must cooperate in this work. As a class we are not qualified to write in popular style, and in the past we have not troubled ourselves very much about such matters; but we can furnish facts and sound opinions to those who have the work and responsibility of popular presentation, and we should stand ready, each in his own community, to share in such cooperative effort.

*Second*—An awakening of the financial interests of the country to the fact that the ways of chemistry are not mysterious but applied common sense which constitutes a sure guide.

*Third*—Continued worthiness of our own efforts. This is our direct responsibility. Thoroughness of training, untiring zeal in work, aggressive conservatism in counsel, courage in new undertakings, independence in thought, generous cooperation, constant search for truth—these must surely lead us to that vantage ground where we can best serve this our country.

CHAPEL HILL, NORTH CAROLINA

## ORIGINAL PAPERS

### A STUDY OF THE EFFECT OF STORAGE ON MIXED PAINTS<sup>1</sup>

By E. E. WARE AND R. E. CHRISTMAN<sup>2</sup>

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The manufacture of ready mixed paints is a development of comparatively recent years. Pigments ground in oil to be mixed and tinted by the individual painter were much more commonly used than ready mixed paints twenty-five years ago, while it was not at all uncommon practice for the practical painter to mix the dry pigments with oil. It may be possible, if proper precautions be used, and enough time be given, to prepare a satisfactory paint in this way, but extensive investigation has shown that it is much better to grind at least part of the oil with the pigment. The painter to-day has neither the necessary skill nor the unlimited patience required for mixing the dry pigments with the oil, even if it were possible to compound in this manner as satisfactory a product as the paint manufacturer with his years of experience and his intimate knowledge of materials is able to produce by intensive grinding and an intelligent proportioning of the different ingredients.

One of the earliest difficulties encountered in the manufacture and use of ready mixed paints was the tendency of the heavy pigments to settle away from the vehicle if the paint were permitted to stand any time before use. It was soon discovered, however, that the addition of small amount of water containing a suitable emulsifying agent helped to prevent this settling of the pigment. But while eliminating one source of difficulty, the practice has brought on other troubles, a satisfactory remedy for which has never as yet been advanced.

Some emulsified mixed paints, if left to stand for several years, will show evidence of a deterioration which manifests itself in one of two ways, either through the formation of an amorphous soapy blanket between the settled pigment and the supernatant vehicle, or by the gelatination of the entire paint to a mass of about the consistency of soft putty, the vehicle seemingly having entirely disappeared. The first case is usually spoken of as "skinning" and the second as "puttying."

These phenomena have given the paint manufacturer much trouble, and consequently have been the incentive for considerable experimental work in an effort to compound a paint formula that will show them to a minimum extent. While it has been quite generally acknowledged that neither trouble will occur in the absence of water, it has been felt that water exerted only a secondary influence, the principal cause of deterioration lying in some action between the pigment and the oil of the vehicle. Most of the published data has been compiled as a result of investigation along this line.

<sup>1</sup> Presented at the 8th Annual Meeting, American Institute of Chemical Engineers, Baltimore, January 12-15, 1916.

<sup>2</sup> Holder of the Acme White Lead and Color Works Fellowship in Chemical Engineering at the University of Michigan, 1915-1916.

In 1911 Gardner,<sup>1</sup> in studying the possible effect of pigments upon the paint vehicle, ground the more common ones, both the active and the inert, in raw linseed oil and compared the ash content of the oil before grinding and after it had remained in contact with the pigments for a month. The oils from the mixes containing white lead, zinc oxide and red lead showed an appreciable increase in this ash value, and Gardner advanced the opinion that these pigments have the power of saponifying the oil with the formation of their respective soaps. He stated that the inert pigments have little action by themselves and when mixed with active pigments tend to retard the action of the latter. A few months later Sabin<sup>2</sup> published a reply in which he questioned both of these theories.

In a later publication Gardner<sup>3</sup> described the effects of pigments upon linseed oil after a storage of two years. Various pigments were ground in a good raw oil without drier or thinner, using a sufficient amount of oil to bring the mixture to the desired consistency. The most marked effect on the oil was the change in its iodine number, which was lower in all cases after storage. The oil of the red lead mix showed a final iodine number of 135.4, while in the other cases the value had dropped to approximately 160 from an original value of 181. The acid content of the oil was affected to the greatest extent in the paints containing white lead, red lead, and basic chromate of lead, but to a considerable extent also by both carbon black and graphite. He concluded that the perfect condition of these experimental mixtures warrants the manufacturer in assuming that any properly prepared combination pigment paint may be safely stored in cans for long periods without bad effects, provided that the oil used be of normal grade. He also concluded that the action of the free acids upon the pigments was the real cause of the hardening.

The results of work by Boughton<sup>4</sup> along similar lines are somewhat at variance with those of Gardner in that they show a change in iodine value of not more than ten points in any case, while the only sample in which there was any marked change in the ash content of the oil is the one containing corroded white lead.

In a more recent publication Gardner states<sup>5</sup> that the oil in paint is hydrolyzed by a fat splitting enzyme, lipase, liberated in seeds of the oil-producing type. He claims that the seed is not always steamed before expression to a temperature that will kill all of the microorganisms, and spores which pass into the oil soon develop the enzyme. He further states that the fatty acids formed are partially neutralized by the basic pigments whereby lumps of an insoluble

<sup>1</sup> THIS JOURNAL, **3** (1911), 628.

<sup>2</sup> *Ibid.*, **3** (1911), 790.

<sup>3</sup> *J. Frank. Inst.*, **174** (1912), 415-423.

<sup>4</sup> THIS JOURNAL, **5** (1913), 282.

<sup>5</sup> *J. Frank. Inst.*, **177** (1914), 533.



fatty acid soap are formed. He recommends heating cloudy oil to at least 100° C. before shipping, in order to kill all microorganisms.

#### EXPERIMENTAL

In considering this important problem the authors felt that it might be possible to get a clearer idea of the underlying causes of these deteriorating influences if paint specimens in which the action was pronounced could be procured, and the different products contained therein isolated and examined. Accordingly an effort was made to collect a number of samples of standard commercial paints which had been in storage for considerable time. Those actually used in this investigation had been on the shelves for from 2 to 8 years.

The blanket effect of "skinning," which was very pronounced in some of the samples, was studied first. The paints in which this had occurred were all composite-base paints which had originally contained a small amount of water, while one also contained a considerable proportion of gloss oil.

The oil extracted from the pigment and with the thinner completely distilled off showed an average iodine number of 181 and an acid value of 15. The ash content was low, running about 1.5 per cent and consisting mainly of lead oxide, with some manganese and zinc. The recovered oil was clear and of good color.

Samples of the skin were repeatedly washed with petroleum ether until all adhering oil and pigment were removed. The composition of this skin was variable, the weight of the oxides ranging from 13 to 16 per cent, the average of a number of samples being about 14 per cent. The proportions of the different oxides varied within narrow limits; but a typical analysis, corresponding to 14 per cent oxides, showed:

PbO..... 12.0    ZnO..... 87.0    R<sub>2</sub>O..... 1.0

The zinc oxide was similarly predominant in all samples analyzed, indicating that it was the active agent in the formation of the skin.

The free acids were liberated from the skin by heating with a dilute solution of mineral acid without access of air, the fatty acids dissolved in ether and the ether solution evaporated under vacuum.

In the first experiments hydrochloric acid was used as the liberating agent, which procedure gave free fatty acids exhibiting the following constants:

Neutralization Value	Saponification Value	Iodine Value
166 to 167	203 to 205	170 to 178

Such abnormal differences between the neutralization and saponification values clearly show, according to Browne,<sup>1</sup> the presence of an unsaturated lactone. The amount of this lactone was estimated according to the method of Lewkowitsch<sup>2</sup> and found to be 20 per cent of the total acid. As the purified lactone was liquid it seemed hardly probable that it was formed as a product of reaction during storage of the paint, for in that case it would have remained in solution in the oil rather than have been precipitated in the skin. It was no doubt formed during our manipula-

tion when the fatty acid was freed from the zinc soap, the action being accelerated by the presence of the resulting zinc chloride which acted as a condensing agent. Zhukov and Shellakov<sup>1</sup> studied a similar reaction and came to the conclusion that zinc chloride has the power of throwing the double linking along the carbon chain until it reaches the gamma position, where it is converted into the lactone. Concentrated sulfuric acid exerts a similar influence, although the dilute acid has no action.

The acids of the skin when liberated by dilute sulfuric acid proved to be more nearly the usual linseed oil acids, as indicated by the following constants:

Neutralization Value	Saponification Value	Iodine Value
193.5	203.0	181.0

This remaining difference between the neutralization and saponification values showed that the free acids still contained some lactone, probably due to the condensation of a small amount of gamma hydroxy acid which may have been present, and which, on liberation, changed immediately to the lactone.

The Gusserow-Varrentrapp or lead-salt-ether method for the separation of solid and liquid fatty acids showed a solid acid content in the skin of 10-12 per cent, a figure not inconsistent with that of 7.5 per cent ordinarily given for raw linseed oil.

Samples of the skin were dissolved in hot alcohol-ether solution, and gave upon titration an apparent neutralization value as high as 168. This at first suggested the possibility that the skin was a product of the coagulation of a colloidal suspension of pigment and fatty acid, but experiments to establish this failed to yield definite results and were abandoned.

On extracting the skin with hot absolute alcohol the entire mass was dissolved. On cooling, a white flocculent material composed of metallic soaps and hydroxides was precipitated, while the residue in the filtered solution, upon evaporation of the alcohol, was recovered as free acids. An extraction with ether failed to show the presence of these free fatty acids and it was decided that during the extraction with alcohol the soaps had been hydrolyzed. This same condition undoubtedly existed when the skin was titrated with dilute KOH in determining its acid value, which would account for the high value obtained. Weaker hydroxides, Ba(OH)<sub>2</sub> and NH<sub>4</sub>OH, acted similarly, as did an absolute alcohol solution of KOH. To check these observations, a pure zinc soap of linseed oil was prepared. This soap exhibited the same tendency to hydrolyze, giving an apparent acid value indicating complete hydrolysis as figured from the formula of zinc linoleate.<sup>2</sup>

Since in the skin or blanket of a mixed paint the metallic soaps present are mostly all those of zinc, which are completely hydrolyzed in analysis, the determination of the acid number of this material does very little toward establishing its constitution.

However, it seems reasonable to assume that the skin consists almost entirely of the neutral metallic soaps of zinc and lead, for any free acid present should be perfectly soluble in the oil which is in contact with

<sup>1</sup> THIS JOURNAL, 7 (1915), 30.

<sup>2</sup> "Chemical Technology of Oils, Fats and Waxes," 1, 423.

<sup>1</sup> J. Russ. Phys.-Chem. Soc., 40, 930-9.

<sup>2</sup> Ware and Christman, next issue of THIS JOURNAL.

the skin. Also if the total weights of the zinc and lead soaps be calculated from the oxides contained in the ash as given above, using 275.5 as the average molecular weight of the fatty acids, they are found to check up to the original weight of the sample taken for analysis.

As a further proof of the identity of the skin as a zinc soap of linseed oil a comparison was made of the melting points of the skin and of the zinc linoleate. The somewhat higher melting point of the former, 81, as compared with 76 for the linoleate, may be accounted for by the presence of the other metallic soaps.

It is not probable that these precipitated metallic soaps that go to make up the skin result from the saponification of the neutral glycerides by the pigments alone, although at different times writers have stated that white lead has this power of saponifying the oil to form a lead soap. Such reactions may occur at high temperatures, but it is doubtful if they proceed to any extent at ordinary temperatures. The results obtained by Gardner and Boughton do not necessarily signify that even the slight changes in the characteristics of the oil as obtained by them are due entirely to the pigment, since the action of any water present must be taken into consideration.

It is possible that the accelerator necessary to this metallic soap formation is lipase, as claimed by Gardner, but it is the opinion of the writers that, although the action of lipase may at times be considerable, it is of secondary importance in the reactions taking place in the ordinary mixed paint. The occasional presence of lipase, the fat-splitting enzyme, in linseed oil has long been established. Zymogen, in the flaxseed, under favorable conditions, is capable of forming the enzyme, and it is of real importance in expressing the oil that the seeds be heated to a high enough temperature to kill any microorganisms present, not only to prevent the formation of lipase in the oil, but also to insure its absence from the press cake. The enzyme has the ability to act upon the cyanogenetic glucoside, linamarin, present in the cake, and, with the aid of water, to convert it into prussic acid, making the cake entirely unfit for cattle food.

However, the authors do not consider that the presence of a fat-splitting enzyme in linseed oil is a frequent cause of trouble. Even when using cold-pressed oil trouble arising from the action of lipase would not be common, for, as shown by Tanaka,<sup>1</sup> the enzyme lipase is inactive in the presence of even dilute alkali, a material which is commonly present as a constituent of the commercial emulsifying agent. And if the action of the lipase be so pronounced it should show in the stored oils as well as in the paints made from these oils.

As a further evidence of the exceptional, rather than common, occurrence of this enzyme in linseed oil, cultures were made according to the method recommended by Gardner, using several different commercial oils and one sample of foots. In no case was any growth apparent after 72 hrs.

The authors believe that the really important hydro-

lyzing influence is the emulsifying agent. The sodium hydroxide present in the solution has the power of saponifying linseed oil at ordinary temperatures, while the sodium soap so formed, acting as an emulsifying agent, tends to keep the water and oil in contact, giving a better opportunity for further action.

The alkali soaps are at least partially hydrolyzed in water solution and, as the acid formed is soluble in the oil present, there may be a partial recovery of the alkali which furthers the reaction by forming more soap; and we might say that the governing factor in establishing the limit to which hydrolysis will proceed will be the amount of water present. That the same saponification takes place with other alkaline agents is evidenced by the following compilation of data:

Water	ADDITIONS TO OIL		Time Hrs.	Temp. °C.	Per cent Saponified
	Na <sub>2</sub> CO <sub>3</sub>	Others			
100 g.	3 g.	.....	2	70	1.5
100 g.	.....	.....	2	70	0.5
100 g.	3 g.	.....	18	70	10.0
100 g.	0	3 g. Casein	18	70	1.3
1 g.	0	3 g. ZnO	18	70	2.2
1 g.	0	3 g. White Lead	20	70	2.3
100 g.	3 g.	3 g. ZnO	20	70	5.3
100 g.	3 g.	.....	22	70	30.4
100 g.	3 g.	.....	22	70	0.8

These results show that the water itself has a small action upon the linseed oil. The carbonate has a marked effect, although the so-called active pigments are almost without effect. The differences in activity between the saponifying agents should be even more marked at ordinary temperatures than at the elevated temperatures employed in this experiment.

When ready mixed paints are stored, the first general reaction is this hydrolysis of the oil by the water, accelerated by the presence of the alkali and perhaps affected to some extent by the pigments. This hydrolysis is necessarily slow since the water and oil are immiscible, and before any large amount of acid is formed the pigment has settled, leaving the clear vehicle above. The acid coming in contact with the top of the settled pigment reacts with the basic materials present, of which zinc oxide is the most active, and forms the corresponding metallic soaps. Originally two molecules of water had hydrolyzed the oil and formed two molecules of the acid, and upon the reaction between these two molecules of acid and the metallic oxide, one molecule of water is liberated. In computing the amount of hydrolysis under such conditions it may be shown that with an amount of water such as is sometimes present in mixed paints it is theoretically possible to get complete hydrolysis of all of the oil. Although this is a condition that does not occur in the average paint the speculations are not greatly overdrawn, and the possibility of injury to mixed paint by the use of improper emulsifying agents is clearly shown.

The zinc soap formed on the neutralization of the acid by the zinc oxide of the pigment is almost completely insoluble in the cold vehicle and is at once precipitated on top of the partially settled pigment. The white lead also unites with the acid, with the formation of the more soluble lead soap, part of which is carried down by the zinc, and so helps to build up the peculiar skin over the pigment. The reactions

<sup>1</sup> J. Coll. Eng. Tokyo, 6, 1912.



between the acid and the pigments take place readily so that the oil never shows a pronounced free acid value. This value, previously cited as approximately 15, is corrected to 8 when allowance is made for the difference due to the dissolved soaps hydrolyzed during analysis.

Some of the water is probably carried along with the settling pigment resulting in a similar hydrolysis of the oil in the bottom of the can. The metallic soap formed in the midst of the pigment may be the cause of the non-caking of the pigment in stored mixed paints. The opportunities for reaction in the presence of the great excess of pigment are very good, and the tendency is in favor of the formation of the basic soap rather than the neutral soap as present in the skin. Upon extraction of the settled pigment with either the presence of the basic soap was inferred from the fact of its relatively slight solubility. The extracted oil was clear and of good color, with an apparent acid value of 16.8. Upon correction for the ash content of 1.16 figured to hydrolyzable metallic soap, the true acid value would be about 10. The pigment residue from the extraction still contained some fatty acid compounds, the freed fatty acids checking to 2.14 per cent. These were no doubt present as the basic soaps and would represent a weight of 2.76 per cent if figured as the basic zinc soap and 3.8 per cent if figured as the basic lead soap.

As a further evidence of the plausibility of the above analysis of conditions it is possible to synthesize the zinc oxide fatty acid blanket if a small amount of oxide be allowed to stand undisturbed in contact with oil containing a large amount of free linseed oil acids. If one gram of zinc oxide is placed in the bottom of a flask and covered with acid, within 24 hrs. the zinc oxide will swell out through conversion to the soap, giving the characteristic lumpy appearance of the "skin."

This zinc soap is quite insoluble in oil or naphtha, though soluble to an appreciable extent in turpentine. The insolubility of the soap may explain why the constants of the oil in the zinc oxide linseed oil storage tests conducted by Gardner and by Boughton showed no marked changes.

If a small amount of white lead be treated with excess acid in the same manner as succeeded in developing the linseed zinc oxide skin, we find that the action is much slower and several weeks' time is necessary before there are any definite indications of reaction. The lead soap formed is of a finer structure and does not show the same tendency toward coagulation or lumping.

#### PUTTIED PAINT

The similarities in the reactions giving a puttied paint to those just reviewed is quite apparent. Several cans of the worst cases of puttying were studied, in which the entire liquid portion had seemingly gone solid to a dense soapy mass. These paints were of a grade inferior to that of the paints exhibiting skinning, in that they contained more water as well as considerable rosin in the form of gloss oil.

The oil extracted from the paint and with the thinner distilled off was clear but slightly dark in color.

The analytical constants of the oil were as follows:

Apparent Acid Value	Saponification Value	Iodine Value	Ash
33.0	177.0	184.0	4.5

An analysis of the acids of the oil by the Twitchell volumetric method indicated the presence of 14 per cent of rosin acids. The ash consisted mainly of zinc oxide with some lead and lime. These oxides were present as a mixture of linoleate and resinate, a separation of which was not feasible. Assuming the same extent of hydrolysis in the determination of the acid number as had been proven in the cases of the soaps previously examined, the free acid content was shown to be negligible.

In these puttied paints the pigment had settled to some extent and it was found convenient to work with the upper layer, which was puttied vehicle containing a comparatively small amount of pigments. This was quite variable in composition, the percentage of free pigment increasing toward the bottom of the can. The amount of free pigment and of zinc soap being the important determinations, these were ascertained within sufficiently close limits by shaking the sample with cold ether, weighing the residue, liberating the acids in this residue and calculating the zinc linoleate from these acids. The zinc soap of the oil is almost entirely insoluble in cold ether while the resinate of zinc is quite soluble under the same conditions, and since the samples taken were in themselves quite variable the results were as reliable as could be expected. Near the top of the puttied vehicle the pigment constituted 10 to 15 per cent and the zinc soap 20 to 25 per cent of the total. Deeper in the layer the pigment content increased to 25 per cent while the zinc soap content decreased to 15 to 20 per cent. The relative amounts of oil, thinner and resinate of zinc were not determined. The pigments separated from these samples analyzed about 75 per cent zinc oxide.

If a small amount of zinc oxide be allowed to remain in contact with raw linseed oil containing rosin dissolved in petroleum thinner, in a very short time the oxide dissolves to a clear solution. The only apparent change in the solution is an increase in the viscosity. The same condition holds when free oil acids are substituted for the raw oil. There is no tendency toward the formation of the skin; in fact a sample of the skin previously formed dissolved completely in a naphtha solution of rosin upon standing over night.

The assumption is that the rosin acid displaces the oil acids from their zinc soaps with the formation of zinc resinate, which is somewhat soluble in naphtha and considerably soluble in turpentine, ether, and linseed oil.

The paints containing gloss oil seem to be the most susceptible to livering, which may be explained as follows: Although the rosin is usually limed there still remains considerable free rosin acid whose combination with basic pigments takes place in a short time. The resinates so formed are soluble in the vehicle but increase its viscosity to a point that delays the settling of the pigment. The hydrolysis of the oil

proceeds as in the case of the skin formation except that, as there is generally more water and more alkali present, the action is faster. The freed acid comes into immediate contact with the unsettled pigment forming the metallic soaps, particularly that of zinc.

The vehicle portion becomes constantly thicker until we have a condition approaching that of a colloidal gel formed from the finely divided zinc soap precipitating from the viscous solution of zinc resinate. This gel has occluded or adsorbed the remaining oil and what little thinner may have been present. Since, during the progress of the reactions, the acids and the pigments are in intimate contact, the opportunity for neutralization is much better than is the case with the skinned paints, which accounts for the low free acid content of the extracted oil. If the rosin of the gloss oil be highly limed or for any other reason the pigments should settle before the oil acids form to any extent, the action is apt to be one of "skinning" rather than "puttying."

An experimental mixture of oil, acids, rosin, pigments, and petroleum thinner, corresponding to the analysis of the puttied vehicle, resulted in a livered paint which, although not so hard as the samples investigated, was in every way comparable to them. Another sample, similar in composition to the mixture showing skinning, when continually shaken to prevent settling, livered in a very short time.

#### CONCLUSIONS

Although the use of emulsifying agents in paint grinding is quite generally recognized as necessary, their action in preventing the hard settling of the pigment has not as yet been satisfactorily explained.

Certain of the emulsifying agents hydrolyze the oil of the paint, the fatty acids subsequently forming insoluble zinc and lead soaps, which, if free to precipitate, form a skin on the surface of the settled pigment.

If, because of the presence of dissolved resins formed from added gloss oil, or for any like reason, the viscosity of the vehicle be increased to the point where the pigments and the metallic soaps formed from the hydrolyzed oil are not free to settle, there is formed a gel or "livered" vehicle.

These conditions may be remedied by the use of a protective colloid containing no water, such as aluminum palmitate or oleate, or by the use of an emulsifier containing water, but in which the active agent exerts no saponifying action on the linseed oil.

As the probable reason why emulsified oil paints do not settle hard is that there is present in the partly settled pigment a lead or zinc linoleate, it may be advantageous to grind paints in an oil of fairly high acid content, or to add the optimum amount of lead or zinc soap to the pigments ground in a neutral oil, as a means of inhibiting the dense settling of the pigment.

Experimental formulas compounded in an effort to establish the relative values of the various emulsifying agents, while they show promise of interesting and valuable results, have not as yet been under observation for a sufficiently long time to warrant definite conclusions being drawn from them.

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#### THE USE OF BARK FOR PAPER SPECIALTIES<sup>1</sup>

By OTTO KRESS<sup>2</sup>

In the manufacture of paper from wood pulp, if the bark is not carefully removed preliminary to the pulping of wood by either chemical or mechanical processes, it appears in the pulp and produces small specks in the finished paper, detracting from the appearance and value of the sheet. Some kraft mills do not clean their wood preparatory to pulping, depending on the alkaline digestion to destroy the bark. This practice is followed only to a very limited extent as the high consumption of chemicals in the pulping of bark and unevenness in shade and uniformity of the resulting pulp are decided drawbacks. The loss in barking will depend on the nature and condition of the wood, and on the method of barking of the wood, and will vary from 10 to 25 per cent, based on the weight of the rough wood. According to the census of 1911 of the Department of Commerce, there were consumed in the United States 4,328,052 cords of pulpwood, of which 280,534 cords were classified as slabwood and other mill waste. Practically all of this wood was cleaned and barked before pulping. The bark, as removed at the mill, is saturated with water and even with heavy pressing can be made only about 50 per cent dry, so that it is of comparatively little value as fuel. One mill that brought this matter to our attention loaded the daily waste from the drum barking of 100 cords of spruce wood into gondola cars, and disposed of it by filling in low places around the mill. They experienced difficulties from the odors of the decomposing bark, from fires which are apt to occur and which are hard to control, while the cost of removal was estimated at from \$15 to \$20 a day.

Large quantities of waste bark in the tanning industry are likewise awaiting successful utilization. Waste tan bark from the leaches is about 35 per cent dry, and has an estimated fuel value of \$0.60 in comparison with \$3.00 for bituminous coal.<sup>3</sup> The latest census figures from the Department of Commerce and Labor on tan bark production for 1909 showed a production in the United States of 698,365 tons of hemlock bark and 324,070 tons of oak bark, valued at \$9,968,710. The production since then, however, is reported to have diminished steadily, because of the increased use of chemical tanning agents, and accurate data as to the present amount is not available. Such minor uses for the waste bark as that in the white lead industry, runways for stables, etc., take but a very small amount of the bark, leaving the balance for fuel after the tannin extraction.

Other sources of waste bark in the United States are the lumbering of redwood, cedar, etc., where the bark is a decided detriment both in the lumbering operation and at the sawmill. The Forest Products Laboratory in attempting to utilize these wastes for pulp and paper purposes first attempted to reduce the bark by chemical pulping. A decided drawback is

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<sup>3</sup> *J. Am. Leather Chem. Assoc.*, **11**, 361.



the small yield and very heavy chemical consumption. As the various waste barks such as spruce, redwood, extracted hemlock bark, etc., all have different properties, it was next attempted to reduce them to a pulp condition by simple mechanical reduction in the beater and Jordan and after mixing with various longer fibred pulps, to run them over our experimental machine into various paper products. The apparatus used in these experiments at the laboratory was a 40-lb. beater, a small Jordan, and a 15-in. experimental Pusey and Jones Fourdrinier machine.

#### EXPERIMENTAL

A paper was made at the laboratory on the basis of 80 per cent extracted hemlock bark and 20 per cent kraft pulp which showed such remarkable impregnation towards tars, asphalt, etc., that it appeared advisable to make further tests on a mixture of hemlock bark and rag stock to try and cheapen the felts used for roofing and shingle stock. A coöperative study was undertaken with a company manufacturing roofing felts to work this out on a commercial scale. Samples made at the laboratory on a basis of 60 per cent rag stock and 40 per cent waste hemlock bark, showed a good strength and good saturation. A factory trial was then arranged for and roofing felt was made on a 114-in. trim cylinder machine. The beaters in this trial were loaded very heavily, using 9800 lbs. of 33 per cent dry bark in the ordinary 1200-lb. beater. The bark was beaten for one-half hour with the roll down to reduce the larger pieces, and then dropped into a separate chest from which it was pumped to a Jordan and dropped into the machine stuff chest. Felt ends were used for convenience instead of rags. They were opened up in the beater, dropped into a separate beater chest, brushed lightly in a separate Jordan, and then mixed with the ground bark in the machine stuff chest. The percentages of rag and bark were controlled by regulating the amount put through the separate rag and bark Jordan, the discharges from which were mixed in the machine stuff chest. The mill in which this trial was made ordinarily makes chip and box board, and to avoid unnecessary dirtying of the machine, only the two end vats of the possible five were used. Various runs estimated up to 80 per cent bark and 20 per cent felts were made, and no difficulty was experienced in passing the paper over the machine or in drying. Using two vats, only thin felts could be made of an average calipre of 40 to 45 points. The backwater, while reddish in color from the soluble coloring matter removed from the bark, was comparatively free from fiber. In this trial 6000 lbs. of finished felts were made, and the rolls were later impregnated and finished into roofing at two different plants.

Felt made on the basis of 80 per cent bark would of course be too weak to stand up under the weakening action of the hot asphalt and would break under the tension of pulling the felt through the saturating tank. Felt carrying this high percentage of bark was made at this trial in order to bring out to the maximum extent the difficulties that might be expected in the mill production.

A coöperative study was then undertaken by the laboratory with the saturating plant, a felt mill and a tannery to develop the practical use of tan bark in the manufacture of roofing felts. At the present time, the coöperators are using at certain mills having an average daily production of 50 tons of felt, approximately 60 tons of dry bark a week, which is shipped, 40 per cent dry, from the tannery. It is reported by the coöperators that roofing felt is being successfully made and offering no undue difficulties in the saturating plant on a furnish in which tan bark is used up to 20 to 30 per cent. The average price of rags for the manufacture of felts at the present time is \$40.00 a ton, and conversion loss is estimated to average 25 per cent. The value of waste bark for fuel as already stated is \$0.60 per wet ton, 35 per cent dry, in comparison with bituminous coal at \$3.00 per ton. To this must be added the cost of handling the bark into the cars, the profit to the tannery, the expense of plant facilities necessary in changing the tanner's fuel to coal and in rearranging side tracks and loading facilities, and the freight rate to the felt mill. If this freight rate is high, it would appear to be advisable to consider the cost of drying the spent bark from a 66 per cent moisture content to about a 15 per cent content, and thus avoid the freight on the water. Modern drying apparatus has made possible the cheap drying of raw materials to a remarkable degree. This drying might offer difficulties in obtaining the necessary minimum car weight, as the spent bark is bulky.

One of the difficulties still to be overcome which, however, we feel can be easily solved, is the controlling of the percentages of bark and rag stock run onto the felt machine. At first the bark, after passing through the bark Jordan, was mixed with the beaten rags in the beater rag stuff chest, then pumped through the rag Jordan to the machine chest. This offered considerable difficulty, as any variations in pumping, in the level of the stock in the chests, etc., caused a variation in the percentage of bark in the finished felt. In order to hold the percentage of bark constant the Jordaned bark may be pumped to a separate chest with overflows arranged at 10, 20, 30 per cent, etc. The bark can then be run by gravity to the various rag beaters or the right amount can be run directly into the rag stuff chest in proportion to the amount of rags dropped. Where this development work has been done, the felt is now made on a 72-in. felt machine with a 36-in. cylinder and 46 3-ft. dryers. It has been found by experience that no beater treatment for the bark is required. The bark at the present time is screened through a screen with about a  $\frac{3}{4}$ -in. mesh, and is thrown into the chest. From here it is pumped to the regulating box on the Jordan and the discharge from the Jordan run to the beater rag chest. The mixture of rags and bark after passing through the rag Jordan goes to the machine chest and then onto the machine. The object of the screening of the raw bark is to prevent the choking of the inlet pipe to the Jordan by the larger pieces of bark. The larger pieces which are screened out are thrown into the beater with the rags and reduced to a proper condition in this way. A valve placed on the dis-

charge pipe from the Jordan was found to be a convenient way to regulate the fineness of the stock, as it enables the operator to regulate the time of Jordaning. This direct Jordaning of the bark makes a decided power saving in the beating, for if a considerable replacement of rags is made by the bark, less beaters are required for the same felt output.

No difficulty is experienced in either forming or running the sheet. A little difficulty has been experienced in the proper drying of the felt, when a large percentage of bark is used. In order not to curtail the production by slowing down the machine it would appear advisable, if the mill is so arranged as to permit it, to add some extra driers or arrange for some special drying device. Due to the higher specific gravity of the bark, the finished felts are a trifle heavier, and allowance must be made for this in running the stock. The felt mills to-day are receiving a poor grade of rags, in fact only such rags as can hardly be used for any other purpose. With a more careful selection of the rags, we believe that it will be possible to raise the percentage of bark in the finished felt and still maintain the quality of the finished goods. Further, it is possible that the Jordan is not the best machine to reduce the tan bark to a proper condition; probably a special refining engine will reduce the bark without unduly cutting the fiber found in the bark. The limitation to the use of a higher percentage of bark does not appear to be in the paper mill, but in the lack of strength in the saturating tanks; this is partly due to the moral inertia and prejudice of the men handling the felt through the saturating tanks. A great deal could no doubt be done by using a better grade of rags that could be readily paid for by only a slight increase in the percentage of bark in the finished felt, as there is such a great difference in the cost of rags and bark.

Two other rather interesting and possible uses for waste hemlock and oak bark have been worked on at the laboratory. Two papers were made at the laboratory on the basis of 80 per cent extracted hemlock and 80 per cent extracted oak bark, the balance in each case being unbleached sulfite pulp. These papers were unsized and had a tendency to dust off fine particles of bark on rubbing, which we believe could be overcome by sizing. Two of the rolls were printed on a commercial 12-color wall paper printing machine, the paper taking the colors well. One of the disadvantages of a grade of paper of this type is that the high specific gravity of the bark makes the paper heavy. Hanging is ordinarily made on a furnish of 80 to 85 per cent ground wood, the balance of sulfite, and a decided saving would be made, if a wall paper made on a basis of 80 per cent bark could find application. The paper made with hemlock bark had a decided reddish color, while the oak bark paper was more of a chocolate shade. We have tried out in a preliminary way the color effect of cheap mordants, such as iron sulfate, etc., and find that there is a possibility of changing the shade with very little expense. The present price of this grade of paper was estimated by the wall paper printing concern at \$60 to \$80 a

ton. The papers printed better than the ordinary oatmeal wall paper with which it is compared, and if no undue difficulties are experienced in running it on large and fast commercial machines, it should be decidedly cheaper than the present hanging. This paper would undoubtedly have the disadvantage of increased weight and possibly the disadvantage of dusting off small particles of the bark.

Two rolls of unsized paper were made at the laboratory on the basis of 80 per cent extracted hemlock bark and 80 per cent extracted oak bark, the balance sulfite, and tried out on a commercial machine for making fiber conduits. The paper was run at the mill in competition with their ordinary grade of paper, and impregnated thoroughly; it made a satisfactory conduit which could be machined and which showed up well under the various tests applied. The paper in which bark was used was thinner than the regular grade, and further, was softer, and impregnated more readily, which might require a slight change in the blending of the saturant. A decided drawback lies in the fact that the increased weight of the bark makes the conduit decidedly heavier, thus increasing the freight rate on the finished conduit.

Trials were made at the laboratory on the possible utilization of spruce and balsam bark obtained in the drum barking of pulpwood. These barks differ from waste tan bark in being pitchy, which would exclude their use in any product which subsequently had to be impregnated. Further, any large percentage of spruce bark makes a brittle sheet. For certain purposes such as wall board, where the finished board is usually made by plying together the individual sheets by a binder such as sodium silicate, this tendency towards brittleness is of little consequence. A coöperative study was undertaken with a wall board mill but the work to date has not progressed beyond the laboratory stage. Boards made experimentally on the basis of 80 per cent waste bark, the balance sulfite and kraft, also boards on the basis of 50 per cent bark and 50 per cent ground-wood, were favorably commented on by the mill.

Spruce bark offers some difficulty in mechanical reduction and we believe that the beater will require extra sharp tackle, and a special filling in the Jordan would be a decided help. At the laboratory no difficulty was experienced in reducing spruce bark in 45 minutes in an experimental beater, while on a commercial beater, fitted with dull tackle, a 5-hr. treatment still left the bark in an unsatisfactory condition.

Patent specifications on the use of waste bark for pulp and paper purposes have been submitted to Washington by Mr. Howard F. Weiss, of this laboratory, and myself. If patents for the United States are granted, they will be dedicated to the public. Foreign patents have also been applied for.

#### SUGGESTIONS

There are a great many other possible uses of the various barks which at the present time have either a limited or no value. A fair insulating board has been prepared at the laboratory from the bark of the redwood tree. Other possible uses that suggest them-



selves are the use of spruce or balsam bark from the drum barking of pulpwood which is to be mixed with sulfite screenings and run into car liners. Further, waste hemlock and oak bark might be used in the manufacture of sheathing, carpet liners, bottle wrappers, deadening felts, chip board and box board. A small percentage might be used for board used in stand up boxes where no great bending qualities or high test are required. For indurated fiber ware, such as pails, etc., it might be possible to substitute a large percentage of ground tan bark for the more expensive stock used at present.

The above remarks can be looked upon as only indications of what might be done, as each mill will have to determine whether they can substitute bark in part for a more inexpensive stock, and still maintain the quality and standard of their product. Waste bark can be looked on only as a filler, and must be used with a longer fibered stock to carry it over the machine. Its use will permit a decided saving in many grades of paper products.

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#### THE PROBLEM OF CATALYZER POISONS WITH REFERENCE TO THE HYDROGENATION OF FATTY OILS

By CARLETON ELLIS AND A. A. WELLS

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One of the main difficulties in the hydrogenation, by the aid of nickel catalyzer, of many low-grade oils, such as some of the fish and whale oils, is that the life of the catalyzer is relatively very short. Usually the activity of the catalyzer becomes much slower after two or three batches of oil have been hardened and in some cases it is necessary to prepare fresh catalyzer for every batch of oil treated. On the other hand, when hardening a good grade of oil, such as refined, edible cottonseed oil, the life of a carefully prepared catalyzer is likely to be very long and in some cases an entirely new lot of catalyzer is not required for months in the constant operation of a hardening plant. In these cases the catalyzer is kept in a state of high activity for continued usage by adding a small amount of fresh catalyzer at intervals of one or two weeks.

The fact that in some cases a catalyzer does not last indefinitely and that its life is prolonged in proportion to the purity of the oil, indicates that there are present in some fatty oils certain substances which unfavorably affect the catalyzer, acting as a poison thereto, and sooner or later causing the catalytic agent to become inactive. It has been observed that some kinds or grades of oil may be hydrogenated to an incomplete degree but that they cannot be carried beyond this point, no matter how long the treatment is continued, without change of catalyzer. If to these semi-hardened oils a fresh quantity of catalyzer is added, the hardening will usually proceed practically to complete saturation. In some cases, a fresh quantity of oil may be treated with the seemingly spent catalyzer, when partial hardening will occur. An additional quantity of fresh catalyzer will sometimes carry the

oil so treated, to completion, showing that the substance which affects the catalyzer is apparently taken up by it under these circumstances, thus leaving the oil in condition to be readily hardened. Some oils which ordinarily cannot be hardened without a preliminary purifying treatment, may first be agitated with a spent catalyzer, the catalyzer removed and the oil then incorporated with a fresh quantity of catalyzer when hardening readily occurs.

#### EXPERIMENTAL

From time to time we have had submitted to this laboratory various samples of low-grade oils to be treated with hydrogen. In some cases obstacles were met with in handling these oils and the observations here reported are some of the typical ones which were performed in the attempt to obviate these difficulties.

**COD OIL**—Apparently this oil would have a very wide use, especially in the leather industry, if some cheap method of treatment could be rendered available so that the oil could be easily hydrogenated.

A sample of crude cod oil was freed from fatty acids with a solution of sodium carbonate and after washing free from alkali and soap was treated with hydrogen, using 5 per cent catalyzer prepared from nickel oxide. In most of the laboratory work connected with this investigation, a somewhat larger proportion of catalyzer was used than is customary in commercial operations. This enabled results of a comparative nature to be more quickly obtained. The oxide was reduced in the oil at 260° C. and then subjected to the action of hydrogen at 200° C. for 2 hrs. In several trials, the oil either did not harden at all, or only to a very minor degree. Other forms of catalyzer were equally ineffective.

The oil was then agitated for 1 hr. at 200° C. with freshly prepared copper hydrate, filtered to remove the copper compound and again treated with hydrogen and catalyzer under the same conditions as above. The oil was readily hardened by this treatment. Another sample of the oil, refined as above, was treated with 5 per cent freshly prepared silver oxide at 200° C. for 1 hr. The silver compound was removed by filtration and the clear oil hydrogenated. In a short time this oil was hardened to a melting point of 46° C. on hydrogenating under the same conditions as above.

A slight discoloration of the oil due to this treatment was observed, so another portion of the oil was refined, using caustic soda in place of the sodium carbonate. The color of the oil refined with the caustic soda was better than that obtained with the carbonate.

A sample of this refined cod oil was agitated for 1 hr. with 5 per cent Fuller's earth at 150–200° C., filtered and subjected to the hydrogenation process, employing 5 per cent of catalyzer prepared from nickel oxide. The oxide was suspended in the oil and treated with hydrogen at 260° C. until black in color. The temperature was then lowered to 210° C. and maintained at this temperature for 3 hrs. The oil did not harden. A sample of the refined cod oil was treated with a great excess of catalyzer (10 per cent) prepared by soaking Fuller's earth in nickel nitrate solution in

such proportions that the reduced material contained 20 per cent nickel. This material was dry-reduced in a current of hydrogen at 360° C. and immediately flooded with oil to avoid oxidation. The application of hydrogen was carried out at 200 to 210° C. for 2 hrs. but even with this excessive amount of catalyzer the oil was not hardened. A quantity of cod oil was treated with a commercial sample of copper oxide for 1 hr. at 160 to 170° C. and then hydrogenated with catalyzer prepared from nickel oxide. The catalyzer was reduced in the oil at 250° C. for 1/2 hour and hydrogenation was carried out at 200° C. for 3 hrs. The oil was slightly hardened.

A sample of cod oil (iodine No. 169) which we had attempted to hydrogenate with nickel catalyzer but which did not readily harden, was filtered from the catalyzer and again hydrogenated with a dry-reduced catalyzer on a carrier, using 1 1/2 per cent nickel. The oil hardened to a melting point of 40 to 42° C. The iodine number was 91. Continued hydrogenation for several hours raised the melting point to 44 to 45° C. and the iodine number dropped to 81. The catalyzer was unable to carry the hydrogenation further.

A series of tests were performed to determine the relative value of freshly precipitated copper hydrate as a detoxicating agent. In one test, portions of cod oil were agitated with 5 per cent of freshly prepared copper hydrate, commercial copper carbonate and lead oxide at 180 to 200° C. for 2 hrs. After filtering, these samples were treated with hydrogen using 5 per cent nickel oxide as a source of catalyzer. This was reduced in oil at 250° C. for 1/2 hr. The hydrogenation operation was carried out at 230° C. for 3 hrs. The oil treated with freshly precipitated copper hydrate hardened to a melting point of 53 to 54° C., the oil treated with copper carbonate hardened slightly, while the oil treated with lead oxide did not harden.

As the copper hydrate at times is not readily filtered from the oil after protracted agitation with the latter, the hydrate was precipitated on Fuller's earth in the proportion to give 20 per cent copper. Cod oil was agitated with 1 per cent of this material for 1 hr. at 110 to 120° C. The oil was then filtered and hydrogenated, using catalyzer prepared from nickel oxide. The catalyzer was reduced in the oil in the ordinary manner and hydrogenated at 200° C. for 2 1/2 hrs. From the results obtained the copper hydrate did not appear to be as active in this form.

To determine the most effective temperature for treating the oil with copper hydrate the following tests were performed: Cod oil was agitated with 1/2 per cent of copper hydrate for 1 hr. at room temperature, then was filtered and subjected to the hydrogenation process. Another portion of the oil was treated in a similar manner, except the temperature of treatment with copper hydrate was 50° C. Other portions were treated at 75° and at 110 to 120° C. The samples treated below 110° C. did not harden and metallic mirrors were formed on the walls of the

container during the treatment with hydrogen. The sample which was agitated at room temperature exhibited the most perfect mirror. The oil treated at 110 to 120° C. hardened readily without the formation of a mirror.

The effect of refining cod oil with alkali before hydrogenation, when the copper hydrate treatment is used, is beneficial to the catalyzer as was shown by agitating crude cod oil with copper hydrate at 140 to 150° C. for 1 hr., filtering and then subjecting it to the hydrogenation process, using nickel oxide. The catalyzer was formed in the oil at 250° C. and hydrogenation was carried out at 190 to 200° C. for 4 hrs. The oil was only slightly hardened.

A sample of refined cod oil was treated with Fuller's earth to improve the color. It was then treated with copper hydrate and hydrogenated in the usual manner. As a control a portion of the same oil was treated with copper hydrate and then hydrogenated, omitting the Fuller's earth treatment. The sample which was treated with Fuller's earth hardened slightly more rapidly than the sample which had been treated only with the copper hydrate.

A quantity of the oil under examination was burned in oxygen in a combustion bomb. The contents of the bomb were washed out and examined qualitatively. Sulfates and a trace of iodine compounds were found to be present but no test was obtained for either chlorides or phosphates. Either sulfur in the sulfide form, or iodine could have been responsible for the poisoning action on the catalyzer noted.

**MENHADEN OIL**—A sample of Southern crude fish (menhaden) oil, without refining, was subjected to the hydrogenation process, using nickel oxide reduced in the oil at 250° C. and the hydrogen treatment was carried out at 200° C. for 4 hrs. The oil was not hardened. Another portion of the same oil was agitated with copper hydrate at 135 to 150° C. for 1 hr. and treated under the same conditions as above. The oil was hardened, without difficulty, to a melting point of 45 to 46° C. Another quantity of the same crude fish oil was refined and then treated with copper hydrate. The treated oil was hydrogenated using a catalyzer which had previously been used in cod oil that had been detoxicated with copper hydrate. The oil hardened to a melting point of 52 to 53° C. The catalyzer was apparently not affected by its previous use in cod oil which had been treated with copper hydrate.

**HERRING OIL**—An oil which is available in quantity and which up to the present time has had a very limited field of utility is herring oil. In general, this oil requires more careful detoxicating treatment than cod or Southern fish oil to make it adaptable to the hardening process.

A sample of herring oil which could not be hardened by the usual methods was refined to free it from fatty acids and after treating with copper hydrate for 1 hr. at 110 to 120° C. was subjected to the action of hydrogen in the presence of a catalyzer prepared by reducing nickel oxide in the oil at 250° C. for 1 1/2 hr.



The oil was hydrogenated at 190 to 200° C. for 5 hrs. It hardened to a melting point of 45 to 46° C.

**POURISH OIL** A number of samples of this oil have been examined in this laboratory and have proved somewhat difficult to hydrogenate. In one case, a sample of the oil was agitated with copper hydrate for 1 hr. and then treated with hydrogen, using a catalyzer prepared by precipitating nickel hydrate on a carrier and reducing at 360° C. Hydrogenation was conducted for 5½ hrs. at 180 to 190° C. The oil did not harden. The catalyzer was filtered out and 5 per cent of a mixture of finely-divided nickel-copper hydrate was added. A current of hydrogen was passed

**EFFECT OF HALOGENS, HALOGEN COMPOUNDS, SULFUR, ETC., ON HYDROGENATION OF COTTONSEED OIL**

Catalyzer: Nickel Oxide (5 per cent of the weight of the oil) reduced in oil at 250° C. for ½ hr.

Expt. No.	Substance Added	Per cent Added	Temp. ° C.	Time Hrs.	Effect on Oil
1	Bromine	1.0	200	2	No hardening
1 (CH)		1.0	200	2	
2	Iodine	1.0	200	2	
2 (CH)		1.0	200	2	Oil hardened
3		0.5	200	2½	
3 (CH)		0.5	200	2½	
4	Antimony Bromide	1.0	200	2	Oil hardened
4 (CH)		1.0	200	2	
5	Sodium Chloride	5.0	210	2½	
6	Zinc Chloride	5.0	210	2½	Oil hardened
7		1.0	200	2½	
7 (CH)		1.0	200	2½	
8		0.5	200	2½	Slight hardening
9	Tin Chloride	1.0	200	2	
10 (CH)	Sulfur	0.5	200	2½	
11		0.5	200	2½	No hardening
11 (CH)		1.0	200	2½	
Blank		...	200	2½	
12	Sulfur	0.1	210	3½	Slight hardening
13 (CH)	Red Phosphorus	1.0	200	2	
14		1.0	200	2	
14 (CH)		0.5	200	2	No hardening
15	Sulfur Chloride	1.0	200	2	
15 (CH)		1.0	200	2	
16	(As <sub>2</sub> O <sub>3</sub> )	1.0	200	2	Slight hardening
17	Mercury	1.0	200	2	
Blank		...	200	2½	
18	Lead Stearate	1.0	200	2½	No hardening
19	Lead Oleate	1.0	200	2½	
19 (CH)		1.0	200	2½	

(CH) after an experiment number indicates treatment with copper hydrate before hydrogenation.

through the oil, the temperature of the oil being held at 250° C. for ½ hr., then lowered to 190 to 200° C. and maintained at that point for 3 hrs. The oil hardened to a melting point of 45° C.

Probably the most difficult to handle of all the low-grade oils is that derived from city garbage. There are two methods of reclaiming this grease, one by boiling the garbage with water and allowing the oil to rise to the top when it is drawn off, the other by extracting the oil with solvents. This oil is usually denatured with or contains tar, and as it is derived from all manner of materials which would vary from day to day it is quite probable that no fixed method of treatment can be employed. Up to the present time no entirely satisfactory method has been found to refine and successfully harden this material in a manner capable of general commercial application.

#### EXAMINATION OF COPPER HYDRATE

The copper hydrate which had been used to detoxicate the cod and other oils was examined to determine what bodies were taken up from the oils by the treatment. Fatty material was removed from the copper hydrate by extraction with solvents and the residue was analyzed. Sulfates were found but no evidence

of the presence of phosphates or chlorides was obtained. A blank test on the original copper hydrate showed no sulfates or sulfur present, indicating that sulfur compounds are removed from fatty oils containing them, by treatment with copper hydrate in the manner stated.

#### OTHER CATALYZER POISONS

As various bodies other than those mentioned above are known to poison hydrogenating catalysts, and as the treatment with copper hydrate has been found to remove certain of these poisons or render them non-toxic to nickel catalyzer, the accompanying table has been compiled from an extensive series of tests with such bodies and in some cases the effect of copper hydrate thereon is indicated.

NEW JERSEY TESTING LABORATORIES, MONTCLAIR

#### EXPERIMENTAL NOTES ON THE PREPARATION OF FIRE-PROOF WRITING PAPER

By ROLLIN G. MYERS

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The writer made a careful study of the methods for the preparation of fire-proof writing paper, as well as of the character of the paper obtained by such processes. He extended this work to include the paper produced from crysotile fiber when this was combined, as pulp, with white or lightly tinted precipitated compounds of the metals. These pulps were prepared at about 100° C.

The method used in the preparation of the paper was identical, in many respects, to that employed by the Japanese in the preparation of their hand-made paper from the vegetable and animal fibers. Each sample prepared was tested for porosity, tensile strength and permanence to temperatures varying from 900–1000° C. during a period of about 10 hours: 80 or 90 samples of paper were prepared.

The following inferences appear to be truthful interpretations of the experimental studies:

1—The commercial varieties of crysotile fiber used as raw material in the preparation of the paper were not to be distinguished in respect to mutability at high temperature, porosity, tensile strength and flexibility.

2—Within certain limits, variations in the quantity of the chemical reagents used for a given weight of fiber produced no observable gain in tensile strength and the reduction of porosity in the paper prepared.

3—Tensile strength and closeness of texture of the paper prepared appears to be obtained best from pulps containing precipitated hydroxides, arsenites, silicates and tungstates. Perhaps the best paper prepared, in respect to the properties referred to, was that obtained from a pulp containing a considerable excess of magnesium arsenite in an alkaline mixture. This paper was far in advance of any of the commercial papers examined.

It might be well to note that most of the above

precipitates are flocculent in character, and that increase in closeness of texture and tensile strength is not always concurrent.

4—Substances like kaolin or pulverized mica, when incorporated with the pulps, do not seem to add anything to the paper produced.

5—In all the pulps, there exists a certain amount of adhesion between the fiber and the precipitated substance. This attraction is greatest for the precipitated salts of the more basic metals like calcium and magnesium, and least for the more acid metals like silver or lead. This adhesive effect may be due to some chemical action between the fiber and the precipitate.

6—The degree of porosity of all samples increased rapidly when they were heated for any length of time above 100° C., the cause of the increase of porosity being undoubtedly the contraction in bulk of the precipitated substance in the paper.

7—Tensile strength, and smoothness of surface only, seem to be enhanced by pressing with a warm iron.

8—From the identity of crysotile to "true asbestos" and the general character of the foreign substances used, the indications are pretty clear that no foreign substance either acting by itself or with others can increase the chemical stability of asbestos towards fire.

9—Under the experimental conditions set for the heat or "fire test," i. e., a temperature varying from 900–1000° C. with a time interval of 10 hours, it seems probable that no paper composed of incombustible substances containing molecular water is fire-proof or can be made fire-proof. This inference can be extended to "true asbestos" on account of its general similarity in properties and composition to crysotile.

It is true, however, that several samples of paper prepared by the writer, were not seriously impaired when exposed to a dull red heat for an hour or so. These samples still possessed considerable flexibility and could be handled, if a certain degree of care was used. There are some varieties of "true asbestos" which cling to their zeolitic(?) water with a great deal more persistence than crysotile. Paper made from asbestos of this sort would of course be quite well adapted for the preparation of, e. g., fire-proof records. In general then, when lower temperatures and shorter time limits are considered, it is very probable that an entirely satisfactory fire proof paper can be prepared.

10—In respect to fire-proof inks, solutions of ferric, chromic and cobaltous nitrates and chlorides were used. They stood the "fire test" well. According to Franz Cirkel in the Canadian Government bulletin "Asbestos—Its Exploitation and Uses" no inks up to that time prepared would stand a red heat—excepting perhaps those produced from platinum. For inks other than those prepared from platinum, one condition seems to be necessary, that the acid oxides in the paper should be kept in excess.

## A HIGHLY UNSATURATED HYDROCARBON IN SHARK LIVER OIL

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Although usually small in their quantities, hydrocarbons seem to occur in fatty oils more frequently than hitherto considered. Some of them may possibly be utilized for the identification of individual fats and oils.

P. Matthes and O. Rohdeck<sup>1</sup> isolated a hydrocarbon of the composition  $C_{30}H_{48}$  from cacao butter. It was considered most likely identical with amyrlene. The former chemist, together with H. Sander,<sup>2</sup> obtained a hydrocarbon from laurel oil and named it laurane. It had the composition  $C_{20}H_{32}$  and formed a fine needle crystal of m. p. 69° C. from its alcoholic solution. According to another investigation of Matthes and W. Heintz,<sup>3</sup> a hydrocarbon of the composition  $C_{20}H_{32}$  (m. p. 69° C.) occurs in parsley seed oil and was named by them petrosilene. A hydrocarbon,  $C_{31}H_{50}$  (m. p. 67–68° C.), is stated to occur in kôsam seed oil (Power and Lees).

In the domain of animal oils, especially in insect oils, hydrocarbons occur in considerable amounts and are characteristic of them. So, from chrysalis oil, Menozzi and Moreschi<sup>4</sup> isolated two hydrocarbons: one of them had the composition  $C_{28}H_{46}$ , melted at 62.5° C. and was optically active, while the other melted at 41–42° C. Further, hydrocarbons were obtained from cantharide and Melolontha oils.<sup>5</sup>

The study of substances, beside sterols, in the unsaponifiable matter of oils and fats, so-called "stearyl-free unsaponifiable matter," has lately much attracted the interest of the oil chemist. These substances consist mainly of hydrocarbons, alcohols and ketones. Thanks to the classical researches of Windaus, an effectual means for the separation of sterols from these substances was introduced into fat analysis by the use of digitonin.

The reports of J. Marcusson and G. Meyerheim,<sup>6</sup> as well as P. Berg and J. Angerhausen,<sup>7</sup> have satisfactorily confirmed the importance of the investigation of a stearyl-free unsaponifiable matter. The latter chemists have devised, on the ground of the examination of this matter, a differentiation method of mowrah and shea butters, the distinction of which is not feasible by ordinary fat analysis.

Of marine animal oils, shark liver oil contains, as is well known, a high percentage of unsaponifiable matter, and appears to furnish a very suitable material for the above-mentioned investigation. In the literature of fats, however, we find but meagre descriptions of the oil; some statements even appear to be conflicting at a glance.

<sup>1</sup> Ber., 1908, 41.

<sup>2</sup> Arch. d. Pharm., 1908, 165.

<sup>3</sup> Ber., 1909, 325.

<sup>4</sup> Rend. accad. dei Lincei, 1908, 95.

<sup>5</sup> Mosquito fat is likely to contain hydrocarbon (W. Normann, Chem. Rev., 1913, 187).

<sup>6</sup> Z. angew. Chem., 1914, 201.

<sup>7</sup> Z. Nahr. Genussm., 1914, Bd. 27, 723; Bd. 28, 73, 145.



C. Schaedler<sup>1</sup> and also L. E. Andes<sup>2</sup> described the sp. gr. of shark liver oils to be 0.870–0.875 (highest 0.880) at 15° C., and took oils of higher sp. gr. to be adulterated. G. Hefer,<sup>3</sup> on the other hand, rejected the above statement as incorrect, and assigned the values 0.910–0.916 at 15° C. Both statements are correct, however, as, according to the author's experience, shark liver oils of sp. gr. 0.8644 to 0.9323 at 15° C. were met with, the value varying according to the difference of the genus and species of sharks. The great variation on the other characteristics of the oil recorded in the literature may easily be understood as well.<sup>4</sup> Of the nature of the fatty acids of shark liver oil, no description is found even in the standard works on oils and fats, such as "Lewkowitsch" and "Benedikt-Ulzer."

The unsaponifiable matter of shark liver oil is usually stated to consist of cholesterol. Though cholesterol is invariably found in the oil, this statement is not valid, since substances besides cholesterol, notably hydrocarbons, are found in very large quantities in some shark liver oils.

It should be mentioned that the occurrence of hydrocarbons in shark liver oil has not yet been recognized by the authorities: but in Allen's "Commercial Organic Analysis," Vol. II, Part I (1899), p. 201, the following interesting note is found: The author examined four samples of presumably adulterated shark liver oil (sp. gr. 0.8661–0.8746 at 15.5° C.) and obtained 69.9–83.5 per cent of the ether-extraction residue (unsaponifiable matter). The residue was found to be a bright yellow color like the original oil. It was free from nitrogen and nearly free from oxygen, and gave when heated an unmistakable odor of pine resin. Allen took it, apparently erroneously, to be a mixture of light rosin oil with shale or petroleum lubricating oil, which have been added to the oil as an adulterant. In my opinion, the substances must have hydrocarbons, normally present.

The first report on the occurrence of hydrocarbons in shark liver oil is, so far as I know, the one published by the author some ten years ago.<sup>5</sup> The sample of shark liver oil used for examination was so-called "Kuroko-zamé" oil,<sup>6</sup> obtained from the liver of a shark caught in the Sagami Sea. The oil had the sp. gr. 0.8806 at 15.5° C.; saponification value 66.85, iodine value (Wijs) 281.47, and contained 56.13 per cent of unsaponifiable matter. The unsaponifiable matter was a light yellow oil of iodine value 381, which on brominating in an ethereal solution yielded a white precipitate of bromine addition compound. By elementary analysis, the latter substance was found to consist of 26.93 per cent C, 3.94 per cent H and 69.28 per cent Br, corresponding approximately to an em-

pirical formula,  $C_{10}H_{18}Br_4$ . From this result the author inferred the existence of a highly unsaturated hydrocarbon of the composition  $C_{10}H_{18}$  or  $(C_5H_9)_2$ .

Lately, while engaging in the examination of marine animal oils, the author has often met with shark liver oils of high content of unsaponifiable matter. Hence the previous work was again taken up and has shown that hydrocarbons are important and characteristic constituents of some shark liver oils.

In the present preliminary report, the author describes two remarkable Japanese shark liver oils ("Ai-zamé" and "Heratsuno-zamé") whose contents of unsaponifiable matter amount to about 70–90 per cent. By the present investigation, the unsaponifiable matter of the oils has been confirmed to consist chiefly of hydrocarbons. The oils are therefore not fatty oils, but hydrocarbon oil, in which a comparatively small quantity of glycerides is present.

#### EXPERIMENTAL

##### SAMPLES OF SHARK LIVER OIL USED FOR EXAMINATION

Shark liver oil (Japanese: "Samé-abura") is obtained from the liver of sharks, fish belonging to *Selachoides*. There are a great number of species of shark, but those which are caught for oil-yielding purposes are comparatively limited. The more common oil-sharks of Japan are as follows: Cat shark, Dog shark, Porbeagle, Basking shark, the Squaloid



AI-ZAMÉ (*Squalus mitsukurii*, JORDAN AND SNYDER)  
Scale about  $\frac{1}{10}$

sharks (the most important shark belonging to this class is "Ai-zamé," *Squalus mitsukurii*) and the so-called "Black sharks" (*Genii Zameus*, *Lepidorhinus*, etc.).

As a result of the author's experiments, it has been observed that more or less hydrocarbons occur in shark liver oils of specific gravity lighter than 0.900 at 15° C., the content increasing as the specific gravity becomes lighter. Ai-zamé and Heratsuno-zamé oils are the lightest shark liver oils examined; hence, they contain the highest proportions of hydrocarbons.

AI-ZAMÉ OIL is obtained from the liver of "Ai-zamé," *Squalus mitsukurii* (*Squalidae*), Jordan and Snyder, one of the common squaloid sharks of Japan. The liver of this shark is very rich in oil; hence, the fish is often called simply "Abura-zamé" (Abura = oil, Zamé = shark). There are two or more varieties of *Squalus mitsukurii*. "Ai-zamé" is the name given to a variety which lives in the sea near Tokyo, notably in the Sagami and Suruga Seas. The following samples of the oil were procured:

(1) This oil was prepared in the laboratory (May 7, 1915), from the fresh liver of an "Ai-zamé," caught

<sup>1</sup> The meaning of "Ai" in Japanese is not exactly known. The shark is known as "Tokyo dogfish."

<sup>1</sup> "Technologie der Fette und Oele," 1883.

<sup>2</sup> "Animal Fats and Oils," 1904.

<sup>3</sup> "Technologie der Fette und Oele," Bd. II (1908).

<sup>4</sup> The variation may even be caused by the age and habit of fish, and also by local conditions. Cp. O. Polimanti, *Biochem. Z.*, 1915, 145.

<sup>5</sup> Kōgyō Kwagaku Zasshi, *J. Chem. Ind., Tokyo*, 1906, 953. The report was published in Japanese only.

<sup>6</sup> "Kuroko-zamé" is probably a kind of "Kuro-zamé" (Black shark) of the genus *Zameus* and *Lepidorhinus*. But neither the exact genus nor species is known. (Japanese: "Samé" or "Zamé" = Shark.)

in the Suruga Sea.<sup>1</sup> The fish (male) was 92 cm. in length (measured from tip of snout to root of upper lobe of caudal) and weighed 8.5 kg. The color of the body of the fish was pinkish gray, becoming lighter on the underside. The snout was pointed, the spiracles large, the spines in the two dorsals rather small. The grayish white-colored liver was found to occupy the greater part of the internal cavity, the weight reaching 2120 g., *i. e.*, about 25 per cent of the total body weight. The oil was prepared by carefully heating the chopped material in a porcelain basin on a sand bath, until the moisture had been nearly expelled. The yield of the oil was about 1615 g. The oil is a pale orange-yellow liquid of a peculiar, not unpleasant odor. When spread on the skin, a fishy smell was noticed in a little while. When stirred with a drop of concentrated sulfuric acid, a fine red-dish violet coloration was developed.

(2) This oil was a commercial oil, procured from a fish oil factory at Yui-chō, Suruga (Shizuoka Prefecture). It was a pale orange-yellow oil of properties very similar to Sample 1. The coloration with concentrated sulfuric acid was yellowish brown.

The following values were determined with the above two samples:

AI-ZAMÉ OIL	(1)	(2)
Sp. gr. (15° C./4° C.).....	0.8644	0.8662
Solidifying pt. ....	Below -20° C.	Below -20° C.
Acid value.....	0.00	0.13
Saponification value.....	22.98	28.15
Iodine value (Wijs) (a).....	344.63	330.35
Iodine value (Hübl) (a).....	352.00	333.45
Refractive index (20° C.).....	1.4930	1.4925
Fatty acids.....	10.62%	.....
Neutralization value.....	168.52	.....
Iodine value (Wijs).....	119.25	.....
Glycerol.....	0.52%	.....
Unsaponifiable matter.....	90.17%	87.32%

(a) The time of standing was 2 and 24 hrs. with Wijs's and Hübl's solutions, respectively.

The mixed fatty acids gave, in ether solution, 16.55 per cent of polybromides, which turned black without melting at above 200° C. Glycerol was determined by the bichromate method; it was also qualitatively isolated by the acetone extraction method (Schukoff and Schestakoff). Since its percentage is a little less than the half of that calculated from the saponification value, a small quantity of some esteric compounds besides glycerides is doubtless present in the oil.

HERATSUNO-ZAMÉ OIL—"Heratsuno-zamé,"<sup>2</sup> *Deania eglantina* (Jordan and Snyder), is another squaloid shark which contains a large quantity of liver oil. The sample of the oil used for experiment was obtained from a "Heratsuno-zamé" caught also in the Suruga Sea. The fish (male) had a gray skin and a peculiar flattened head. The spine in the second dorsal was large and curved backward. It had a body length of 71.2 cm. and weighed 1.88 kg. The liver was of a grayish pink color and weighed 407 g. The oil was prepared in the same way as Ai-zamé oil. The yield was 338 g. (Nov. 20, 1915). The oil was a light yellow liquid. Its odor resembled that of Ai-zamé oil. Stirred with a drop of concentrated

sulfuric acid, a violet-red coloration was developed. It had the following properties:

Sp. gr. (15° C./4° C.)..	0.8721	Refractive index (20° C.)	1.4850
Solidifying pt. ....	At 20° C., solidified to a viscous mass	Fatty acids.....	26.59%
Acid value.....	0.49	Neutralization value.....	168.39
Saponification value.....	52.46	Iodine value (Wijs).....	73.35
Iodine value (Wijs).....	261.72	Glycerol.....	0.39%
Iodine value (Hübl).....	259.16	Unsaponifiable matter..	72.88%

The mixed fatty acids gave a very small quantity of ether-insoluble bromine additive compounds which turned black on heating. The glycerol was far less than calculated from the saponification value.

#### DETERMINATION OF UNSAPONIFIABLE MATTER

It is difficult and not in all cases possible to determine quantitatively the content of hydrocarbons in shark liver oils. But in the cases when no other substances besides cholesterol are present in the unsaponifiable matter together with hydrocarbons, the latter may be indirectly determined by deducting the amount of cholesterol from the total unsaponifiable matter. So far as the present shark liver oils are concerned, as will be seen later, the so-called stearyl-free unsaponifiable matter may be taken to be practically identical with hydrocarbons.

(a) DETECTION OF HYDROCARBONS—The following method, essentially a combination of the well-known Spitz-Hönig's and Bömer's methods of determina-



HERATSUNO-ZAMÉ (*Deania eglantina*, JORDAN AND SNYDER)  
Scale about 1/8

tion of the unsaponifiable matter in fatty oil, has been tried with success to decide whether a given sample of shark liver oil contains hydrocarbons or not, and to determine their contents approximately. As cholesterol is very incompletely extracted by petroleum ether from soap solution, the residue of the extraction consists chiefly of hydrocarbons. When the residue has been found to be an oil, the presence of hydrocarbons may be stated with a possible certainty. The absence of hydrocarbons may be usually confirmed by a residue of a small quantity of crystals of melting point above 100° C.

The operation adopted was as follows:

5-10 g. of the sample were saponified with 50 cc. of about normal (96 per cent) alcoholic KOH in a flask with a reflux condenser on a water bath for about 30 minutes to 1 hour. On cooling, the contents of the flask were washed out into a separating funnel with 50 cc. of distilled water and shaken with 100 cc. of petroleum ether (boiling point below 65° C.) for 1 minute.

The emulsion separated quickly into two layers. After standing for about one hour, the lower layer of the soap solution was drawn off into a beaker. The petroleum ether layer was washed successively with 20 cc. of 50 per cent alcohol and distilled water, each two times, and the alcohol washings added to

<sup>1</sup> The date has been mentioned, because the season appears to influence the properties of fish oils.

<sup>2</sup> "Hera" = spatula, in allusion to the flat head of the fish. "Tsunō" = spine; "Zamé" = shark.



the soap solution; then the petroleum ether layer drawn off into a small tared flask, the ether distilled off and the residue dried to a constant weight at 105° C. in a current of dry carbon dioxide gas. This residue consisted mainly of hydrocarbons.

The soap solution in the beaker was heated on a water bath (to expel the greater part of alcohol), then transferred into a separating funnel and extracted with each 100 cc. of ether three times. If an emulsion forms, it may be easily subsided by the addition of alcohol. The ether extracts were united and washed with distilled water; the ether was then distilled off in a tared flask, the residue dried and weighed as above.

As already stated, since cholesterol is extracted only to a small extent by petroleum ether from the soap solution, the residue of the second extraction by ether contains the main part of cholesterol. As a matter of fact, hydrocarbons are not completely extracted by a single extraction with petroleum ether, as may be expected from the distribution law. In the case of the oil of low saponification value, the petroleum ether extract gives the rough content of hydrocarbons. But if the quantity of saponifiable matter is large, considerable proportions of hydrocarbons are retained in the soap solution, so that the above number is not exact even approximately. The total unsaponifiable matter is the sum of the two extraction residues. Since a small quantity of probably hydrolyzed soap is sometimes extracted by ether together with cholesterol, the result is liable to give a little higher percentage of unsaponifiable matter with respect to the ether extract.

The following results (percentages) were obtained with the samples of shark liver oil:

Oil	Petroleum ether extract	Ether extract	Total unsaponifiable matter
Ai-zamé (1).....	87.20	2.97	90.17
Ai-zamé (2).....	83.06	4.26	87.32
Heratsuno-zamé.....	58.20	14.68	72.88

The petroleum ether extracts were faintly yellow to nearly colorless liquid, sometimes with a small deposit of apparently cholesterol crystals. The ether extracts were a pale yellow crystalline mass admixed with more or less liquid constituents (hydrocarbons). A few properties of these extracts were as follows:

Oil	PETROLEUM ETHER EXTRACTS Iodine value (Hubl)	LIEBERMANN'S TEST	MIXED WITH ALCOHOLIC DIGITONIN SOLUTION
Ai-zamé (1).....	370.80	Bluish gray, finally dirty yellowish orange	Almost no ppt.
Ai-zamé (2).....	378.17	.....	Almost no ppt.
Heratsuno-zamé....	360.82	Bluish violet, finally dirty orange	Ppt. formed

Oil	ETHER EXTRACTS	
Ai-zamé (1).....	.....	Reddish violet, finally dark green
Ai-zamé (2).....	187.95	.....
Heratsuno-zamé....	119.80	Violet-red, finally bluish green

The exceptionally high iodine value of the petroleum ether extracts is very characteristic. It indicates the occurrence, in these oils, of a hydrocarbon found by the author in "Kuroko-zamé" oil for the first time (*Loc. cit.*). As may be seen below, this was actually the case with the samples of these shark liver oils.

The presence of stearyl in the ether extracts has been confirmed by the Liebermann and digitonin tests.

**DETERMINATION OF CHOLESTEROL**—Cholesterol was determined by the digitonin method. It has been shown by M. Klostermann and H. Opitz<sup>1</sup> that a part of the cholesterol in cod liver oil occurs in the form of esters; this was also found to be the case with shark liver oil.

For the determination of the total content of cholesterol, 10 g. of Ai-zamé oil, or 5 g. of Heratsuno-zamé oil were saponified with alcoholic KOH, the soap decomposed with dilute sulfuric acid and shaken with ether. The ether layer was well washed with water and then dehydrated by means of anhydrous sodium sulfate. The residue left in a flask by evaporating off the ether was mixed with 50 cc. of 1 per cent digitonin solution in 90 per cent alcohol and vigorously shaken while hot for several minutes. After standing for two or more hours, the content of the flask was filtered in a tared Gooch crucible containing layers of filter paper and cotton. As the digitonide formed an emulsion-like mixture with the hydrocarbons, about 10 cc. of chloroform were next added to dissolve the latter substances. When the precipitate had been transferred into the crucible, it was washed with 90 per cent alcohol and finally with ether. The whole was dried at 105° C. and weighed. Free cholesterol was determined by a similar method by directly treating the original oils with digitonin solution. The weight of cholesterol was calculated from the weight of the digitonide by multiplying by the factor 0.2431. The results obtained were as follows:

PER CENT CHOLESTEROL:	Free	Combined	Total
Ai-zamé oil (1).....	0.09	0.46	0.55
Heratsuno-zamé oil.....	0.61	0.63	1.24

Cholesterol acetate obtained by treating the digitonide with acetic anhydride melted at 112–113° C.

If we assume the unsaponifiable matter of the shark liver oils to consist of cholesterol and hydrocarbons only, then the content of the hydrocarbons is obtained by deducting the content of cholesterol from the total unsaponifiable matter, as follows:

Ai-zamé oil (1), 89.62 per cent      Heratsuno-zamé oil, 71.64 per cent

#### SEPARATION OF HYDROCARBONS

The petroleum ether extracts obtained in the previous experiments were presupposed to be a hydrocarbon or hydrocarbons. In order to determine whether they really consisted of a hydrocarbon or a mixture of hydrocarbons, and if any other constituents are contained in them, the following experiments were performed. Essentially, the volatility of the substances under a reduced pressure was utilized for their isolation and identification.

#### AI-ZAMÉ OIL (1)

**FRACTIONAL DISTILLATION OF STEROL-FREE UNSAPONIFIABLE MATTER**—One hundred g. of the oil were saponified with 10 g. of KOH in 10 cc. of water and 90 cc. of 96 per cent alcohol in a flask. The saponified solution, consisting of two layers (the upper hydrocarbon and the lower, chiefly soap solution), was

<sup>1</sup> *Z. Nahr. Genussm.*, Bd. 27, Heft 10.

transferred into a separating funnel by washing the flask with 100 cc. of distilled water. It was then extracted with 200 cc. of light petroleum ether. The lower soap solution was drawn off, the ether layer well washed with 50 per cent alcohol and water, and then the petroleum ether distilled off.

The crude hydrocarbon thus obtained was mixed with 20 cc. of 1 per cent digitonin solution in 95 per cent alcohol and allowed to stand over night. The lower layer of hydrocarbon was then drawn off; from the upper alcoholic layer, in which the separated digitonide was chiefly suspended, the alcohol was evaporated; the residue was treated with 200 cc. of ether and mixed with the previously drawn hydrocarbon. Since digitonide and digitonin are insoluble in ether, they were deposited from the ether solution as white precipitates; these were filtered off. Finally, the ether was evaporated from the clear ethereal solution, and the stearyl-free hydrocarbon, a pale yellow oily liquid of faint peculiar odor, was left. The yield from 100 g. of the oil was 79 g. (79 per cent by weight) of a colorless liquid.

Fifty grams of the hydrocarbon thus obtained were put in a distillation flask of about 100 cc. capacity, and fractionally distilled under 8 mm. pressure.

The first drop of the distillate was observed at 280° C. bath temperature; the continuous distillation began at 240° C. (temperature of the bath, 288° C.), the thermometer soon rising to 256° C. The specific gravities and refractive indices of the original substance, as well as these fractions, were determined:

FRACTION	1	2	3	4	5	TOTAL
Temperature Oil Bath.....	291	289	289	288	286-7° C.	
Temperature Distillation.....	256	256	256	256	256° C.	
Yield, grams.....	8.0	9.7	9.7	10.4	11.5	49.3
Specific gravity (15/4° C.).....	0.8540	0.8580	0.8589	0.8584	0.8589	(Original) 0.8570
Refractive Index (20° C.).....	1.4925	1.4963	1.4963	1.4962	1.4962	1.4955

Thus, the substance had a constant boiling point and its fractions showed nearly concordant values with respect to specific gravities and refractive indices. It appears, therefore, to consist mainly of a single chemical compound, although a small quantity of a substance of lower boiling point is likely to be present in the first fraction.

The elementary analysis of the substance and of Fraction 3 gave the following results:

0.1785 g. original substance gave 0.5741 CO<sub>2</sub>, 0.1972 H<sub>2</sub>O; C = 87.71 per cent, H = 12.36 per cent.  
0.1816 g. Fraction 3 gave 0.5817 CO<sub>2</sub>, 0.1979 H<sub>2</sub>O; C = 87.36 per cent, H = 12.19 per cent.  
Molecular weight of Fraction 3 (freezing point method, benzene as solvent) = 413.  
C<sub>30</sub>H<sub>50</sub> requires C = 87.72 per cent, H = 12.28 per cent, mol. wt. = 410.40.  
C<sub>30</sub>H<sub>50</sub> requires C = 88.17 per cent, H = 11.83 per cent, mol. wt. = 408.38.

The above results agree more closely with the formula C<sub>30</sub>H<sub>50</sub>.

FRACTIONAL DISTILLATION OF THE OIL—By the later experiments, it has been found that in order to obtain the hydrocarbon in pure state, the previous separation of stearyl-free unsaponifiable matter is not necessary, and the original oil or crude unsaponifiable matter may be directly distilled for this purpose, since cholesterol is nonvolatile at the temperature

and pressure at which the hydrocarbon distills over. Hence the following experiment was tried: 50 g. of Ai-zamé oil (1) were fractionally distilled under 10 mm. pressure. The distillates were colorless and contained a small quantity of free fatty acids, as may obviously be expected; the later fractions were of fairly pure quality.

FRACTION	1	2	3	4	5	TOTAL
Temperature Oil Bath.....	290	292	292.5	295-8	293-303° C.	
Temperature Distillation.....	262-4	264	264-5	265	265° C.	
Yield, grams.....	7.6	8.0	9.0	9.0	7.2	40.8
Acid value.....	0.99	0.21	....	....	....	
Refractive Index (20° C.).....	1.4940	1.4963	1.4965	1.4965	1.4965	

ELEMENTARY ANALYSIS OF THE FRACTION (4). 0.1622 g. gave 0.5183 CO<sub>2</sub> and 0.1765 H<sub>2</sub>O; C = 87.15 per cent, H = 12.18 per cent.

The above composition corresponds to the formula C<sub>30</sub>H<sub>50</sub>.

#### AI-ZAMÉ OIL (2)

The stearyl-free substance was prepared by the same method as from Ai-zamé oil (1). Fifty grams of the pale yellow substance were fractionally distilled at 11 mm. pressure. The first drop was observed at 256° C. (bath 294° C.); then the thermometer rapidly rose to above 260° C. The distillates were colorless.

FRACTION	1	2	3	4	5	TOTAL
Temperature Oil Bath.....	304	300	294	294	295-306° C.	
Temperature Distillation.....	265-268	268	368	268	268° C.	
Yield, Grams.....	10.6	10.6	10.5	10.8	6.5	49.0
Specific gravity (15/4° C.).....	0.8574	0.8584	0.8586	0.8587	0.8546	(Original) 0.8586
Refractive Index (20° C.).....	1.4955	1.4965	1.4965	1.4965	1.4968	1.4960

The elementary analysis gave the following results:

0.1943 g. original substance gave 0.6258 CO<sub>2</sub>, 0.2121 H<sub>2</sub>O; C = 87.84 per cent, H = 12.21 per cent;

0.1932 g. of fraction 3 gave 0.6230 CO<sub>2</sub>, 0.2079 H<sub>2</sub>O; C = 87.94 per cent, H = 12.14 per cent.

Hence, the substance consists of the hydrocarbon C<sub>30</sub>H<sub>50</sub>.

#### HERATSUNO-ZAMÉ OIL

The direct distillation method was adopted with this oil. But, since Heratsuno-zamé oil contains a far higher percentage of esteric compound than Ai-zamé oil, the separation of hydrocarbon was better accomplished by resorting to redistillation: 100 g. of the oil were distilled under 4.5 to 5 mm. pressure; the yield of the distillate was 58 g. The main part distilled at 250-260° C., but it was found that a small fraction distilling at a temperature below 250° C. at 5 mm. was also present. Then, the distillate was well washed with alkali to remove the admixed fatty acids: 40 g. of this refined substance were fractionally distilled under 5 mm. pressure. The distillates were colorless.

FRACTION	1	2	3	4	5	6	TOTAL
Temp. Oil Bath.....	285	288	286	284	285	287° C.	
Temp. Distillation.....	248	248-52	252	252	252	252	
Yield, grams.....	1.4	6.6	7.2	7.2	7.2	7.5	37.1
Sp. gr. (15/4° C.).....	0.8189	0.8581	0.8589	0.8589	0.8589	0.8590	
Ref. Index (20° C.).....	1.4633	1.4950	1.4955	1.4962	1.4961	1.4960	

Fraction 1 had a lower boiling point and considerably lower specific gravity and refractive index. The



properties of the other fractions nearly coincided with those of the hydrocarbon  $C_{30}H_{50}$ , isolated from Ai-zamé oil.

The elementary analysis and molecular weight determination of Fractions 1 and 4 gave the following results: 0.1565 g. Fraction 1 gave 0.4025  $CO_2$ , 0.1028  $H_2O$ ;  $\therefore$  C = 85.82 per cent, H = 13.78 per cent; Mol. wt. = 288.

$C_{28}H_{38}$  requires C = 86.24 per cent, H = 13.76 per cent; Mol. wt. = 278.3.

Fraction 1 was thus confirmed to be a hydrocarbon, but that it really consists of a single compound requires further confirmation.

0.1880 g. Fraction 4 gave 0.6024  $CO_2$ , 0.2066  $H_2O$ ;  $\therefore$  C = 87.39 per cent; H = 12.31 per cent.

This fraction was thus confirmed to be the hydrocarbon  $C_{30}H_{50}$ .

As the result of the above-described experiments, it has been concluded that the stearyl-free unsaponifiable matter of Ai-zamé and Heratsuno-zamé oils mainly consists of a new hydrocarbon of the empirical formula  $C_{30}H_{50}$ . Besides this hydrocarbon, a small quantity of a hydrocarbon or hydrocarbons of lower boiling point is also present in these oils, especially in Heratsuno-zamé oil.

#### PROPERTIES OF THE HIGHLY UNSATURATED HYDROCARBON

So far, it has been shown that a highly unsaturated hydrocarbon,  $C_{30}H_{50}$ , occurs in Ai-zamé and Heratsuno-zamé oils in high proportion. Since the oils consist mainly of unsaponifiable matter, the hydrocarbon is in reality the chief constituent of these oils. A closer study of this interesting hydrocarbon will be very important from technical, and particularly from physiological points of view, as the occurrence of a large quantity of a hydrocarbon in animal oils is a matter of rarity. The experiments with this hydrocarbon, imperfect as they are, are described below:

The sample of the hydrocarbon was obtained from Ai-zamé oil (1): 100 g. of the oil were saponified and the crude hydrocarbon extracted by petroleum ether (yield, 117 g.); 108 g. of this substance were treated with 0.5 g. of digitonin, and 101 g. of the stearyl-free substance were obtained; 100 g. of the latter substance were distilled under 10 mm. pressure. Discarding this first fraction, the distillates of boiling points of 262–264° C. (temperature of the oil bath, 294–296° C.) were collected (yield, 83.5 g.); 80 g. of this distillate were redistilled under 9.5 mm. pressure. Discarding again the first fraction, the distillates of boiling points of 259–264° C. (temperature of the bath, about 300° C.) were collected (yield, 70.3 g.). This substance was used as the sample for investigation. The discrepancy of the boiling points is probably due to the rapid heating of the oil bath.

To confirm the correctness of the formula  $C_{30}H_{50}$ , the following elementary analysis and molecular weight determination were repeated.

(1) 0.1886 substance gave 0.6033  $CO_2$ , 0.2093  $H_2O$ .

(2) 0.1553 substance gave 0.4994  $CO_2$ , 0.1709  $H_2O$ .

C = 87.43 per cent, 87.70 per cent; H = 12.41 per cent, 12.30 per cent.

$C_{30}H_{50}$  requires C = 87.72 per cent, H = 12.28 per cent.

0.4020 substance in 11.7470 benzol gave  $d = 0.42^\circ C$ .

Mol. wt. = 408. Mol. wt. of  $C_{30}H_{50} = 410.4$ .

The hydrocarbon is a colorless, oily liquid which refracts light somewhat strongly. In the pure state, it is nearly odorless; but the distilled sample possesses a faint odor, apparently of decomposition products, which can be removed by washing with alkali. On keeping, it involves an odor which recalls some terpenes. Its taste is peculiar, but not so unpleasant. It is readily soluble in ether, petroleum ether, carbon tetrachloride and acetone; in cold alcohol and glacial acetic acid, it is sparingly soluble. When heated over a flame, the hydrocarbon burns with a smoky, luminous flame, emitting a resinous smell.

**BOILING POINT**—Under ordinary pressure, the hydrocarbon cannot be distilled without decomposition. Boiling point (10 mm. pressure), 262–264° C.; (5 mm. pressure) 252–254° C.

**SOLIDIFYING POINT**—Kept at  $-20^\circ C$ . for one hour, it remained clear; at  $-75^\circ C$ ., it solidified to a white wax-like mass.

**SPECIFIC GRAVITY**—At  $15^\circ/4^\circ C$ ., 0.8587.

**IODINE VALUE**—388.12 (Wijs), 398.70 (Hübl).

Theory requires for  $C_{30}H_{50}I_{12}$ , iodine value = 371.10.

**REFRACTIVE INDEX**—( $20^\circ C$ .) 1.4965.

**OPTICAL ROTATION**—inactive.

**HEAT OF COMBUSTION**—(Hempel's calorimeter), 10,773 cal. per g.

**COLOR REACTION**—By Liebermann's test (solution in acetic anhydride and addition of a drop of concentrated sulfuric acid), the fresh hydrocarbon gave only a faint pink coloration in the lower (acetic anhydride) layer.

**DRYING PROPERTY**—The hydrocarbon dries like the vegetable drying oils. The pure hydrocarbon requires a long time to dry at the ordinary temperatures. That which had been treated with 1 per cent of cobalt resinate, dried in about 10 days (in winter) to a colorless, smooth film which possessed a firmness superior to those of the fatty oils. At  $100^\circ C$ ., a thin layer of the hydrocarbon dried in about 2 hours.

**ACTION OF ACIDS**—Concentrated sulfuric acid attacked the hydrocarbon violently with evolution of heat, changing it to a dark reddish brown mass. Concentrated nitric acid acted not so violently. A very violent reaction was observed by a mixture of concentrated nitric and sulfuric acids.

**ACTION OF ALKALIES**—Even caustic alkalies had practically no action at  $100^\circ C$ .

**ACTION OF SULFUR CHLORIDE**—A yellow solid mass was obtained.

**PICRATE COMPOUND**—No definite compound was obtained.

**BROMIDE ADDITIVE COMPOUND**—0.6326 g. of the hydrocarbon was dissolved in 10 cc. of ether in a flask, the solution cooled with ice, and 0.55 cc. of bromine was added drop by drop. After standing for 2 hours,

the precipitate was filtered on a tared filter paper, washed with about 70 cc. of ether and dried *in vacuo*, over sulfuric acid, until the weight became constant.

The yield of the insoluble bromide was 0.5630 g., *i. e.*, 89.00 per cent of the sample.

0.1467 substance gave 0.1413 CO<sub>2</sub>, 0.0496 H<sub>2</sub>O.

0.1587 substance gave 0.2600 AgBr (Carius method).

C = 26.27 per cent, H = 3.78 per cent, Br = 69.75 per cent.

C<sub>30</sub>H<sub>50</sub>Br<sub>12</sub> requires C = 26.78 per cent, H = 3.72 per cent, Br = 69.50 per cent.

The filtrate from the above precipitate was treated with sodium thiosulfate solution, in order to remove the excess of bromine, washed with water and dried with anhydrous sodium sulfate. On evaporating off the ether, a viscous solid was left, which became a white powder on grinding. The yield was 1.6070 g., *i. e.*, 254.00 per cent of the original sample. The soluble bromide was then treated with a few cc. of ether to remove admixed impurities, and analyzed.

0.1157 substance gave 0.1117 CO<sub>2</sub>, 0.0391 H<sub>2</sub>O.

0.1664 substance gave 0.2710 AgBr.

C = 26.33 per cent, H = 3.78 per cent, Br = 69.30 per cent.

This substance is, therefore, identical with the insoluble portion.

The total yield of the bromide is thus 333 per cent. Theory requires 327.60 per cent, nearly a good accord. The bromine additive compound is a white powder, turning black at about 170° C. and decomposing at 176–177° C. It is sparingly soluble in organic solvents, especially when dried.

The bromide obtained from "Kuroko-zamé" oil described in the introductory note, is the same substance as this brominated hydrocarbon. The analytical results given there correspond more closely with C<sub>30</sub>H<sub>50</sub>Br<sub>12</sub> than C<sub>10</sub>H<sub>18</sub>Br<sub>4</sub>. Therefore, the hydrocarbon in the above-named shark liver oil must have been the hydrocarbon C<sub>30</sub>H<sub>50</sub>.

**HYDROGENATION COMPOUND**—3.3115 g. of the hydrocarbon were dissolved in 30 cc. of ether in a shaking bottle. To this solution, 0.5 g. of Loew's platinum black was added. The bottle was then connected to a gas burette, which in turn was connected with a hydrogen holder. Hydrogen was prepared from pure zinc (Merck) and dilute sulfuric acid, and before entering into the burette, it was washed and dried by bottles containing a solution of potassium permanganate and concentrated sulfuric acid. By vigorously shaking the bottle, hydrogen was conducted into it under the mercury pressure. After 2 hrs. 40 mins., the absorption ended; the volume of hydrogen absorbed, together with a little leakage, was 1120 cc. The hydrogenated compound, left on evaporating off ether, was found to be a colorless oil, resembling in its appearance the so-called liquid paraffin. It had the following properties: Sp. gr. at 15/4° C., 0.8125; b. p. (10 mm. pressure), 274° C.; solidifying pt.: at —20° C. it remained clear and mobile; at —80° C., solidified to a transparent jelly which at —35° C. regained its mobility; ref. index at 20° C., 1.4525. It was not readily acted on by concentrated sulfuric acid, even at 100° C.

**ELEMENTARY ANALYSIS:** (1) 0.1610 substance gave 0.5022 CO<sub>2</sub>, 0.2114 H<sub>2</sub>O.

(2) 0.1910 substance gave 0.5959 CO<sub>2</sub>, 0.2523 H<sub>2</sub>O.

C = 85.07, 85.09 per cent; H = 14.69 per cent, 14.78 per cent.

C<sub>30</sub>H<sub>62</sub> requires C = 85.21 per cent, H = 14.79 per cent.

Molecular weight determination, by freezing point method, 0.2982 substance in 11.1030 benzol, d = 0.31° C. Mol. wt. = 433.

C<sub>30</sub>H<sub>62</sub> requires mol. wt. = 422.5.

The substance has therefore been confirmed to be a compound of the empirical formula C<sub>30</sub>H<sub>62</sub>. As C<sub>30</sub>H<sub>62</sub> is of a type of the general formula C<sub>n</sub>H<sub>2n+2</sub>, it appears that the hydrocarbon C<sub>30</sub>H<sub>50</sub> belongs to the aliphatic compounds.

#### PREPARATION AND APPLICATION OF THE HYDROCARBON

Ai-zamé and Heratsuno-zamé oils are produced in somewhat large quantities in certain districts of Japan, especially in Shizuoka Prefecture. So the preparation of the hydrocarbon is practicable even for commercial purposes; all the more so, as the author has lately ascertained the presence of the hydrocarbon in other shark liver oils besides the above mentioned ones. (See below.)

The preparation of the hydrocarbon is, according to the author's experience, best conducted by distilling the oil under reduced pressure, or by means of superheated steam.<sup>1</sup> Since cholesterol is comparatively nonvolatile, the distilled hydrocarbon contains more or less admixed fatty acids. Therefore, by subsequent washing with alkali, it can be obtained in nearly pure state.

As to the use of the hydrocarbon, only a few experiments have been tried as yet, and exact descriptions cannot be given here. It may be mentioned, however, that for technical purposes, the hydrocarbon may be used for paints, varnishes, lithographic inks, and oil colors. The hydrogenated product, which in its appearance is very similar to so-called liquid paraffins and, at the same time, far more stable for cold, will be a useful material for lubrication of machines.

The medicinal use of the hydrocarbon, possible for the same purpose as cod liver oil, will perhaps be most interesting, but careful researches are necessary to settle this question.

#### CONCLUSIONS

The results of the present investigation have confirmed that two Japanese shark liver oils, Ai-zamé and Heratsuno-zamé oils, contain very high proportions of unsaponifiable matter which mainly consist of a new highly unsaturated hydrocarbon of the formula C<sub>30</sub>H<sub>50</sub>. It will be rather premature to make any further statement, but certainly a remarkable quantity of a hydrocarbon which in reality is the essential constituent of the oil itself, occurs in oils of such vital organs as the liver of the fish. It may be added here from the author's latest experiments that the hydrocarbon also occurs in the liver oils of so-called "Black sharks," basking sharks and another

<sup>1</sup> Japanese Patent, No. 28,143, Aug. 4, 1915.



shark (probably *Triakis scyllium*—Japanese; "Koro-zamé"). Sharks belonging to Squalidae appear to contain the hydrocarbon more frequently. But, the data obtained hitherto are yet too scanty to allow a generalization as to the genus and species of sharks.<sup>1</sup>

To solve the question, why such a hydrocarbon is present in the liver of some fish, is probably very difficult, and presents an important problem for physiological chemistry. It is interesting to note that the bromine content of the bromine additive compound of the hydrocarbon is nearly identical with those of the polybromides of the highly unsaturated fatty acids<sup>2</sup> in marine animal oils, *viz.*, about 70 per cent.

In the case of the present shark liver oils, the place of the highly unsaturated fatty acids is taken, as it were, by the hydrocarbon of a nearly equally high unsaturation. The liver is a storage organ for fat and consequently a source of energy of the fish. If a speculation may be allowed, the hydrocarbon, which evolves far more heat of oxidation than the glycerides, must have been formed in the liver of the fish from the necessity of local conditions. Little as the habit of the sharks is known, it is pretty certain that they are comparatively deep sea dwellers.

For technologists, the hydrocarbon is not less important. The "drying" properties of glycerides (vegetable drying oils) and certain phenols, such as Urushiol,  $C_{20}H_{30}O_2$ , the chief constituent of Japanese lacquer, are well known, but yet those of the hydrocarbons have not been investigated.

In a second paper on this subject, the author hopes to publish the results of the latter experiments, performed on other shark liver oils, and an examination of the further properties of the hydrocarbon.

**ADDENDUM**—After the foregoing report had been written, the author read a paper by H. Mastbaum (Lisbon), entitled "Hydrocarbon in Fish Liver Oils," through *Chemical Abstracts*, 10, No. 2, just arrived. The author has examined two liver oils from *Centrophorus granulosus* and *Scymnus lichia*, and found 80–90 per cent of oil with the characteristic of mineral oil. The unsaponifiable portion of the oil from *Scymnus lichia* is said to have boiled at 205–330° C. (under the ordinary pressure?). As no analytical result of the unsaponifiable matter is given, it is not possible to decide whether they contained the hydrocarbon  $C_{30}H_{50}$  or not. But, as the former shark belongs to Squalidae, the hydrocarbon in the oil is doubtless the same. From this report, it may be seen that the liver oil of foreign squaloid shark also contains hydrocarbon. Although not the only one of

the kind, the family Squalidae seems to have a more important relation to the hydrocarbon than other families. From such reasons, and particularly from the fact that the author has discovered the hydrocarbon first in the liver oils of the squaloid sharks, he proposes the name "*Squalene*" for the hydrocarbon.

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## AERATION METHOD FOR AMMONIA

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Investigations in soil biology require frequent exact determinations of ammonia in the presence of organic nitrogenous compounds. The problem is therefore the same as that encountered in general biological chemistry with the additional difficulty that large amounts of solutions must be used in soil biological work because of the smaller percentage of ammonia in the material under examination. For instance, in biological chemistry, in the determination of ammonia in urine, 25 to 50 cc. portions of urine are taken, whereas in soil biology 250 cc. of soil extract or of physiological solution are frequently necessary to give a measurable amount of ammonia nitrogen.

The matter of the separation of ammonia from organic nitrogen has been the subject of a very large amount of study by biological chemists. The tendency of all recent work has been toward the use of an air current to transfer the ammonia from cold alkaline solution into acid receivers and determination of the ammonia by titration (or Nesslerization) of the receiver contents. The use of larger amounts of solutions naturally renders the removal by the air current slower. Moreover the matter of the kind and concentration of alkali is still a matter of controversy among workers in this field. Obviously, the lowest hydroxyl ion concentration compatible with complete removal of ammonia under workable conditions is desirable since decomposition of the organic nitrogenous material is roughly proportional to the concentration of hydroxyl as ion.

The use of different alkalies, and their effect on the rapid removal of ammonia from large amounts (250 cc.) of solution by means of a vigorous air current, and its subsequent quantitative collection and measurement constitutes the experimental work reported in this paper. It was desired to obtain a method by which the ammonia can be recovered in a period of 2½ to 3 hrs. and, if possible, the use of an alkali imparting a low concentration of hydroxyl as ion to the solution.

## HISTORICAL

Folin<sup>1</sup> outlined a method for determining ammonia in urine: 25 cc. of urine were aerated for 1 to 1½ hrs. over 1 g. of sodium carbonate and 8 to 10 g. of sodium chloride. The rate of air used was 600 to 700 liters per hour. The ammonia was absorbed in standard acid and titrated with standard alkali. He devised the well-known Folin absorption tube by which he was able to get complete absorption of the ammonia. He used MgO for some determinations

<sup>1</sup> Oils prepared from the following sharks have been found not to contain the hydrocarbon. Cat shark (*Heterodontus japonicus*), Blue shark (*Isurus glaucus*), Porbeagle (*Lamna cornubica*), Saw shark (*Pristiophorus japonicus*), Hammer-headed shark (*Sphyrna zygaena*), and Angel-fish (*Squatina japonica*). Nor has the hydrocarbon been found in the liver oils from the following rays: Ray (*Raja kenoi*), Sting-ray (*Dasyatis akajoi*), Eagle-ray (*Myliobatis tobiei*), and *Discobatus sinensis* (Japanese; "Uchiwa-zamé").

Shark liver oils from probably *Squalus sucklii* contained 12.00 to 21.64 per cent of unsaponifiable matter, not volatile at 300° C. under 10 mm. pressure. The nature of the substance has not yet been ascertained. Details will be published in a next report.

<sup>2</sup> Acids of the series  $C_nH_{2n-8}O_2$  and  $C_nH_{2n-10}O_2$ .

<sup>1</sup> Folin, *Z. physiol. Chem.*, 37 (1912), 161.

of ammonia in pure solutions and complete recovery was obtained. However, no data are reported for aeration of urine over  $\text{MgO}$ . Steel<sup>1</sup> proposed the use of sodium hydroxide and saturation of the solution with sodium chloride, but this alkali has been subsequently shown to be stronger in its action on organic nitrogenous compounds than the sodium carbonate.

Kober<sup>2</sup> recommended the use of the air current for the transfer of ammonia from the strongly alkaline solution of the Kjeldahl method, to the standard acid. He does not report the rate of aeration but states that the rate is increased as much as possible without losing any of the absorbing acid in the cylinder. The distillation is complete in one hour. After the aeration is complete the acid is titrated with standard alkali. Kober and Graves<sup>3</sup> report further work on this same point. The rate of aeration used was 500 liters per hour. The rate was measured by displacement of a known volume of water by the air current drawn by the pump. They were able to remove large quantities of ammonia in one hour.

Pennington and Greenlee<sup>4</sup> report some determinations on chicken meats. They determined the loosely bound nitrogen in protein-rich tissues of meats. The work reported was done on chicken meats which had undergone some bacterial and enzyme decomposition. Twenty-five grams of chicken meat were suspended in 250 cc. water and 5 g. of  $\text{MgO}$  added. The suspension was aerated and the ammonia absorbed in standard acid. The rate of aeration was about 1,250 liters of air per hour through each aeration flask.

Potter and Snyder<sup>5</sup> report on the determination of ammonia in soils by aeration over sodium carbonate. They show conclusively that the alkali as recommended by Steel<sup>6</sup> for determining ammonia in urine, decomposes organic nitrogenous compounds of the soil and give ammonia. They ascribe this largely to the decomposition of acid amides. Acetamide failed to give a very appreciable amount of ammonia when aerated with sodium carbonate. They conclude that sodium carbonate will not decompose acid amides to yield ammonia as does sodium hydroxide. They aerated 25 g. of soil in 50 cc. of ammonia-free water and about 2 g. of sodium carbonate for a period of 19 hrs. The rate reported in this work was 250 liters per hour. At the end of the aeration period the acid solutions were titrated with standard alkali. The results are reported for 100-g. samples of soil. The average amount of ammonia found was about 1 to 1.4 mg. per 100 g. of soil. They added quantities of ammonia to soil and in most cases they were able to recover better than 99 per cent of the added ammonia. The addition of the salts  $\text{NaCl}$  and  $\text{K}_2\text{C}_2\text{O}_4$  did not aid in the recovery of the ammonia of the soil.

We find very little attention has been given to the liberating of ammonia from solutions by  $\text{MgO}$ . Other

alkalies have been used and it is well established that large quantities of ammonia can be determined by aeration and in a comparatively short time when the rate of aeration is high. The rate of aeration has been slow in most cases and the quantity of solution aerated has been small except in Kjeldahl determinations. The lack of a uniform method of measuring the rate of aeration makes any correlation of the work from different laboratories hard.

#### EXPERIMENTAL

**AMMONIA-FREE WATER**—The distilled water used in this work was prepared by double distillation of live steam through dilute  $\text{CuSO}_4$ , and this then passed through a scrubber before condensation. The water showed no traces whatever of ammonia with Nessler's reagent, and was neutral to methyl red.

**AMMONIA-FREE MAGNESIA**—The magnesium oxide was calcined before being used.

**AMMONIA SOLUTIONS**—The ammonia solutions were prepared from ammonium sulfate and standardized by distilling over  $\text{MgO}$ . For small quantities of ammonia  $N/50$   $\text{H}_2\text{SO}_4$  was used and for larger quantities  $N/10$   $\text{H}_2\text{SO}_4$  was used.

**INDICATOR**—Methyl red was used as the indicator in all titrations. The  $\text{CO}_2$  was expelled from all solutions before titrating.

The method of measuring the rate of aeration is that suggested by Kober.<sup>1</sup> Attention is called to the fact that the tube through which the water passes should be sufficiently large to prevent the speed of the pump being checked at any time. Theoretically, the friction of the water passing through any tube would retard the rate of flow. However, in the apparatus used in this work tubes of 11 mm. internal diameter were employed, and when this apparatus operated in series with the aeration flasks, there was no perceptible decrease in the rate of bubbling in the latter.

The measurement of the air should give the amount which actually passes through the apparatus and not that amount which the pump is capable of pulling when there is no load. The rate as measured by some workers does not give the amount of air which passes through the apparatus. They measure the capacity of the pump and take this value for the rate of aeration used. Measured through the apparatus, the rate would be found very much lower. This important point has been overlooked by workers in this field and renders impossible the comparison of results from different laboratories.

The rate of aeration reported in this work gives the amount of air which passed through the apparatus. The Crowell pump, which was used, was capable of handling 2100 liters of air per hour, with no load. However, when drawing air through the apparatus, the rate was reduced to 1080 liters per hour, because of the resistance of the solutions in the ten flasks.

The first work was carried on with sodium carbonate as the alkali. Five hundred cc. Kjeldahl flasks were used as aeration flasks and the regular Folin tubes

<sup>1</sup> Steel, *J. Biol. Chem.*, **8** (1910), 365.

<sup>2</sup> Kober, *J. Am. Chem. Soc.*, **30** (1908), 1131.

<sup>3</sup> Kober and Graves, *Ibid.*, **35** (1913), 1594.

<sup>4</sup> Pennington and Greenlee, *Ibid.*, **32** (1910), 561.

<sup>5</sup> Potter and Snyder, *This Journal*, **7** (1915), 221.

<sup>6</sup> *Loc. cit.*

<sup>1</sup> *Loc. cit.*



and cylinders as receivers. The results were highly unsatisfactory. Mr. J. J. Kennedy, working in this laboratory, obtained results which lead him to believe entrained alkali was being carried over into the receiving flasks. This point was confirmed by later work. The results appear in Table I. After aeration was complete and the excess acid titrated the titer solutions were then distilled over MgO into standard acid and the excess acid again titrated.

TABLE I

Nitrogen by	Direct Titration Mg.	Distillation over MgO Mg.
1.....	24.12	24.44
2.....	25.00	24.48
3.....	24.69	24.45
4.....	24.77	24.40

An attempt was made to prevent the carrying over of the alkali. Many different kinds of traps were used but none sufficed to cause the complete deposition of the alkali. Further work with sodium carbonate was abandoned and attention was then paid to the use of MgO. By using MgO we hoped to remove dangers from entrained alkali, at the same time reduce the hydroxyl ion concentration, and thus reduce the danger of decomposition of organic nitrogenous compounds of the soil.

Trouble was experienced from incomplete absorption. The Folin tube was found to be of no value for such a rapid rate of aeration as was used in this investigation. The air passed from the bottom of the bell in large bubbles and escaped from the solution without complete washing.

A  $\frac{5}{8}$  in. bulb perforated with  $\frac{1}{2}$  mm. holes, the use of 225 cc. of approximately  $N/10$   $H_2SO_4$  contained in a 500 cc. Kjeldahl flask and the distillation of the receiver contents over MgO gave far better results, but absorption was as yet not quite complete.

This showed that complete absorption could not be obtained without thorough scrubbing of the air as it passed through the acid solution, and this can not be obtained without the use of a tower. Carbon dioxide towers, both the Reiset and Camp forms, were tried but the diameter of these towers was too small. The rapid air current jerked the absorbing liquid out at the top. Larger towers,  $1\frac{1}{2}$  in. in diameter, were prepared and used. The acid solution was drawn up on top of the column of beads where it spattered badly. The absorption was complete but the spattering caused a loss in some cases. Glass rods about  $1\frac{1}{2}$  in. in length were then substituted for the beads. The acid did not draw up on top of this coarse material.

The tower finally adopted for the work is shown in Fig. 1. The main part of the tube is  $1\frac{1}{2}$  in. in diameter and 15 in. long. It is closed at the bottom with a glass stopcock of 3 mm. bore. The side arm has a bore of 8 mm. C and E are glass rods held in

place by baffles made from rubber gasket. The purpose of the baffle at E is to stop any acid which spatters from the lower part of the tower. The tower is connected with the aeration flask as shown in the figure. The aeration bulb D should be well perforated so that complete stirring of the solution will be obtained, and should extend well to the bottom of the flask. The tubes connecting the flask are 5 mm. bore.

**PROCEDURE**—In the tower are placed 15 cc. of approximately  $N/10$   $H_2SO_4$  and 15 cc. distilled water. The ammonia solution is placed in the Kjeldahl flask and made to a volume of 250 cc. A few drops of oil and the MgO are then added. Determinations are run in a series of four. The rate of aeration is measured at the beginning of each determination.

The air was washed through 25 per cent  $H_2SO_4$ . Trouble was experienced in securing complete recovery of the ammonia from the first flask which the air entered. It seemed this might be due to the  $CO_2$  of the air since it would react with the magnesium oxide in solution and the rapidity of ammonia liberation would be thus greatly checked. During the aeration enough  $CO_2$  would be drawn into the solution to react with about 1 g. of MgO. When 30 per cent solution of NaOH was used to remove the  $CO_2$  from the air no further trouble was experienced. The air is washed with the NaOH before washing with acid.

Several determinations showed the best period of aeration to be  $2\frac{1}{2}$  hrs. When the aeration is complete the air current is reduced and the stoppers loosened, beginning at the flasks farthest from the pump.

A Kjeldahl flask is placed under the tube of the tower and the acid solution is emptied into it. The tower is then washed with about 150 cc. distilled water, using about 50 cc. portions. The stopcock is closed before each washing in order to allow the water to run back into the side arm. Three such washings were found to remove all traces of ammonia, a fourth showing no ammonia with Nessler's reagent.

The solution is then distilled over MgO into standard acid and the excess acid titrated. The boiling should be continued for 30 mins. The liquid in the titration flask, which becomes hot from the steam, is cooled under running water before titration. In making this distillation over MgO it has been found that direct distillation into the acid without the use of a condenser is more satisfactory than using the Kjeldahl distilling apparatus provided with block-tin condensing tubes. Quartz<sup>1</sup> tubes were used in this work. Hard glass tubes well seasoned will suffice for many determinations. It is only where one works with small quantities of ammonia and the use of  $N/50$  acid that the very insoluble quartz tubes are necessary.

Some determinations were made to ascertain the amount of MgO necessary to liberate all the ammonia. It was found that 0.2 g. of MgO was sufficient to liberate 25 mg. ammonia nitrogen when the  $CO_2$  is removed from the air before entering the flasks. It

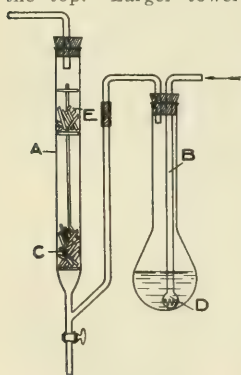


FIG. 1

<sup>1</sup> Allen, THIS JOURNAL, 7 (1915), 251.

is not necessary that an exact amount of MgO be added and for most determinations 0.5 of a gram is entirely sufficient. Large quantities, as 10 g., which are often used in distillation over MgO, are not necessary and should be avoided.

The results obtained from a number of determinations are reported in Table II. For quantities of

TABLE II—MILLIGRAMS AMMONIA NITROGEN FOUND, AND ERRORS  
TAKEN, 23.92 TAKEN, 5.045 In soil, 12.84 } 17.880  
Added, 5.040 }

Found	Error	Found	Error	Found	Error
23.91	-0.01	5.001	-0.044	17.88	0.00
23.88	-0.04	5.010	-0.035	17.89	+0.01
23.88	-0.04	5.048	+0.003	17.85	-0.03
23.91	-0.01	5.035	-0.010	17.89	+0.01
23.90	-0.02	5.080	+0.035	17.85	-0.03
23.93	+0.01	5.054	+0.009	17.85	-0.03
23.90	-0.02	5.045	-0.000	17.91	+0.03
23.89	-0.03	5.054	+0.009	17.92	+0.04
23.90	-0.02	5.001	-0.044	17.84	-0.04
23.95	-0.03	5.015	-0.030	17.92	+0.04
Deviation . . .	-0.013		-0.0117		0.000
Probable error	±0.018		±0.0195		±0.02

5 mg. or less,  $N/50$   $H_2SO_4$  was used and for quantities above 5 mg.,  $N/10$   $H_2SO_4$  was used. The results need no discussion and they show the accuracy of the method. The ammonia in 250 cc. of the soil extract was first determined and then a known quantity of ammonia added and the total ammonia determined.

#### SUMMARY

I—Ammonia can be determined by aeration over MgO.

II—A standard method of measuring the rate of aeration should be adopted.

III—The Folin tubes are of no value for aeration work when the rate is as rapid as was used in this work.

IV—Complete absorption cannot be obtained unless the air is scrubbed well as it passes through the absorbing liquid.

V—The absorbing tower as used in this work gives complete absorption.

VI—One-half gram of MgO gives as satisfactory results as larger quantities.

VII—Two and one-half hours is sufficient to recover large quantities of ammonia from 250 cc. portions of solution when 1080 liters of air per hour are used.

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#### NITRATES AND OXYGEN DEMAND

By F. W. BRUCKMILLER

Received June 9, 1916

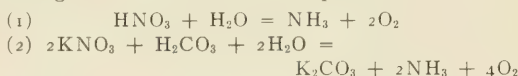
The determination of oxygen demand in sewages by the so-called saltpeter method depends upon the oxygen value ascribed to the nitrogen in the nitrate radical. Two values have so far been proposed, one by Lederer<sup>1</sup> and one by Hale.<sup>2</sup> The former assumes that 1 nitrate nitrogen is equivalent to 2.5 atoms of oxygen, while the latter assumes that 1 nitrate nitrogen is equivalent to 4 atoms of oxygen.

The process of nitrate reduction is a biologic one, and in order for it to go on successfully three conditions must prevail: namely, presence of organic matter, nitrates and bacteria. The products of reduction depend upon the kind of bacteria present. The re-

duction may be such that (1) the nitrates are reduced to nitrites only; or (2) the oxygen is taken from the nitrates and nitrites for the formation of ammonia; or (3) the nitrates and nitrites are reduced with evolution of NO and  $N_2O$ ; or (4) the nitrates and nitrites are reduced to gaseous nitrogen.

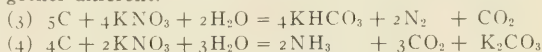
The energy for carrying on the reduction is obtained from easily assimilated carbon compounds and the amount of reduction is directly proportional to the organic matter present. A number of such compounds so readily utilized by denitrifiers are produced by the action of putrefactive organisms upon the complex insoluble compounds in animal and vegetable tissues, humus and undigested material in feces.

Any equations, therefore, devised to explain the reduction of nitrates must necessarily consider carbonaceous matter. Such equations, therefore, as the following<sup>1</sup> hardly represent the true course of the reaction since they do not take into consideration the reducing action of the carbon compounds:

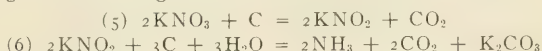


These equations might possibly represent the part nitrates play in the electrolytic action in the corrosion of iron, but they hardly apply to the biologic reduction of nitrates in sewages.

If it is necessary to represent the biologic reduction by a chemical equation the following<sup>2</sup> can be used to picture the facts in the case, although the exact nature of the reaction in actual conditions might be altogether different.



Analyzing this last equation by splitting it into its supposed successive reactions as they might occur we get the following:



In Equation 5, 2 nitrogens give up 2 oxygens. In Equation 6, 2 nitrogens give up only 3 oxygens (one of them staying with the potassium to form the  $K_2CO_3$ ), and 3 oxygens are taken from the water in order to carry the reaction to completion. In the complete reduction, therefore, 8 oxygens are required; that is, 1 nitrogen is equivalent to 4 oxygens.

The same conclusion can be obtained without the aid of equations and without recourse to the idea that oxygen must always be associated with oxidation and reduction. Oxidation can be defined as an increase in positive valence or a decrease in negative valence on the element oxidized; reduction as the converse.<sup>3</sup> In going from  $NO_3$  to  $NO_2$  or  $NH_3$ , nitrogen changes in valency. The nitrogen in nitrate has 5 positive valences; in ammonia 3 negative; in nitrite 4 positive; and in nitrogen gas no valence. The change from nitrate to ammonia is 8, to nitrite is 2, and to nitrogen 5, which being interpreted in terms of oxygen with 2

<sup>1</sup> Hale, THIS JOURNAL, 7 (1915), 763

<sup>2</sup> Marshall, "Microbiology," 1912, 264.

<sup>3</sup> Cady, "Inorganic Chemistry," 1912, 255

<sup>1</sup> J. Infect. Dis., 14, 488.

<sup>2</sup> THIS JOURNAL, 7 (1915), 762.



valences means 4, 1 and  $2\frac{1}{2}$ ; that is, if the reduction all proceeded to gaseous nitrogen the equivalents of oxygen available for each nitrogen in nitrate is  $2\frac{1}{2}$ ; if only ammonia was formed, 4 equivalents would be available; and if only nitrites 1 equivalent.

Assuming that the reduction goes to nitrites and ammonia, the oxygen available will be dependent upon the quantity of nitrites and of ammonia produced. If we start with one equivalent of nitrogen as nitrate, and assume varying percentages of  $\text{NO}_2$  formed we can get the oxygen value for the different percentage combinations of  $\text{NO}_2$  and  $\text{NH}_3$  present.

TABLE I

Eqvt. $\text{NO}_2$ formed.....	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Eqvt. $\text{NH}_3$ formed.....	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0.0
Eqvt. O available.....	4.0	3.7	3.4	3.1	2.8	2.5	2.2	1.9	1.6	1.3	1.0

If 50 per cent of the nitrogen goes to  $\text{NH}_3$ , the oxygen equivalent is 2.5.

Since bacteria in sewage vary, the percentages of reduction products obtained will not only vary with different sewages but will vary from day to day with the same sewage. That this is true is shown by the experiments of various investigators. Letts, Blake, and Totton<sup>1</sup> found that nitrogen is evolved, sometimes free and sometimes as nitric oxide. Guth and Keim<sup>2</sup> report the same products. Both of these investigators were unable to demonstrate an increase in free ammonia. Hoover<sup>3</sup> reports an increase of free ammonia and nitrites. Lederer<sup>4</sup> reports an increase of nitrites and free ammonia, the latter varying from 20 to 50 per cent.

TABLE II—FORMATION OF FREE AMMONIA DURING SALTPETER OXYGEN CONSUMPTION (a)

No.	Temp. of Incubation	Time of Incubation	N as free $\text{NH}_3$ Before	After	Per cent Increase
1.....	37° C.	3	7.2	9.2	30
2.....	37	3	8.3	12.4	41
3.....	37	3	12.4	14.4	16
4.....	37	3	10.8	15.2	40
5.....	37	3	14.0	16.4	15
6.....	37	3	12.0	14.8	23
7.....	20	5	7.2	10.0	40
8.....	20	5	8.8	11.6	24
9.....	20	5	12.4	12.8	3
10.....	20	5	10.8	15.2	50
11.....	20	5	14.0	18.0	29
12.....	20	5	12.0	17.6	47

(a) Lederer, *Am. J. Pub. Health*, **5**, 358.

Unfortunately, the quantity of nitrites and initial nitrates were not given, so the value of the nitrogen in terms of oxygen could not be calculated from these products.

In our laboratory, we have been unable to demonstrate the presence of any free nitrogen or nitric oxide. Nitrites and ammonia were found to be the only products of reduction.

TABLE III—REDUCTION PRODUCTS OF SALTPETER TREATMENT

SERIAL NO.	1	2	3	4	5	6	7	8	9	10
Incubation Temp.....	37	37	37	37	37	20	20	20	20	20° C.
Incubation Time.....	5	5	5	5	5	0	10	10	10	10
PER CENT INCREASE: Nitrogen.....	0	0	0	0	0	0	0	0	0	0
Ammonia.....	40	51	47	46	52	49	45	42	51	47

The increase in ammonia, however, may come from the hydrolysis of proteins and other complex nitrog-

enous organic compounds present in sewages, so that any calculations based on the increase in free ammonia are not very dependable. If, however, we can get comparable results on the reduction of nitrates and the reduction of available oxygen in absence of nitrates, we will have dependable data from which the oxygen equivalent of nitrogen in nitrates can be calculated. Such comparisons have been made by Hale and Melia, by Lederer<sup>2</sup> and by the writer.<sup>3</sup>

Hale and Melia could get consistent results with the sewage on which they were working only by assuming that one nitrogen was equivalent to 4 oxygens, basing their assumptions on Equations 1 and 2 above. From the considerations herewith presented, the nitrate must have been all reduced to  $\text{NH}_3$ , no nitrites being formed, in order for this value to be true.

Lederer, however, could get checking results with the dilution and nitrates method, by assuming that 1 nitrate nitrogen was equivalent to 2.5 oxygens. This is strictly in accord with his observations that both nitrites and ammonia are formed in the nitrate reduction. He further assumed that one nitrite nitrogen was equivalent to  $1\frac{1}{2}$  atoms of oxygens. According to the consideration that the nitrogen is the oxidizing agent, one nitrite nitrogen is equivalent to one oxygen.

Rideal<sup>4</sup> in his text book allows 2.5 atoms of oxygen for one atom of nitrogen, and Hoover at the Columbus Sewage Testing Station has employed the same value.

The weight of evidence, therefore, seems to be in favor of 2.5 atoms of oxygen for every nitrate nitrogen. The conclusion, however, can not be drawn that this value is applicable to all sewages. The most that can be said is that the percentages of reduction products in each of the sewages so far worked on were about the same, namely, about a 50 per cent increase in free  $\text{NH}_3$ . Other investigators might find a different oxygen value for nitrogen.

That is, each sewage, depending upon the bacteria and organic matter present, will reduce nitrates differently. The safest thing, therefore, in oxygen demand work is to determine experimentally the oxygen value for the nitrogen in nitrates for the sewage in question. This can be done best by conducting very carefully parallel determinations, using nitrates in one and oxygen in the other, as the oxidizing agent. All the precautions mentioned by Lederer<sup>5</sup> and others<sup>6</sup> should be followed in running the "Dilution" method.

From the data thus obtained, the oxygen equivalent of nitrogen in nitrate can be readily determined, and from the evidence so far presented the value obtained should not differ far from 2.5.

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<sup>1</sup> THIS JOURNAL, **7** (1915), 763.

<sup>2</sup> J. Infect. Dis., **14**, 487.

<sup>3</sup> THIS JOURNAL, **8** (1916), 403.

<sup>4</sup> "Sewage," 3rd Ed., **1906**, 131.

<sup>5</sup> THIS JOURNAL, **6** (1914), 882.

<sup>6</sup> Bruckmiller, *Ibid.*, **8** (1916), 403; **7** (1915), 762.

<sup>1</sup> Chem. News, **88** (1903), 182.

<sup>2</sup> Gesundh. Ing., **35** (1912), 52.

<sup>3</sup> Engineering News, **68**, 192, 452.

<sup>4</sup> Amer. J. Pub. Health, **5**, p. 357.

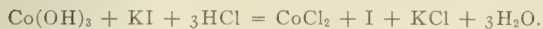
# A NEW VOLUMETRIC METHOD FOR THE DETERMINATION OF COBALT

By W. D. ENGLE AND R. G. GUSTAVSON

Received May 11, 1916

As the quantitative determination of nickel and cobalt in the presence of one another is difficult, this investigation was undertaken to find, if possible, simpler methods than those commonly used. It was hoped that volumetric methods might be found whereby either of these metals might be easily determined in the presence of the other. A very satisfactory method for cobalt has been found, but in the case of nickel nothing better than the methods already in use has so far been discovered.

In the presence of sodium or potassium hydroxide both nickel and cobalt are oxidized to trivalent oxides or hydroxides by various oxidizing agents, but neither trivalent nickel nor cobalt forms stable salts with acids. Both nickelic and cobaltic hydroxides, when treated with acids and potassium iodide, liberate iodine and form the nickelous or cobaltous salts, *e. g.*,



Of these two metals, cobalt is the more easily oxidized, and when oxidized, forms the more stable compounds. For example, cobalt sulfate treated with potassium hydroxide and hydrogen peroxide gives cobaltic hydroxide, while nickel under the same treatment is not changed even at the boiling point. A. Metz<sup>1</sup> uses this fact as a basis for the determination of cobalt. The difficulty in completely removing the excess of hydrogen peroxide either by boiling or filtering and washing, is an objection to this method. After trial of a number of oxidizing agents, sodium perborate proved to be the best, both because it completely oxidizes the cobalt without affecting the nickel and also because any excess of the reagent is readily decomposed by boiling.

The method recommended is as follows: The ore, or other material, may be dissolved with acids and the metals of the copper and iron groups and also manganese removed by standard methods. The solution so obtained may contain nickel and cobalt, zinc, and the metals of the alkalies and the alkaline earths, but must be free from any substances capable of liberating iodine from an acid solution of potassium iodide. This solution, with a volume of about 100 cc., is made acid with dilute sulfuric acid, using about 5 cc. in excess, and 1 or 2 g. of dry sodium perborate added. After agitation and solution of the perborate, sodium hydroxide is added to strong alkaline reaction and the mixture boiled for 10 min. to decompose the excess of perborate. The solution is now cooled to room temperature and, after 1 g. potassium iodide has been added, acidified with dilute sulfuric acid. After solution of the precipitate, the liberated iodine is titrated with a standard solution of sodium thiosulfate, using starch paste as an indicator.

As it is difficult to secure a cobalt compound of known cobalt content, it is recommended that the

sodium thiosulfate solution be standardized by means of potassium dichromate in the usual manner. Since  $1\text{K}_2\text{Cr}_2\text{O}_7 = 6\text{I} = 6\text{Co}$ , the  $\text{K}_2\text{Cr}_2\text{O}_7$  factor of the thiosulfate solution multiplied by 1.207 gives its cobalt factor.

If a cobalt compound of known purity is available, it may be used to standardize the sodium thiosulfate solution by taking a weighed quantity and treating, as in the regular method, with sodium perborate and sodium hydroxide. After boiling for 10 mins., cool, add potassium iodide and acidify with dilute sulfuric acid; titrate the free iodine with the thiosulfate solution and compute its factor. By this method 0.1613 g. of cobalt as cobalt sulfate required 35.25 cc. of the sodium thiosulfate solution, making its factor 0.004575 while its factor as determined by the potassium dichromate method was 0.004568.

The results of a few of the analyses of mixtures of cobalt and nickel are given in Table I. The cobalt used was a solution of pure cobalt sulfate containing 0.00978 g. of cobalt per cc. The nickel used was a solution of nickel sulfate free from cobalt and contained 0.00908 g. of nickel per cc. The titrations checked one another within a 0.1 cc. and wide variations in the amounts of the sulfuric acid, sodium perborate, etc., used did not affect the results. It may be noted that the process is accurate for widely different amounts of cobalt and also in the presence of large quantities of nickel.

TABLE I.—DETERMINATION OF COBALT IN THE PRESENCE OF NICKEL

Expt. No.	GRAM NICKEL	GRAM COBALT	
	PRESENT	Present	Found
1.....	0.0454	0.000	0.000
2.....	0.0908	0.000	0.000
3.....	0.0000	0.0489	0.0492
4.....	0.0000	0.0489	0.0487
5.....	0.0908	0.0489	0.0490
6.....	0.0454	0.0489	0.0491
7.....	0.4540	0.0489	0.0491
8.....	0.4540	0.0489	0.0495
9.....	0.0908	0.0978	0.0977
10.....	0.0908	0.0978	0.0982
11.....	0.0000	0.1467	0.1470
12.....	0.0908	0.1467	0.1466
13.....	0.0000	0.1956	0.1950
14.....	0.2270	0.1956	0.1955
15.....	0.0000	0.2445	0.2439

The following points in this analysis must be carefully observed to obtain accurate results: It is necessary to add the sodium perborate to the acid solution and then make alkaline. Attempts to add the perborate to the alkaline solution resulted in incomplete oxidation of the cobalt when the amount present was more than 0.050 g. It is necessary to add the potassium iodide before adding the dilute sulfuric acid for the solution of the cobaltic hydroxide, otherwise the results will be low. This method does not require the filtration of the cobaltic hydroxide, which is important not only in saving time, but in increasing the accuracy, as this compound tends to pass through the filter during the last part of the washing.

It was attempted to determine nickel and cobalt together by an analogous method using more powerful oxidizing agents such as bromine water and sodium persulfate. These experiments were not successful, due to the difficulty of completely removing the excess of the oxidizing agent. The nickelic and cobaltic hydroxides, which are readily formed, require filtra-



tion and excessive washing and even after prolonged washing the results were usually high. Cobalt free from nickel gave good results when oxidized with bromine water, but even here the washing required was excessive and the method is much inferior to the one given above using sodium perborate.

In conclusion we would state that cobalt may be determined in the presence of nickel by oxidation in alkaline solution with sodium perborate, removing the excess of the perborate by boiling, and after the addition of potassium iodide and dilute sulfuric acid, titrating with a standard sodium thiosulfate solution.

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### THE COMPOSITION OF SOUND AND FROZEN LEMONS WITH SPECIAL REFERENCE TO THE EFFECT OF SLOW THAWING ON FROZEN LEMONS

By H. S. BAILEY AND C. P. WILSON

Received May 29, 1916

#### INTRODUCTORY

The work described below was undertaken as a result of the freeze of January 6, 1913, which destroyed a portion of the citrus crop of Southern California and was especially severe on lemons.

While no temperature charts were made at San Dimas, the district from which the material was collected, Mr. Woods, foreman of the San Dimas lemon house, says: "On the 6th of January, the day preceding the freeze, there was a very high wind and the temperature went below the freezing point early in the evening. A low temperature was maintained until 6.30 next morning, when it began to move up."

That the injury to lemons, which almost always follows a heavy freeze, is due to a rapid thawing of the frozen fruit, rather than to the low temperature to which they have been subjected, seems to be the general opinion of citrus growers. This assumption is apparently substantiated by the fact that in groves where a night of frost is followed by a warm, bright day, the damage is greater than in orchards which have suffered an equally low temperature during the night but warmed up more slowly the following day. In other words, when a cloudy morning or a heavy smudge blanket keeps the groves cool until toward noon, the fruit is less injured by a freezing night than if the sun comes out hot early in the day. This is in harmony with the well-known fact that living animal tissues suffer greater injury from freezing if the thawing out be rapid than when it takes place gradually.

In the hope of obtaining further data upon the effect of gradual thawing upon frosted citrus fruit, Mr. Horsford, Manager of the San Dimas Lemon Association, had a quantity of the fruit which was frozen on the night of January 6, 1913, picked, beginning at 7 o'clock the following morning and continuing nearly all that day. This was stored as fast as gathered in the packing house at a temperature of 45 to 50° F., where it would thaw slowly. At the time the freeze occurred there was already in storage in his house a quantity of sound lemons picked two days previously and several boxes of these were set

aside for comparison later with frozen fruit. To supply the third set of samples, that of frozen fruit thawed rapidly, several trees were left unpicked in the orchard, from which were gathered the frosted lemons for storage. An opportunity was thus afforded to make a comparative study of fruit picked before the frost, and therefore, normal; fruit picked and stored immediately after the frost; and frozen fruit remaining on the trees. All this fruit came from the same grove of Eureka lemons.

#### DESCRIPTION OF SAMPLES ANALYZED

One packing box of fruit picked January 4, two days before the freeze, and one box picked January 7, the day after the freeze; were selected and placed side by side in storage at a temperature of 45 to 50° F. Beginning January 16, a sample of a dozen or more lemons was taken at random from each box and another dozen picked fresh from the grove. These were wrapped in the regular tissue paper wrappers, packed in a wooden box, and sent by express to the Citrus By-Products Laboratory in Los Angeles, and analyzed as soon as possible after being received. Similar series of samples were taken at intervals of about a week until the first of May following.

#### METHODS OF ANALYSIS

**SPECIFIC GRAVITY OF FRUIT**—When received, the lemons were weighed on a torsion balance and immediately put in a battery jar filled with water and covered with a ground glass plate to remove all surplus water. The fruit was then taken out and the jar refilled with water, the amount thus required being equal to the volume of the fruit. From the weight of the fruit and volume of water it displaced, the specific gravity was calculated.

**APPEARANCE OF FRUIT**—The lemons were cut in halves with a sharp knife and the condition of the cell structure noted. Perfect lemons, showing no evidence of having been frosted, are designated as "Sound," those in which about 20 per cent of the cells appeared desiccated, that is, dried and shriveled, due to having been injured by the frost or the resulting thawing of the frozen tissues, "Slightly frozen." The remainder, where the cut surface showed more than 20 per cent of the cells affected, were considered badly frozen and so denoted.

**PERCENTAGE OF JUICE**—After this examination the half lemons were wrapped in a heavy canvas press cloth, 24 in. square, and squeezed in a hydraulic press with about 1500 lbs. pressure. The juice and pulp were collected and weighed separately and the percentage of each obtained. Owing to the fact that an appreciable amount of juice was absorbed and retained by the press cloth, the more exact figure for the quantity actually present in the fruit was obtained by deducting the weight of the pulp from that of the original lemons. This figure, divided by the weight of fruit pressed, gives the calculated percentage of juice and is the value so tabulated. These figures were used in calculating the percentage of citric acid in the fruit, which probably makes these latter values a little higher than would be obtained had the samples been larger.

**SPECIFIC GRAVITY OF JUICE**—The specific gravity of the juice was determined at 20° C. by means of a spindle.

**ACIDITY OF JUICE**—Immediately after taking the specific gravity 10 cc. of the juice were pipetted from the cylinder and titrated against  $N/2$  sodium hydroxide solution, phenolphthalein being used as an indicator. From the specific gravity and the acid equivalent thus obtained, the percentage of acid as citric, plus one molecule of water, was calculated.

**SOLIDS IN JUICE**—Solids were determined in the juice by drying 10 cc. in lead dishes for 8 hrs. in an air bath at about 95 to 100° C. Owing to the difficulty in controlling the oven and the action of the acid on the metal dishes, the solids determinations are probably only approximations.

#### ANALYTICAL RESULTS

The results are given in the accompanying tables and show the effect of the frost on the stored and unstored fruit. It is true that the sound lemons were in storage two days earlier than the frozen ones, but this would have very little, if any, effect upon the relative condition of the two lots at the time the first analysis

figures obtained for the entire sample. Too much importance must not be given to the individual determination.

As has already been intimated this work was undertaken without previous preparation, on the spur of the moment, when the material became available. It is perfectly obvious that instead of the small samples of a dozen lemons, at least an entire box should have been used for each analysis, but under the circumstances samples of this size were out of the question.

TABLE II—COMPARISONS OF SPECIFIC GRAVITIES, JUICES AND CITRIC

Date Anal- ysis	SPECIFIC GRAVITIES OF FRUIT			ACID CONTENTS JUICE YIELD Per cent			PER CENT CITRIC ACID In Juice In Fruit					
	SU	FS	FT	SU	FS	FT	SU	FS	FT	SU	FS	FT
1/21	0.933	0.914	0.837	49.6	42.4	41.1	6.5	6.9	5.1	3.2	2.9	2.1
1/25	0.913	0.886	0.789	37.4	39.5	31.9	7.2	6.6	5.3	2.7	2.6	1.7
2/3	0.920	0.886	0.779	42.1	35.9	26.5	7.1	7.3	5.3	3.0	2.6	1.4
2/7	0.940	0.923	0.710	44.8	34.3	28.7	6.8	6.9	4.5	3.0	2.4	1.3
2/13	0.952	0.920	0.729	41.4	33.9	25.3	7.0	6.8	4.7	2.9	2.3	1.2
2/18	0.951	0.904	0.701	46.2	45.5	29.8	7.3	7.2	4.8	3.4	3.3	1.4
2/25	0.944	0.870	0.724	42.8	35.2	28.4	7.2	6.6	4.1	3.0	2.3	1.2
2/27	0.931	0.898	0.773	40.1	35.6	31.6	7.4	6.8	4.9	3.0	2.4	1.5
3/4	0.926	0.882	0.730	41.4	36.9	26.3	7.3	7.6	4.8	3.0	2.8	1.3
3/7	0.967	0.894	0.714	42.7	32.4	26.3	7.3	7.2	3.7	3.1	2.3	1.0
3/11	0.913	0.870	0.713	40.2	36.7	33.3	7.4	7.1	4.1	3.0	2.6	1.4
3/14	0.949	0.879	0.682	40.7	35.3	30.0	7.4	7.3	3.7	3.0	2.6	1.1
4/9	0.954	0.920	0.713	39.7	37.3	26.1	8.2	7.8	4.7	3.3	2.9	1.2
4/16	0.934	0.840	0.753	44.1	33.9	34.8	8.3	7.3	4.1	3.7	2.5	1.4
4/25	0.968	0.918	0.766	48.3	39.4	35.0	7.6	7.6	4.1	3.7	3.0	1.4
5/2	0.991	0.889	0.722	33.3	36.5	31.6	8.1	7.4	4.3	2.7	2.7	1.4

TABLE I—ANALYSES OF UNFROZEN LEMONS, FROZEN LEMONS THAWED SLOWLY AND FROZEN LEMONS ALLOWED TO REMAIN ON THE TREES

			Sp. Gr.	PER CENT OF JUICE Ob- tained	Sp. Gr.	PER CENT IN JUICE	Per cent Citric Acid		
Fruit	Date of Picking (a)	Time (b)	Lemons		Juice	Citric Acid Solids			
SU	Jan. 4	15 days	0.933	9.0	49.6	1.041	6.5	8.8	3.22
FS	Jan. 21		0.914	23.1	42.4	1.041	6.8	9.5	2.92
FT	Jan. 16		0.837	29.4	41.1	1.037	5.1	8.8	2.10
SU	Jan. 4	19 days	0.913	27.0	37.4	1.040	7.2	9.5	2.69
FS	Jan. 25		0.886	30.0	39.5	1.040	6.6	9.5	2.61
FT	Jan. 24		0.789	24.9	31.9	1.036	5.3	8.9	1.69
SU	Feb. 4	28 days	0.920	27.6	42.1	1.038	7.1	9.1	2.99
FS	Feb. 3		0.880	27.7	35.9	1.041	7.3	9.8	2.62
FT	Feb. 1		0.779	19.1	26.5	1.038	5.3	9.9	1.40
SU	Jan. 4	32 days	0.940	37.1	44.8	1.036	6.8	9.6	3.05
FS	Feb. 7		0.923	31.1	34.3	1.037	6.9	9.0	2.37
FT	Feb. 6		0.710	26.2	28.7	1.032	4.5	8.0	1.29
SU	Jan. 4	38 days	0.952	28.7	41.4	1.040	7.0	9.0	2.90
FS	Feb. 13		0.920	33.9	39.9	1.038	6.8	9.4	2.30
FT	Feb. 12		0.729	21.2	25.3	1.032	4.7	8.3	1.19
SU	Jan. 4	40 days	0.951	37.1	46.2	1.041	7.3	9.5	3.37
FS	Feb. 7		0.904	21.1	45.5	1.038	7.2	9.3	3.28
FT	Feb. 14		0.701	19.9	29.8	1.032	4.8	7.9	1.43
SU	Jan. 4	50 days	0.944	33.1	42.8	1.040	7.2	9.1	3.08
FS	Feb. 25		0.870	35.2	41.4	1.040	6.6	9.1	2.32
FT	Feb. 20		0.724	24.1	28.4	1.030	4.1	8.4	1.16
SU	Jan. 4	52 days	0.931	30.6	40.1	1.042	7.4	9.6	2.97
FS	Feb. 27		0.898	30.3	35.6	1.040	6.8	9.2	2.42
FT	Feb. 26		0.773	28.5	31.6	1.031	4.9	7.6	1.55
SU	Jan. 4	57 days	0.926	33.6	41.4	1.044	7.3	9.9	3.02
FS	Mar. 4		0.882	23.6	36.9	1.045	7.6	9.9	2.80
FT	Mar. 3		0.730	21.6	26.3	1.033	4.8	7.6	1.26
SU	Jan. 4	60 days	0.967	27.6	42.7	1.042	7.3	9.5	3.12
FS	Mar. 7		0.894	26.2	32.4	1.044	7.2	9.9	2.33
FT	Mar. 7		0.714	21.1	26.3	1.028	3.7	6.5	0.97
SU	Jan. 4	64 days	0.913	25.4	40.2	1.042	7.4	9.3	2.97
FS	Mar. 11		0.870	25.0	36.7	1.045	7.1	9.9	2.61
FT	Mar. 10		0.713	33.3	33.2	1.032	4.1	7.3	1.36
SU	Jan. 4	67 days	0.949	27.1	40.7	1.042	7.4	8.1	3.01
FS	Mar. 14		0.879	23.2	35.3	1.046	7.3	8.4	2.58
FT	Mar. 12		0.682	19.0	30.0	1.030	3.7	6.8	1.11
SU	Jan. 4	93 days	0.954	27.7	39.7	1.046	8.2	9.7	3.26
FS	Apr. 9		0.920	33.4	37.3	1.046	7.8	9.6	2.91
FT	Apr. 7		0.713	23.7	26.1	1.032	4.7	6.9	1.23
SU	Jan. 4	100 days	0.934	31.8	44.1	1.050	8.3	10.2	3.66
FS	Apr. 16		0.840	30.3	33.9	1.046	7.3	9.4	2.47
FT	Apr. 15		0.753	32.4	34.8	1.031	4.1	6.8	1.43
SU	Jan. 4	109 days	0.968	35.3	48.3	1.048	7.6	10.5	3.67
FS	Apr. 25		0.918	37.8	39.4	1.046	7.6	10.2	2.99
FT	Apr. 23		0.766	27.5	35.0	1.026	4.1	6.8	1.43
SU	Jan. 4	116 days	0.991	32.3	33.3	1.046	8.1	9.3	2.70
FS	May 2		0.889	31.7	36.5	1.045	7.4	10.0	2.70
FT	May 1		0.722	30.2	31.6	1.030	4.3	7.2	1.37

(a) SU, stored unfrozen fruit; FS, frozen stored fruit; FT, frozen fruit left on tree (picked generally 1 or 2 days before analysis).

(b) Time between freeze and analysis, and date of analysis.

was made, 15 days after the freeze. Owing to the small samples used for analysis, peculiarities in individual lemons had an undue influence upon the

Disregarding then the great irregularities in the individual figures, it is evident that the frozen fruit stored immediately after freezing is much more like the unfrozen fruit than like the frozen fruit left on the trees. The specific gravity of the fruit and the percentage of acid in the juice are nearly the same for the two lots in storage, while these values for frozen fruit left on the trees are considerably lower. The percentage of juice in the frozen fruit in storage is about a mean between that of the unfrozen fruit in storage and the frozen fruit on the trees.

The figures show that the frozen fruit which remained in the orchard is not nearly so rich in citric acid as the sound fruit or as that frozen but immediately placed in cold storage. This fact is of special importance to those interested in the manufacture of citrus by-products, and is fully confirmed by the work, on a much larger scale, of the By-Products Laboratory in the manufacture of citric acid from the frozen fruit of the 1913 crop. The amount of citric acid in the juice of one ton of frozen lemons, taking the figures from twelve runs of fruit between January 18, 1913, to May 19, 1913, varied from 14.03 lbs. to 30.14 lbs., with an average of 20.16 lbs. Corresponding figures on four runs of sound lemons from April 18, 1914, to June 8, 1914, were 42.75, 49.44, 46.56 lbs. citric acid in juice of one ton of lemons. In this connection, however, it should be mentioned that there is apparently no decrease in the oil content of lemons due to freezing, and that ton for ton the more frozen and consequently lighter the fruit the greater the yield of oil. It has been pointed out that the frozen fruit remaining on the trees decreased in specific gravity and its juice in percentage of solids and acidity. Thus the increasing lightness in the orchard fruit is evidently due both to the decrease in the amount of juice actually present and the percentage of total solids in the juice.



There is but little change in the specific gravity of the fruit held in storage during the first 60 to 70 days, and even up to the end of the experiment the increase is slight and may be accounted for by a normal drying-out or withering of the fruit. But with the fruit that remained on the tree there is at first a very marked decrease in specific gravity and then apparently a gradual increase. It was noticed in cutting this orchard fruit that during the latter half of the observation period the lemons appeared to be filling out a little.

#### SUMMARY

In so far as a preliminary experiment of this kind can be considered as giving definite results, the following conclusions may be drawn:

I—The lemons that remained on the trees after being frozen retained less juice and considerably less acid than the fruit picked immediately after being frozen and stored at a temperature of 45 to 50° F.

II—The frozen fruit left on the trees decreased rapidly in specific gravity due to the loss of juice and acid and the formation of thick, puffy skins, dried-up cells and hollow centers.

III—Lemons picked immediately after being frozen and stored under ordinary packing house conditions retained somewhat less juice than the unfrozen fruit, but the composition of the juice was nearly the same, and in weight and appearance the slowly thawed lemons compared well with normal fruit.

We wish to acknowledge our indebtedness to Mr. G. W. Hosford of the San Dimas Lemon Association for his valuable suggestions and hearty coöperation, and to the association for so generously supplying us with the fruit used in this investigation.

BUREAU OF CHEMISTRY, WASHINGTON

### AN IMPROVED METHOD FOR THE DETECTION OF ARACHIDIC ACID

By ROBERT H. KERR

Received May 16, 1916

The method described below for the detection of arachidic acid in peanut oil and mixtures of oils containing peanut oil has been found to offer certain advantages over the Renard method adopted by the Association of Official Agricultural Chemists. These advantages consist in greater convenience, lessening of the number of operations, reducing the amount of attention required, and avoidance of the use of ether.

#### REAGENTS

*Potassium Hydroxide Solution*—Dissolve 100 g. of stick potassium hydroxide in 100 cc. of water.

*Magnesium Acetate Solution*—Dissolve 10 g. of magnesium acetate in a mixture of 100 cc. distilled water and 100 cc. of 95 per cent alcohol.

*Acetic Acid Solution*—Mix 50 cc. glacial acetic acid with 150 cc. of 95 per cent ethyl alcohol.

*Sulfuric Acid Solution*—Mix 50 cc. concentrated sulfuric acid with 150 cc. of distilled water.

*90 per cent Ethyl Alcohol* (by volume).

#### METHOD

Weigh out 20 g. of the oil to be tested in a 300 cc. Erlenmeyer flask, pour in 200 cc. of 95 per cent ethyl alcohol, and heat to boiling on the steam bath. When the alcohol is boiling add 10 cc. of the potassium hydroxide solution. Saponification begins immediately and is soon complete. After the saponification has been completed add a few drops of phenolphthalein and neutralize the excess alkali with the alcoholic solution of acetic acid. Next add 50 cc. of the 5 per cent magnesium acetate solution and heat the whole mixture to boiling. Allow to cool to room temperature with occasional shaking and then place in a refrigerator at a temperature of 10 to 15° C. and leave until next day. Filter off the solution, wash the precipitate twice with 50 per cent alcohol and three times with distilled water, and return to the flask in which precipitation took place. Pour 100 cc. of hot distilled water into the flask and add sufficient dilute sulfuric acid to decompose the magnesium salts. Heat until the separated acids form a clear layer. Cool the flask, pour off the acid solution, add 100 cc. of hot water. When the fatty acids have melted and solidified, pour off water as before. Free the cake of acids of water as far as possible by draining; dissolve in 100 cc. of 90 per cent alcohol and separate the arachidic acid by crystallization, according to the present provisional method of the Association of Official Agricultural Chemists as given in *Bulletin 107*, Revised, Bureau of Chemistry, p. 146.

The method as outlined above has been used on a number of samples of peanut oil and mixtures of peanut and other vegetable oils. The results obtained are qualitative only, no attempt having been made to apply the method for quantitative purposes. It has been found to be capable of detecting 5 per cent of peanut oil in olive oil, cottonseed oil, soy bean oil and corn oil. These results are quite as good as the best which have ever been obtained with Renard's method.

BUREAU OF ANIMAL INDUSTRY, WASHINGTON

### THE HYDROLYSIS OF ETHYL-SULFURIC ACID AND THE ASSAY OF AROMATIC SULFURIC ACID, U. S. P.

By W. B. D. PENNIMAN, W. W. RANDALL, C. O. MILLER AND L. H. ENSLOW  
Received September 1, 1916

Aromatic sulfuric acid is a mixture of sulfuric acid, ethyl-sulfuric acid, certain aromatics and alcohol. It is prepared by bringing together, according to the U. S. Pharmacopoeia, 111 cc. of concentrated sulfuric acid and 700 cc. alcohol, and, after the mixture has cooled, adding 50 cc. of tincture of ginger, 1 cc. of oil of cinnamon, and sufficient alcohol to bring the total volume up to one liter. The proportion of ethyl-sulfuric acid present depends upon the strength of the sulfuric acid and alcohol used and upon the length of time the mixture remains hot, and probably increases the longer the liquid stands, even when cold.

The Pharmacopoeia (Eighth Revision) is not concerned with the ethyl-sulfuric acid: its only demand is that the mixture shall contain not less than 20

per cent, by weight, of sulfuric acid,  $\text{H}_2\text{SO}_4$ , after the ethyl-sulfuric acid has been completely hydrolyzed by the action of water.

The method of assay made standard by the Pharmacopoeia has varied in some of its details with each of the recent editions. In the Eighth Revision (September, 1905) the analyst was directed to mix 10 g. of aromatic sulfuric acid with 30 cc. of water and to boil this mixture "for several minutes," after which the total acid present (assumed now to be sulfuric) was to be determined by means of titration with a standard solution of alkali. In the Supplementary Revision of 1907 the only change made was that the words "for four hours" were substituted for "for several minutes." In the Ninth Revision, about to appear, the requirement will be "free sulfuric acid and ethyl-sulfuric acid together equivalent to not less than 19 per cent nor more than 21 per cent of  $\text{H}_2\text{SO}_4$  (98.09)." The method of assay is also changed and directs that a known weight (which will be about 9 grams) of aromatic sulfuric acid shall be mixed with six times its volume of water, boiled for six hours in a flask fitted with a reflux condenser, and later titrated with standard solution of alkali.

In an article published four years ago, L. A. Brown<sup>1</sup> called attention to the fact that the methods of assay given in the U. S. Pharmacopoeia (8th Revision, 1905, and Supplementary Revision, 1907) fail to determine all the sulfuric acid present. Accordingly, Brown advocated a method in which all free acid present (sulfuric and ethyl-sulfuric) is first determined by titration; by the action of hydrochloric acid and barium chloride the alkali sulfate and ethyl-sulfate thus formed are converted into barium sulfate and the yield of the latter salt determined by weighing. It is thus possible to determine the total acid present, calculated as sulfuric, and also the proportion of ethyl-sulfuric acid.

In trying out this method, Brown analyzed a "standard sample of aromatic sulfuric acid," but does not inform us what its acid strength actually was. By the U. S. Pharmacopoeia method the percentage found was 18.40 in each of two determinations; by his method the percentages found were 20.18, 19.73, and 19.80, respectively. Again, he records the results obtained on analyzing by both methods a series of commercial samples, but as we have no means of knowing the actual strength of any of these, the only safe conclusion we can draw is that the U. S. Pharmacopoeia method is faulty and that Brown's method is more nearly accurate; we are not in a position to say that a satisfactory method has been found. Only where a series of assays upon a sample of known strength yield closely agreeing results are we to claim that the goal has been attained.

Brown concludes from his work that diethyl sulfate is one of the constituents of aromatic sulfuric acid, at any rate after long standing. If, as seems to the present writers, this conclusion has for its basis the fact that his analytic method failed to show the presence of all the sulfuric acid originally used, it rests

upon a doubtful foundation. The work of Claesson<sup>1</sup> and that of Villiers<sup>2</sup> seem to prove that, in order that diethyl sulfate shall be formed, absolute alcohol and very concentrated sulfuric acid must be employed, and that diethyl sulfate decomposes comparatively readily when heated with either water or alcohol. The fact that it yields alcohol and ethyl-sulfuric acid when heated in the presence of water, would appear to disprove Brown's assumption that such part of the sulfuric acid as could not be recovered as such, was locked up in the form of diethyl sulfate at the end of the boiling process.

It fell to the chemists of this bureau this summer to determine the strengths of a large number of samples of aromatic sulfuric acid purchased from retail druggists. Making use of the U. S. Pharmacopoeia (1907 Revision) method, it was soon found that few of the samples would show results which could be considered as satisfying the demands of the Pharmacopoeia. Table I gives the percentage figures for a series of samples of various strengths as found by this method and, below them, the figures obtained by the method soon to be described.

TABLE I—PERCENTAGES OF TOTAL ACID ASSUMED TO BE SULFURIC, BY TWO METHODS

Sample	11297	11300	11388	11391	11393	11394	11395	11396	11397	11398
U. S. P. (1907)	23.68	17.13	16.77	11.86	15.92	14.30	15.00	15.76	12.96	17.34
Maryland	25.58	19.08	19.76	14.24	21.74	17.76	18.09	19.91	16.79	20.29
Diff.	1.90	1.95	2.99	2.38	5.82	3.46	3.09	4.15	3.83	2.95

It will be seen that, if judged by the U. S. Pharmacopoeia method, only one out of the ten samples is satisfactory, and that the other nine give figures from 2.66 to 8.14 per cent too low. On the other hand, judged by the improved method, three samples are satisfactory, two approximate 20 per cent, and the worst is 5.76 per cent short of the required amount.

Our attention having been called to the revised method to become standard with the publication of the Ninth Revision of the Pharmacopoeia, a series of assays upon samples of unknown strength was carried out, the amount of added water being increased to 6 volumes and the time of boiling with reflux condenser lengthened to 6 hrs. Under "Ninth Revision Method" in Table II are given the results of duplicate assays and the differences between them, while another column contains the figures found by our revised method:

TABLE II—PERCENTAGE OF TOTAL ACID, ASSUMED TO BE SULFURIC

Lab. No.	NINTH REVISION A	U. S. P. METHOD B	DIFF.	MARYLAND METHOD
11051	10.39	11.49	1.10	12.47
11092	15.89	20.70	4.81	23.22
11101	16.48	18.45	1.97	20.41
11108	15.82	17.65	1.83	18.56
11112	22.72	23.90	0.18	23.97
11122	13.66	14.50	0.84	15.24
11125	17.90	18.75	0.85	20.59
11128	26.19	26.90	0.71	27.57
11139	17.60	18.40	0.80	19.84
11148	24.52	24.30	0.22	25.53
11151	30.92	31.80	0.88	32.72
11166	14.24	14.60	0.36	17.01
11175	16.74	17.25	0.51	19.40
11184	11.85	14.75	2.90	16.16
11190	22.90	23.00	0.10	25.26
11195	27.02	27.80	0.78	28.52

It will be noted that parallel determinations by the new U. S. Pharmacopoeia method rarely showed

<sup>1</sup> THIS JOURNAL, 4 (1912), 512.

<sup>1</sup> J. prakt. Chem., [2] 19, 257; Ber., 13, 1699.

<sup>2</sup> Bull. soc. chim., 34, 26.



satisfactory agreement, and that, judged by our method, all these results are too low.

For a thorough study of the two standard (U. S. P.) methods of assay, there was prepared a standard aromatic sulfuric acid, in accordance with the Pharmacopoeia. A careful specific gravity determination was made in the case of the acid, of the alcohol and of the final product; and a weighed amount of the sulfuric acid used was titrated against standard alkali solution. From these data the percentage of total acid, assumed to be sulfuric, in the product was calculated to be 20.14. With this standard material the three series of experiments indicated in Table III were conducted.

TABLE III—EFFECT OF VARIOUS TREATMENTS

Results in Percentages Total Acid, Assumed to be Sulfuric					
(1) BOILED UNDER REFLUX CONDENSER			(2) SLOW EVAPORATION IN THE COLD		(3) BOILED UNDER REFLUX CONDENSER
No.	Hrs.	Water Added	No.	Hrs.	Results
1	2	17.23	1	24	17.23
2	1	17.56	2	48	17.23
3	2	17.67	3	72	17.23
4	4	18.32	4	144	19.64
5	6	18.81			
6	12	19.49			
7	18	19.63			
8	24	19.79			
		6 Vols.			Results
		17.23			10
		17.67			20
		18.32			25
		18.81			30
		18.70			40
		19.63			50
		19.85			60
		19.90			70
					19.41

It will be seen that in Series 1 all the sulfuric acid was not recovered even after 24 hours' boiling. While, on the whole, better results were obtained when a larger proportion of water was added to decompose the ethyl-sulfuric acid, this outcome may be chargeable to some other cause.

In Series 2, weighed amounts of the standard aromatic sulfuric acid (to each of which 6 volumes of water had been added) were placed, cold, in a vacuum desiccator over sulfuric acid and left for different periods of time before titration. The results seem to show that the decomposition of the ethyl-sulfuric acid begins only after a certain concentration has been reached, and then proceeds slowly towards completion. This will be referred to again.

Series 3 had to do with the effect of varying proportions of water to acid, time of heating remaining constant. In each case 5 g. of aromatic sulfuric acid were boiled for 6 hrs. in a flask under a reflux condenser, after the addition of the quantities of water indicated. The results fail to show that any appreciable advantage is to be secured by the addition of 6 volumes of water in place of 3.

Finally, two 5-gram quantities of the standard aromatic sulfuric acid were each mixed with 15 cc. of water: one was titrated at once, the other after standing in the cold for 48 hrs. In each case the percentage of total acid, assumed to be sulfuric, was 16.96.

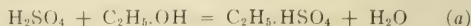
As a result of these various experiments, the following conclusions appear to be justified:

1—The ethyl-sulfuric acid in aromatic sulfuric acid is not appreciably hydrolyzed on standing mixed with cold water.

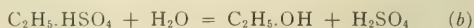
2—This ethyl-sulfuric acid is slowly hydrolyzed, after dilution with water, as a result of prolonged boiling under a reflux condenser, the decomposition never, however, becoming complete, no matter how much water may have been added. Hence the Pharma-

copoeia method will always give low results, the actual figure obtained being apparently dependent largely upon the rate of boiling and the efficiency of the condenser.

These same conclusions might be drawn as the result of the following considerations: The reaction between sulfuric acid and alcohol is expressed by the equation



The acid must be at least fairly strong and the alcohol must not contain much water. Again, ethyl-sulfuric acid is decomposed, to some extent perhaps in the cold, to a large extent when heated, in contact with water, with the formation of sulfuric acid and alcohol,



The reaction is reversible, and should be expressed as follows:



Reaction (a) begins upon mixing the acid with alcohol, and continues. The accumulation of water, however, soon starts reaction (b), which develops until, in a given period of time, as much ethyl-sulfuric acid is being decomposed as is being formed. After this point has been reached, the composition of the mixture remains constant and equilibrium is established among the four reacting substances. The relative amounts of sulfuric and ethyl-sulfuric acid in the resulting mixture will therefore depend, physical conditions being the same, upon the amount of water originally present in the sulfuric acid and in the alcohol. It is a well-known fact that fuming sulfuric acid and absolute alcohol yield a high proportion of ethyl-sulfuric acid and that dilute sulfuric acid has little or no effect upon alcohol.<sup>1</sup> Could we remove the water as fast as it is formed in accordance with reaction (a), we should be able to secure a 100 per cent yield of ethyl-sulfuric acid. Similarly, were we able to remove the alcohol formed in reaction (b) as fast as it is produced, we should secure a complete decomposition of the ethyl-sulfuric acid present. Now this is just the problem before us. The U. S. Pharmacopoeia assay method is not successful, because it fails to bring about the removal of the alcohol already present as such in the aromatic sulfuric acid, or that is being formed through hydrolysis of ethyl-sulfuric acid. The reflux condenser, in so far as it is efficient, prevents the escape of the very reagent whose presence renders impossible the completion of the reaction.

Even the best of our water-jacketed condensers probably allows the escape of slight quantities of alcohol-vapor, and hence in process of time the hydrolysis may be complete. The experiments reported in Table IV were undertaken to see if evidence of a state of equilibrium among the four reacting substances could be secured. Five-gram quantities of aromatic

<sup>1</sup> Thus in one of our experiments dilute sulfuric acid (1 of acid to 36 of water, by volume) was boiled continuously for 6½ hrs. with a mixture of alcohol and extract of ginger; samples were removed from time to time and titrated. Not the slightest change in the strength of the acid could be detected.

sulfuric acid were heated with 3 volumes of water in sealed glass tubes, in a bath of boiling water, for different periods of time, after which the tubes were cooled and opened and their contents titrated. (The percentage of acid in this preparation, after complete hydrolysis, was 24.94.)

TABLE IV—TIME REQUIRED FOR EQUILIBRIUM

Hrs. heated	1	2	3	4	5	6	7	8
% Acid found	18.57	21.66	21.77	22.60	24.08	24.10	24.08	24.10
% of Total								
Acid recoverable }	74.46	86.85	87.29	90.61	96.55	96.63	96.55	96.63

Apparently equilibrium in the system—sulfuric acid, ethyl-sulfuric acid, alcohol, water—for the concentrations peculiar to these experiments and at the temperature of boiling water, was attained after ten hours' heating. From this time on about 3.4 per cent of the sulfuric acid present remained in the form of ethyl-sulfuric acid, in spite of the presence of a relatively very large volume of water.

The problem is, therefore, after all very simple. We have only to heat a weighed quantity of aromatic sulfuric acid, after dilution with water, in such fashion that the alcohol vapors may escape, and for such a time that all ethyl-sulfuric acid shall have been decomposed.

In Table V are given the results of a series of experiments in which some of the ideas expressed above were tested. In each case 5 g. of the standard aromatic sulfuric acid (20.14 per cent) were heated with 30 cc. of water, the period of heating ranging from 2 to 8 hrs.

TABLE V—COMPARISON OF RESULTS USING REFLUX CONDENSERS OR WATCH GLASS COVERS ON FLASKS, AND HEATING BY FREE FLAME OR ON WATER BATH

Heated Hrs.	REFLUX CONDENSERS		WATCH GLASS COVERS	
	Free Flame	Water Bath	Water Bath	Water Bath
2.....	18.74	18.73	17.53	17.58
4.....	18.97	19.18	17.88	17.86
6.....	19.46	19.34	17.86	18.01
8.....	19.61	19.44	18.50	19.14

It is clear that much better results are obtained by the watch glass method, than where a condenser is used; also that continuous heating for more than two hours was necessary, in this method, to bring about the hydrolysis of all the ethyl-sulfuric acid.

A weighed amount of the standard aromatic sulfuric acid was mixed with 3 volumes of water and slowly boiled for 3 hrs. in a flask fitted with a Hempel tube and condenser. The alcohol was thus slowly distilled off and the water vapor, condensed in the Hempel tube, returned to the flask. Titration of the residual liquid gave for the total acid percentage, calculated as sulfuric, 19.94, instead of 20.14, actually present.

Two flasks, each fitted with a wide tube about 15 in. long, which served as a condenser, and each containing a weighed amount of the standard aromatic sulfuric acid diluted with 6 volumes of water, were each heated over a small flame in a Kjeldahl rack. The alcohol vapors slowly distilled off, while the water vapor was for the most part condensed in the glass tubes and ran back. On titrating, the liquid whose volume had been reduced to about 15 cc. gave 20.06 per cent; the other, reduced to about 25 cc., gave 19.88 per cent, acid calculated as sulfuric. Repeating the experiment in such fashion that the liquid volume

was reduced in each flask to not more than about 10 cc., the figures obtained were 20.12 per cent in each case. These, as well as many other results obtained later, show, as was found by Kastle and Fraser<sup>1</sup> and by Brown,<sup>1</sup> that the hydrolysis of ethyl-sulfuric acid proceeds more rapidly when the solution is concentrated than when it is dilute.

These experiments indicated that satisfactory results might be looked for if the heating were so conducted that all free alcohol present might quickly evaporate and the aqueous solution of ethyl-sulfuric acid left be kept concentrated and hot, until hydrolysis is complete. A large excess of water serves no useful purpose, as the following experiments (Table VI) suggest: Three portions of an aromatic sulfuric acid, which contained 24.95 per cent of total acid calculated as sulfuric, were diluted with large quantities of water and distilled rapidly. This process removed the free alcohol, of course, but failed to break down the ethyl-sulfuric acid satisfactorily.

TABLE VI

No.	Aromatic sulfuric acid Grams	Water added Cc.	Time Min.	Distillate Cc.	Acid and Water Residue Cc.	Ratio acid Water in Residue	Total acid Found Calc. as H <sub>2</sub> SO <sub>4</sub>
1	10	160	30	100	70	1:6	19.43
2	10	115	25	100	25	1:1.5	19.71
3	5	160	45	150	15	1:2	20.31

The least satisfactory result was obtained where the largest proportion of water remained at the end of the experiment. Although the concentration was ultimately greater in (2) than in (3), yet the last result was the best, probably because much more time had been given for hydrolysis to take place.

## METHOD ADOPTED

Eight 5-gram portions of our standard aromatic sulfuric acid (20.14 per cent) were diluted each with 6 volumes of water and heated in open beakers upon a strongly heated water bath for different periods of time. The results appear in Table VII. Evidently, as soon as

TABLE VII

No.	1	2	3	4	5	6	7	8
Time, hrs.	1/2	1	1 1/2	2	2 1/2	3	3 1/2	4
Total acid Calc. as H <sub>2</sub> SO <sub>4</sub>	17.23	17.23	17.23	17.45	20.14	20.14	20.14	20.14

the proper concentration of acids and water is secured, the hydrolysis of the ethyl-sulfuric acid is fairly rapid and soon becomes complete, provided the water in the bath is kept vigorously boiling. If the beakers are covered with watch glasses, naturally more time will be required for completing the reaction than if the escape of vapor is unimpeded.

It may as well be pointed out here that, although ethyl-sulfuric acid may be quantitatively converted, in the presence of water, into sulfuric acid and alcohol, a similar statement may not be made with respect to its alkali salts. Aqueous solutions of the latter are but slightly, if at all, affected by boiling. Even when heated in the presence of sulfuric acid and water, the decomposition of alkali ethyl-sulfates into sulfuric acid, sulfate and alcohol, is very slow. Ostwald pointed out many years ago<sup>2</sup> that ethyl-sulfuric is a far stronger acid than sulfuric; and our work, in so far as it may be

<sup>1</sup> THIS JOURNAL, 4 (1912), 512.<sup>2</sup> J. prakt. Chem., [2] 28, 449; 29, 385.



said to furnish evidence on this point, bears out this statement. One of the methods of assay which we attempted to employ was this: A known weight of aromatic sulfuric acid, diluted with water, was titrated while cold; an amount of sulfuric acid exactly equivalent to the alkali used in the titration was then added, and the liquid heated in an open beaker on the water bath. A second titration, it was hoped, would now show the total acid present to be sulfuric, and a comparison of the two titrations would tell us what amount of ethyl-sulfuric acid was originally in the mixture. But in this we were disappointed. The original diluted aromatic sulfuric acid contained 5.12 per cent total acid calculated as free sulfuric. The first titration showed 4.37 per cent; after heating  $2\frac{1}{2}$  hrs., the second titration showed 4.50 per cent; after  $3\frac{1}{2}$  hrs., 4.94 per cent; and after  $4\frac{1}{2}$  hrs., 4.94 per cent. The presence of alkali ethyl-sulfate thus greatly retarded, if it did not altogether prevent, the conversion of all the acid present into sulfuric.

It is difficult to say how long a given sample of aromatic sulfuric acid must be heated in the presence of added water in order that the hydrolysis of the ethyl-sulfuric acid may be assumed to be complete. In addition to the physical conditions of the experiment, we must naturally take into account the proportion of ethyl-sulfuric acid present in the mixture. Certainly in most cases four hours' heating in an open beaker on a water bath, in which the boiling is vigorous, will be found ample. In Table VIII are some results obtained with samples of unknown strength, where the periods of heating were not the same. The figures represent the percentage of total acid, assumed to be sulfuric, as found by titration.

Lab. No.	U. S. P. (1916) METHOD		FLASK WITH AIR CONDENSER OVER FREE FLAME		OPEN BEAKER ON WATER BATH	
	Time	Results	Time	Results	Time	Results
11038	6 hrs.	22.20	$1\frac{3}{4}$ hrs.	24.54	4 hrs.	24.83
11047		22.16	$1\frac{3}{4}$	24.57	4	24.63
11051		10.39	$3\frac{1}{2}$	11.83	$3\frac{1}{2}$	12.47
11085		20.90	$1\frac{3}{4}$	22.25	4	21.96
11092		20.70	$1\frac{3}{4}$	22.22	4	23.22
11190		23.00	$1\frac{3}{4}$	24.95	4	25.26
11195		27.80	$1\frac{3}{4}$	28.37	4	28.52
11261		28.58	$4\frac{1}{2}$	32.49	$4\frac{1}{2}$	32.53
11563		35.28	4	35.81	4	35.77

It will be noted that, speaking generally,  $1\frac{3}{4}$  hours' boiling in a flask was not sufficient. In the case of No. 11051, the boiling was longer continued but was so slow that the volume at the end of  $3\frac{1}{2}$  hours' heating was only slightly reduced and, hence, the reaction was incomplete. The U. S. P. method gave low figures in every case.

It seemed to us desirable to study the hydrolysis of ethyl-sulfuric acid in the case of samples of aromatic sulfuric acid which had not been recently prepared. Accordingly a series of samples, put at our disposal by an important drug manufacturing house, were assayed, with the results given in Table IX.

Apparently the age of the sample affects very slightly, if at all, the hydrolysis of the ethyl-sulfuric acid present. It would also appear that, in order to meet the U. S. P. assay requirement, more sulfuric acid had been used in the manufacture of these preparations than corresponds to 20 per cent by weight.

TABLE IX ANALYSES OF A SERIES OF MANUFACTURERS' SAMPLES

A—Percentages obtained by the chemists of the manufacturing firm at the time of the preparation of the samples in question, the U. S. P. method having presumably been used. B—Figures obtained by us by the use of the same method.

C and D—Results obtained with open beakers on the water bath, according, respectively, as 3 or 6 volumes of water were added for hydrolysis.

E—Results of direct titrations, made after dilution with water but without previous heating.

F—Percentages of the total sulfuric acid which have been converted into ethyl-sulfuric acid in the respective samples.

No.	Age	A	B	C	D	E	F
1.....	$41\frac{1}{2}$ mos.	19.90	25.40	27.56	27.56	19.11	15.3
2.....	$37\frac{1}{2}$	19.00	25.85	27.49	27.43	19.93	13.7
3.....	35	19.60	27.30	28.38	28.65	21.34	12.6
4.....	$33\frac{1}{2}$	19.70	26.51	27.69	27.69	20.05	13.8
5.....	27	20.10	23.89	26.02	25.95	18.67	14.0
6.....	25	20.40	27.25	28.49	28.65	20.85	13.5
7.....	22	21.00	27.41	28.86	28.86	20.95	13.7
8.....	16	19.80	26.32	27.86	27.90	20.00	14.1
9.....	13	19.50	26.24	27.07	26.95	19.53	13.8
10.....	8	21.00	25.67	26.71	26.65	19.41	13.6
11.....	$1\frac{1}{2}$	20.00	23.78	25.05	25.00	18.21	13.6

In conclusion, we have thought it well to put on record the results of a progressive distillation of aromatic sulfuric acid which had been diluted with over three times its volume of water. Our object was to show that hydrolysis hardly begins until after the removal of the alcohol present as such in the mixture, and that thereafter the increase in the proportion of free sulfuric acid keeps pace with the removal of alcohol by distillation.

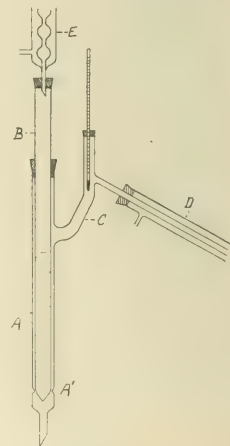
As the apparatus used possibly exhibits some points of novelty, a short description of it may not be out of place. The boiling liquid was contained in a round-bottomed flask through the stopper of which were fitted:

(1)—A thermometer whose bulb was in the boiling liquid.

(2)—A tube through which an aliquot of the liquid could be withdrawn by means of a pipette, and

(3)—The distilling tube shown in the figure.

The inner tube *B* (about  $27 \times 2$  cm.), closed at the bottom and provided with a reflux condenser, *E*, at the top, has an outside diameter about 4–5 mm. less than the bore of the outer tube *A*; the latter is provided at *A'* with three "dimples" which hold *B* in place, and a side-tube, *C*, which contains a thermometer and connects with a condenser, *D*. The tube *B* is partly filled with the same liquid which it is proposed to distil off from the flask—in this case alcohol. The mixed vapors of alcohol and water rise into the annular space between *A* and *B*, where the water is condensed on coming in contact with *B* and flows back; as soon as the alcohol in *B* is heated to boiling the alcohol vapor from the flask passes into *C* and so to the condenser *D*. To secure a constant boiling temperature for the condensing tube *B*, a bundle of



capillary tubes closed at the top and projecting above the liquid surface are placed in *B*.

In order to give an idea of the efficiency of this apparatus, the following may be stated:

Redistilled alcohol was put in *B* and a mixture of 10 cc. alcohol and 240 cc. water was boiled in the flask; when 10 cc. of distillate had been collected, the operation was stopped. The distillate proved to be 95.6-per cent alcohol and there was no alcohol in the residual liquid in the flask.

A mixture of 180 cc. aromatic sulfuric acid and 580 cc. water was placed in the flask and boiled. Ordinary alcohol was placed in *B*. At the end of each half-hour the thermometer readings and the volume of the distillate were noted, after which 5 cc. of the mixture were withdrawn from the flask, cooled, diluted and titrated, while the distillation was resumed. In Table X are given the results. The respective weights

TABLE X

Time Hrs.	Distillate Cc.	Thermometer in vapor	Reading in boiling liquid	Weights of $H_2SO_4$ in 2 cc. of Liquid Free Combined	Ratio of Free to Total $H_2SO_4$ Per cent
0.0	0.0	78°	89.10°	0.0488	0.0343
0.5	43.50	78	91.40	0.0532	0.0328
1.0	80.00	78	93.50	0.0593	0.0314
1.5	109.20	78	95.90	0.0652	0.0304
2.0	129.60	78	97.90	0.0721	0.0255
2.5	141.80	78	99.30	0.0758	0.0231
3.0	148.70	78	99.80	0.0821	0.0181
3.5	152.20	78	100.10	0.0870	0.0152
4.0	154.30	74	100.30	0.0888	0.0147
4.5	155.80	69	100.50	0.0917	0.0118
5.0	156.30	60	100.70	0.0939	0.0093
5.5	156.90	60	100.85	0.0956	0.0088
6.0	157.20	50	101.00	0.0964	0.0073
6.5	157.50	48	101.15	0.0991	0.0050
7.0	157.70	48	101.30	0.1003	0.0034
7.5	157.80	48	101.45	0.1005	0.0029
8.0	158.40	48	101.70	0.1010	0.0019
8.5	158.80	48	101.85	0.1020	0.0015
9.0	159.00	48	101.90	0.1033	0.0003
9.5	159.00	48	102.05	0.1040	0.0000
10.0	159.00	41	102.10	0.1040	0.0000
10.5	159.00	40	102.10	0.1040	0.0000

of "free  $H_2SO_4$ " and "combined  $H_2SO_4$ " were obtained in this way: the 5 cc. of liquid withdrawn from the flask were made up to 25 cc. with water; of this dilute solution 10 cc. were titrated at once and 10 cc. were completely hydrolyzed in an open beaker on the water bath and then titrated. From the data thus secured the amount of free sulfuric acid and that of the ethyl-sulfuric acid present in each 2 cc. of the liquid in the flask are calculated.

It will be noted that throughout the distillation the temperature of the vapor in the side-tube *C* never rose above 78°; after the bulk of the alcohol had been removed, the reading of this thermometer slowly fell, since the quantity of vapor passing through *C* became less and less and the loss of heat through radiation from the thermometer bulb was not compensated for. At the same time the temperature of the boiling liquid slowly rose as alcohol was distilled off. The sum of the "free" and the "combined" acid also slowly increases, for the percentage of total acid in the boiling liquid rises as the alcohol is removed. Finally, we may note that under the conditions of the experiment over 9 hrs.' boiling was needed for the complete hydrolysis of the ethyl-sulfuric acid present.

LABORATORY OF THE MARYLAND STATE  
DEPARTMENT OF HEALTH, BALTIMORE

## RENNIN—A NOTE AND A CORRECTION

By HOWARD T. GRABER

Received May 27, 1916

Rennin is not official in the sense that it is recognized by either the United States Pharmacopoeia or the National Formulary, hence there is a wide variation in the article as found upon the market, as well as in the methods used for its standardization. It is universally recognized as a milk coagulant and all methods use milk as a medium for standardization.

In 1911 I published an article<sup>1</sup> entitled "Some Observations upon the Assay of Digestive Ferments." In this article I included the assay used by me in the standardization of rennin. There was an error in this script which has since been corrected. This error to which I want to call especial attention was in the amount of milk specified to be used for the test. It was just twice the volume intended, so that the results by this error were just half what they should be, or in other words the rennin seemed to be just half its real strength. I have tried other methods proposed, but I recommend the method as published by me both for its simplicity of operation and the reliability of the results obtained when one uses a standard of known value as control.

The enzyme rennin, like all other enzymes, is distinctly specific in its reaction and it shows its selective characteristics as to the nature of the proteid, temperature and reaction of the media as well as the presence or absence of organic and inorganic salts, especially those of calcium and the phosphates. Results often vary when samples of milk are used from different cows, as well as different lots from the same cow, and the best results are obtained when using a mixture from the milking of many cows. There also seems to be a seasonal variation in the ability of the milk to coagulate.

The following table gives the results of many of the tests:

DATE	ASSAY 1:30,000 in Min. Sec.	MONTHLY AVERAGE	DATE	ASSAY 1:30,000 in Min. Sec.	MONTHLY AVERAGE
4/1 to 4/15/14		7.5	11/ 5/15	10 30	
8/ 7/14	10 30		12/ 3/15	10 30	
10	7 30	9	22	11 30	
15	7 30		23	8	10.5
9/ 1/14		9	24	10	
1/24/15	16	13.75	27	13 30	
21	11 30		28	7 30	
2/16/15	8 30	9.25	29	11	
22	10		30	11	
3/ 8/15	10	11	31	11	
31	11		1/ 3/16	10 30	
5/ 5/15	8 30		4	11	10.5
13	11 10		5	10	
17	11	10.3	6	11 30	
27	10 45		7	11	
29	10 45		8	10	
30	10 10		2/14/16	11	11
6/ 1/15	9 5		3/ 6/16	10	
7	11		7	9 45	
12	8 30		8	7 30	
17	10 15	10.6	9	7 30	
22	12		10	5 30	
23	12		11	9 30	
29	11 30		12	9 30	7.5
7/ 2/15	8 45		14	8	
7	8		23	11 15	
9	8	9.3	24	7	
10	8 45		28	4	
21	12		29	6	
22	10		30	4	
			31	7	

Several years ago I selected a rennin to be used as a standard in the assay of this enzyme, and I have

<sup>1</sup> THIS JOURNAL, 3 (1911), 919.



followed it quite consistently ever since. In the spring of the year 1914 it was tested for a period of 14 days and was found to assay 1 : 30,000 in 7½ min. and was accepted as such. In every assay made since then it has been run as a check upon the unknown sample.

There are 74 assays here enumerated extending over a period of about 2 years. A series of 14 assays in April, 1914, averaging 7½ min.; a second series of 14 in December, 1915, and January, 1916, averaging 10½ min., and a third series of 14 assays in March, 1916, averaging 7½ min.

This is certainly a very interesting state of affairs and the natural question to be asked is, "What is the cause of this variation?" There are many causes: some are known and some we are still studying.

My experience seems to show that the rennin coagulates more quickly in the fall and spring than in the winter and summer, and this fact seems to prove my contention that there is a seasonable variation in the milk.

There may be several explanations of this phenomenon. The cattle may get more exercise and more organic and inorganic salts in the spring, summer and early fall, than in the winter, hence their milk supply may vary, especially in relation to its coagulability. If this be so, the question rises, why does not the summer supply show this same increment in coagulability? My answer is that it would if we could regulate the supply, but during the hot summer months the milk is so prone to temperature changes that this offsets the other advantages. Then, too, the period of lactation is an important consideration and milk will show great variations in composition during this time.

It is an established fact that the rennet coagulation proceeds in three<sup>1</sup> stages: (1) The calcium casein is changed into the para casein; (2) the rennet enzyme seems to act upon the insoluble calcium salts of the milk, converting them into a form sufficiently soluble to enable them to coagulate the calcium para casein; (3) the true coagulation.

It is the second change or conversion of insoluble calcium salts to soluble salts which seems to retard the progress of coagulation, and I have noticed that in those cases where the time of coagulation was prolonged, the viscosity of the milk gradually changes; it seems to thicken and acts as if it almost wants to coagulate, but something seems to hold it back—either calcium salts are lacking or the insoluble calcium salts are with difficulty made soluble and available. I have also noticed that if a milk, acting in this manner, is divided into two portions, to one of which a soluble calcium salt is added, the coagulation period is much advanced in this portion when compared with the portion to which no soluble calcium salt has been added. Hence my statement that the seasonal variation in milk is an important factor.

There are other factors which, without a doubt, influence this coagulation period. Various samples of milk will show a variation in the fat content and

although the large creameries standardize the per cent of fat in their milk, the smaller creameries do not, and the inclusion of a superabundance of fat globules in one sample of milk undoubtedly will have some bearing upon the ease of coagulation.

The effect of bacterial content is an important factor. The milk examined by the Detroit Board of Health ranges in bacterial count from 3,000 to 1,500,000 bacteria per cc., which variation must certainly exert some influence upon rennet action.

The range of reaction of the milk within the perceptible limits of litmus test is an important item for consideration. In some cases I have found that a milk which has started to sour and thus had developed acidity above normal, seems to accelerate the coagulation period of rennin; in other cases it has inhibited it.

The "hydrogen-ion" concentration, a fact overlooked in the past by most of us but receiving more or less consideration at present, may help us clear up some of these peculiarities in enzyme activity. I look forward to the time when we can eventually adopt a standard milk of normal hydrogen-ion concentration and adjust our enzyme solution to a hydrogen-ion concentration found to give its optimum activity, and thus have our method under absolute and scientific control.

Until such time as this arrives, the results here enumerated lead me to say, "Know your standard." Do not adopt it on a single test or even a single series of tests, but follow it through a series of months as I have mine, then assign a strength which seems a fair average.

The method I use for testing follows, with the correction before cited.

(1) Only fresh, whole, unpasteurized milk is to be used, preferably from a herd of many cows.

(2) *Milk*—Heat 2 qts. gradually to 43° C.; mix well and take 1 qt. for the unknown sample and the other for the standard. Do not overheat the milk and if by chance it has been heated high enough to produce a thin skin, discard and use a new lot.

(3) *Rennin Solution*—Dissolve 0.4843 g. rennin in 150 cc. distilled water, mix thoroughly by inversion gently, and take 10 cc. for a test (10 cc. upon 1 qt. of milk gives a proportion of 1 : 30,000). Do not shake the rennin solution violently or the agitation will injure the strength of rennin.

(4) Measure 10 cc. rennin solution into a wide-mouth precipitating jar of about ½ gal. capacity; add 1 qt. of milk at 42° C., mix thoroughly by pouring rennin solution and milk 3 times from one jar to another, taking time with stopwatch after the first pouring. The milk should now be just 40° C. Keep the temperature at this point and test the milk for curd formation at half-minute intervals by tipping the precipitating jar forward gently; note the time required to separate the casein from the liquid whey; report the sample as 1 : 30,000 in this time.

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<sup>1</sup> Allen's "Commercial Organic Analysis," 8, 126.

## PEPSIN—A RESUME OF TESTS

By HOWARD T. GRABER

Received May 27, 1916

In a previous article<sup>1</sup> entitled "Some Observations upon the Assay of Digestive Ferments," I called attention to the great variation in the apparent strength of a sample of pepsin due to the age of the egg used in the test, and showed that eggs between the ages of 5 to 7 days leave the least residue when used in testing the strength of the pepsin. I therefore recommended, for uniformity in results, that chemists adopt age limits for their eggs when testing pepsin, and it is interesting to note that the Revision Committee of the Pharmacopoeia, having confirmed these findings, have adopted this egg limit in their revised test for pepsin. The revised wording, which I have every reason to believe will appear in the U. S. P. IX test for pepsin, will state: "Immerse a hen's egg, which should not be less than 5 nor more than 12 days old."

After having determined the large factor which the age of the egg bears in the assay of pepsin, it was of interest to me to know how my results would vary when choosing my eggs as to age and when going into the open market and buying "strictly fresh eggs" from a reliable dealer.

I have compiled the results from a series of many tests. Part of these tests were made with eggs of known age (5 to 12 days), and the balance with so-called "strictly fresh eggs." The pepsin used in all these tests was a sample found to leave a residue of about 1 cc. under ideal conditions and was chosen because of the fact that it is easier to note slight differences in strength with a residue of 1 cc. than with a smaller residue.

Assay Date 1915	Age of Eggs Days	Residue Cc.	Assay Date 1915	Age of Eggs Days	Residue Cc.	Assay Date 1915	Age of Eggs Days	Residue Cc.
2/13	7	1.25	4/3	8	0.75	6/2	10	0.6
15	7	0.6	8	9	0.75	7/2	10	0.4
19	7	0.9	9	10	0.45	24	12	0.4
20	7	1.25	10	8	1.5	8/2	10	1.0
22	7	1.25	12	8	1.0	4	10	0.95
25	10	1.0	13	9	0.6	6	10	1.0
26	5	1.0	14	8	0.5	10	7	0.8
4	10	1.25	15	9	1.5	9/3	7	0.75
5	9	1.0	26	7	0.3	6	7	0.8
8	7	0.5	27	8	0.25	9	7	1.0
			29	9	0.4	10	8	1.0
10	9	1.0	5	9	0.35	14	9	0.8
12	6	1.0	7	10	0.5	16	8	0.8
17	9	1.0	8	8	1.25	17	7	0.9
20	8	1.0	14	11	1.25	18	7	1.0
26	6	1.5	21	11	0.65	20	8	0.65
31	7	0.55	22	7	0.55			
			26	10	0.25			

Table I includes a series of 50 assays from eggs of known age, and of this series we find:

28 assays (56 per cent) below 1 cc.  
40 assays (80 per cent) not more than 1 cc.  
10 assays (20 per cent) above 1 cc. Of the latter 10, just 2 are 1½ cc.

<sup>1</sup> This Journal, 3 (1911), 919.

TABLE II—PEPSIN TESTS ON EGGS OF UNKNOWN AGE BUT GUARANTEED "STRICTLY FRESH"

Assay Date 1915	Residue Cc.	Assay Date 1915	Residue Cc.	Assay Date 1915	Residue Cc.	Assay Date 1916	Residue Cc.	Assay Date 1916	Residue Cc.
9/23	1.0	10/25	0.7	12/2	0.85	1/10	1.0	2/10	1.0
28	1.0	29	0.6	3	0.4	13	0.6	11	1.0
10/4	0.9	11/15	0.5	8	0.4	14	0.9	14	1.75
5	2.25	9	0.5	9	0.9	17	1.25	15	2
7	2.25	11	0.5	10	0.3	19	0.3	18	1
8	2.5	16	0.7	17	0.5	28	0.65	21	1.75
13	2.25	17	2.0	20	0.7	2/5	2.5	23	1
14	1.25	22	0.45	23	0.8	7	3	25	2.25
17	1.75	26	0.3	28	2.0	4	2	28	0.9
20(a)	0.75	29	0.2	29	1.25	6	1.0		
				31	0.3				

(a) Source of supply changed.

Table II includes a second series of 50 assays from eggs supposedly fresh, but of unknown age. Here we find:

25 assays (50 per cent) below 1 cc.  
32 assays (64 per cent) not more than 1 cc.  
18 assays (36 per cent) above 1 cc.

Of these last 18 assays with a residue more than 1 cc., the largest residue recorded was 3 cc. Whether the eggs used in this test were too fresh, or, on the other hand, older than the age limit previously described, I did not determine.

The two tables show well the advantage accruing in choosing eggs of known age, and in the testing of pepsin as well as with rennin, I repeat my caution—"Know your standard." Always use a standard pepsin as control, whose strength you have tested under different conditions as to age of eggs, etc., and draw your conclusions as to the strength of the unknown samples from the deportment of said control.

In concluding, I wish to state that in the above assays the conditions such as temperature, agitation, reaction, etc., were under absolute control, and the error due to the personal equation has been eliminated as far as possible.

Another fact brought out in this connection which I have not heard discussed is this: If we can determine the strength of pepsin by the age of the egg, the contrary is also true. We can approximately determine the age of a number of eggs by testing against a pepsin of known strength. If the residue is much more than experience has shown the control to run with eggs 5 to 12 days old, it is natural to assume that it is due to one of two causes: Either the eggs are absolutely fresh, or they are more than 12 days old. If they are too fresh and one has supply enough, they can be kept for 5 or 6 days and another assay made. If with this second assay a marked decrease in the amount of residue is shown, the eggs can be considered as strictly fresh. If the residue continues to increase, they were more than the age limit to start with and hence not strictly fresh.

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## LABORATORY AND PLANT

## ARTIFICIAL GAS-FIRED FURNACE STALLATION

By CHARLES E. RICHARDSON  
Received August 14, 1916

One of the largest, if not the largest artificial gas-fired furnace installation in this country has been made in the plant of the Eddystone Ammunition Corporation, Eddystone, Pa., for the purpose of hard-

ening and tempering (or drawing) 3-in. shells. The installation consists of three hardening furnaces and three tempering furnaces. One hardening and one tempering furnace are at present under construction and two each at present in operation. The furnaces are arranged in units—one hardening and one tem-



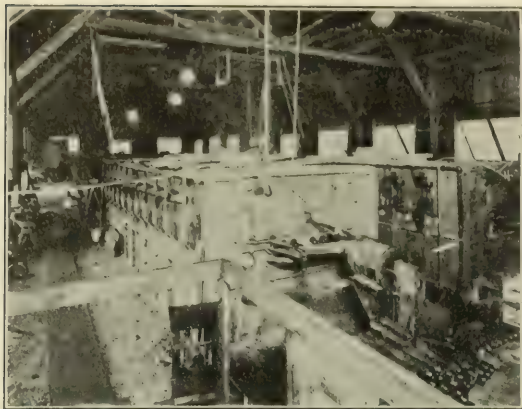


FIG. I—VIEW TAKEN FROM CONTROL PULPIT

Showing front (or charging end) of Hardening Furnaces, with pushes in place. Tempering furnaces can be seen in center on left behind Hardening Furnaces with oil-quenching tanks between. Note red flash lights in front of furnaces, covered conduits for piping and pyrometer locations.



FIG. III

Same view as Fig. I, but taken from opposite side, showing on left (inside of railing) the control pit. Note indicating and recording pyrometers, valves and flashers.

pering furnace comprising a unit. Each unit is designed to turn out 5,000 shells in a 20-hr. day. The full capacity of the installation (3 units) would be 15,000 shells per 20-hr. day.

The furnaces are operating at the high average efficiency of 32 per cent—furnace efficiency meaning the percentage of available heat units in the fuel consumed which are actually absorbed by the work being done, in this case heating steel.

The furnaces, designed and installed by the Surface Combustion Company of New York City, are fired by the surface combustion high-pressure system—a process whereby gas under pressure is made, by means

of a special governor, to inspire all the air necessary for complete and perfect combustion, maintaining, automatically, constant mixture proportions and eliminating all motors, blowers and air piping (Fig. II).

Gas under a pressure, ranging from 10 to 25 lbs. per sq. in. passes cock, A, continues through strainer, B, and enters nozzle, C. A portion of the pressure energy of the gas in passing from nozzle, C, into throat, D, is transformed into velocity energy. The pressure head on air opening, E, is thereby reduced, causing

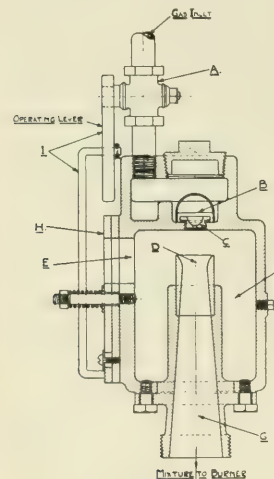


FIG. II

air to flow first into air-chamber, F, and from thence into throat, D, where it joins with the gas. The high velocity at the throat, D, mixes the air and gas thoroughly and the velocity head of the mixture is transformed back into pressure head by the pressure tube, G. The mixture then continues to the burner.

The burners are inserted at the sides of the furnaces and incline downward. The homogeneous mixture of air and gas from the inspirator is forced through the burners at a velocity greater than the rate of flame propagation and each flame strikes a baffle consisting of carborundum or other refractory material resting on the bottom of the furnace. This material attains an intense heat which is radiated very evenly upon the shells, from off the arched top of the furnace.

Each furnace is approximately 22 ft. long, 8 ft. wide and 7 ft. high (outside dimensions) and is set on a slight slope. The furnaces are encased in cast iron casings held together by heavy tie rods and are mounted on concrete foundations. The heavy fire brick linings are backed up by Sil-O-Cel, giving plenty of insulation. This cuts down the radiation losses and protects the operators from the heat. The furnaces are as air-tight as possible. To prevent leakage of cold air, which would produce an oxidizing effect and, by its cooling action, lower the furnace efficiency, a slight furnace back-pressure is maintained. As in all surface combustion work the furnaces are so designed as to develop and utilize the maximum possible amount of radiant heat. The flues are arranged so as to distribute the hot gases uniformly and to release them at the lowest possible temperature. The hardening furnaces are equipped with 22 high-pressure burners, and the tempering furnaces with 18. All piping is laid in conduits having removable covers, thereby eliminating all overhead work. To give an idea of the simplicity of the system the largest pipe used is a 2 in. Each burner is fed by a 1/2-in. pipe from a 1-in. manifold.

The fuel is a 580 B. t. u. gas (a mixture of water and coal gas), supplied by the Philadelphia Suburban Gas and Electric Company, Chester, Pa. The gas is delivered and metered under a pressure of 25 lbs. It is metered by a Rotary pressure meter and a Bailey flow meter. Each unit consumes an average of 3,300 cu. ft. of gas per hr., turning out 240 shells per hr., or 8

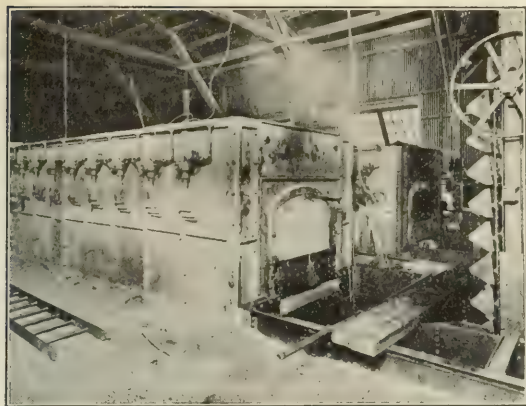


FIG. IV

Rear (or discharge end) of Hardening Furnace. Hot shells pop out of opening, covered by iron flap on hinge, into oil-quenching tank. They are removed from tank by elevator conveyor to drain tables, and are then fed into Tempering (or drawing) Furnace.

shells every 2 minutes. Therefore, when all these units are running at capacity, 9,900 cu. ft. of gas per hr. would be consumed, and for a day of 24 hrs., 237,000 cu. ft. of gas, and for 300 such days approximately 70,000,000 cu. ft. of gas. (While shells are turned out during only 20 hrs., the furnaces are kept hot the entire 24 hrs.) The cost of gas in this case is based on a sliding scale rate. The approximate average rate for this work is 43 c. per M. cu. ft.

#### METHOD OF OPERATION

The shells made are 3 in. in diameter and approximately  $8\frac{1}{2}$  in. long. They vary in weight from 8 to 11 lbs. The hardening is done at an average temperature of  $1500^{\circ}\text{F}$ ., and the tempering (or drawing) at an average of  $1100^{\circ}\text{F}$ . Each shell is in each furnace for a period of approximately one hour.

Running through each furnace are 8 steel angles which act as troughs to carry the shells. An air cylinder with an arm attached to the piston rod acts as a pusher. A man stands in front of each furnace and feeds shells into the angle troughs. Every 2 minutes the pusher pushes the shells ahead the length of a shell. This causes 8 shells to discharge into the oil-quenching bath located at the discharge end of the hardening furnaces, from which they are taken when sufficiently cool and fed into the tempering furnaces in exactly the same manner.

Frequent flue gas analyses have shown oxygen = 0.0, carbon monoxide = 0.0, and an average of 15.2 carbon dioxide. This shows that the heat is generated with 100 per cent efficiency having no excess air or unburned gases. For the purpose of minimizing the scaling of the shells and to lengthen the life of the angle troughs the furnace is operated with a slightly reducing atmosphere-carbon monoxide reading between 0.3 and 0.5 per cent. This is done to be on the safe side, as an oxidizing atmosphere would be very injurious in this operation.

#### CONTROL

All of the furnaces are controlled from a central control pulpit. Each furnace is controlled by a sin-

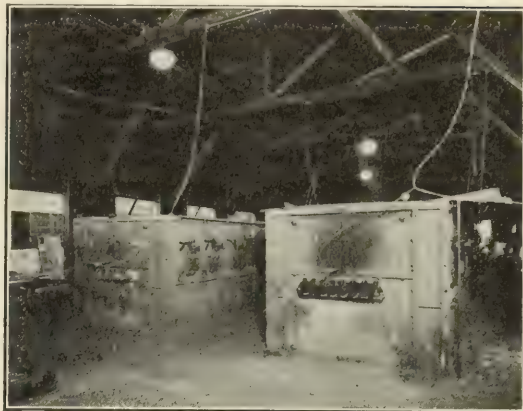


FIG. V

Rear (or discharge end) of Tempering (or drawing) Furnaces. Shells pop out of tubes with flap covers to keep out air.

gle valve which regulates the pressure supplied. The maximum pressure is 25 lbs. and the minimum 5 lbs. The average operating pressure is 15 lbs. All pyrometers, both indicating and recording, are also located in this pulpit. This allows one man to operate easily all of the furnaces. This feature has resulted in considerable saving of labor, since frequently as many as 8 men have been necessary to care for burners and the control of temperatures on a similar number of furnaces of the same size, fired by oil. This feature also allows much more accurate and careful control as evidenced by the practically straight line pyrometer charts which are secured daily. There is also located in this pulpit the electric flasher, which times the charging operation. This machine flashes a red light in front of each furnace every 2 minutes, which flash is the signal for the men to operate the pushers. The furnace operator in the control pulpit, each shift, receives his temperature and time instructions and is able to follow these instructions with the greatest accuracy without moving a step. This pulpit is the brains and heart of the heat-treating building, clock, bells, etc., all being located there.

#### COMPARISON WITH FUEL OIL

These furnaces are installed in the face of the competition of fuel oil costing 0.045 per gal. Several oil-fired furnaces of practically the same size and doing the same work were in operation prior to the installation of these furnaces. One of these oil-fired furnaces was carefully tested, over a period of several days, the oil being measured in a calibrated tank. Subsequent tests of the gas-fired furnaces have proven conclusively (as was believed in the beginning) that the operating cost of the gas-fired layout is very considerably lower than that of the oil. While it is not argued that all furnace operations can be done more economically with this system of gas-firing, still it has been proven beyond doubt that quite a percentage of large furnace work can be done considerably more economically than with oil. Generally speaking, 600 B. t. u. gas at 50 c. per M. compares very favorably with



0.01 per gal. oil in a good many cases, using the surface combustion, high-pressure system in properly engineered and designed furnaces.

For a plant putting in new furnaces where all the necessary equipment must be purchased, the initial cost of installation of this system of gas-firing will be found fully 30 per cent less than the cost of the necessary equipment, including furnaces, for an oil-fired installation. This system of gas-firing, eliminating, as it does, all air or steam supply and the consequent equipment for such, can be compared very favorably with even considerably higher priced fuels, as air and steam and the handling of them cost money, which is just as valuable as the money paid out for the actual fuel. The above figures, however, do not include any of these considerations but are based on straight fuel against fuel costs.

LONG ISLAND CITY  
NEW YORK

### SOME FEATURES OF SWIMMING POOL CONTROL<sup>1</sup>

By W. LEE LEWIS<sup>2</sup>

Received June 19, 1916

The responsibility for careful sanitary supervision on the part of those in charge of indoor swimming pools is increasing with the rapid increase in the number and patronage of these pools. Twenty years ago there were few indoor tanks. To-day, every up-to-date gymnasium gives a large place to this splendid feature of physical training. Almost every men's club, many large hotels and some of the larger passenger steamers, maintain swimming pools. Moreover, there is a growing tendency among educational institutions to require swimming as a part of the curriculum. This is true among the secondary schools of New York State and practically so at Northwestern University. The University of Illinois requires of its men students the ability to swim fifty yards. Princeton and Wisconsin require one hundred yards, and the navy a quarter of a mile. Obviously, enforced usage means definite legal responsibility for accidental infection traceable to faulty sanitary control.

Likewise, it must be noted that, through health departments, school instruction, government publications, the press, etc., the general public is gaining a new knowledge of sanitary matters, and sanitary standards in all things are rising rapidly.

The possibilities of an indoor swimming tank becoming unhygienic are apparent when one considers the intensive usage of a relatively small body of water and the absence of sunlight, fresh air, sedimentation and the various forces operative in the self-purification of outdoor waters. Furthermore, the coughing and spitting of the average swimmer is most favorable to contamination of the water with those disease germs typical of the respiratory tract, as those of tonsillitis, pneumonia, common colds and sore throat.

Possible swimming pool infections might be grouped

<sup>1</sup> Presented at the 52nd Meeting of the American Chemical Society, Urbana-Champaign, April 18 to 21, 1916.

<sup>2</sup> Assistant Professor of Chemistry, Northwestern University, and City Chemist, Evanston, Ill.

under three heads: gastro-intestinal, respiratory and venereal.<sup>1</sup> To the second group should be added eye infections and possible infections of the skin and outer ear. Organisms causing such trouble would include *staphylococcus*, *streptococcus*, *pneumococcus*, *B. coli*, *B. typhosus*, *gonococcus*, etc.

In respect to intestinal infections, it has been repeatedly established that these may follow bathing in contaminated water.<sup>2</sup> An excellent review of the literature bearing upon this point may be found in a recent article by Mannheimer.<sup>3</sup> In view of the demonstration of *B. coli* in swimming pool waters by practically every worker in the field, the possibility of transmission of gastro-intestinal diseases is apparent. One point, in this connection, is the increasing recognition of typhoid carriers. Since the discovery of the famous "Typhoid Mary,"<sup>4</sup> who infected 26 persons, some fatally, studies have been made showing the prevalence of such types.

Rosenau<sup>5</sup> states that "4 per cent of all typhoid fever patients continue to discharge typhoid bacilli in the urine and feces during and after convalescence." Albert states that 1 person in every 1000 of population is a carrier. Studies by Lumsden and Anderson,<sup>6</sup> on the Washington population during which the feces of 1000 healthy persons were examined, led them to conclude that 0.3 per cent of the general population discharge typhoid bacilli.

The American literature records no cases that have come to the author's notice of actual diseases of this group proved to have originated in swimming pools.<sup>7</sup> Klein and Schütz,<sup>8</sup> however, reported cases of typhoid fever in 6 soldiers who had bathed in water close to the mouth of a city drainage canal; 34 cases of enteric fever were reported among soldiers who had bathed in a swimming pool which derived its water from a polluted source.<sup>9</sup> About 10 per cent of the men using the pool became infected, while only 1 case developed among those who did not use the pool. Baginsky<sup>10</sup> demonstrated 6 cases of typhoid infection as coming from a swimming tank.

The epidemiology of swimming pools offers more direct evidence of infection from diseases in the second group. Baginsky<sup>11</sup> reported several cases of rhinitis from a swimming tank. Fehr<sup>12</sup> reported a number of cases of conjunctivitis among users of a public bath in Berlin. Burrage<sup>13</sup> notes mild epidemics of

<sup>1</sup> Atkins, *Proc. Ill. Water Supply Assn.*, 1911.

<sup>2</sup> Jager, *Z. Hyg.*, 12 (1892), 525; Pfuhr, *Deutsche, Militärärztl. Wochenschr.*, 17 (1888), Heft 9; Schäfer, *Ibid.*, 17 (1888), Heft 5; Lenhartz, *Münch. Med. Wochenschr.*, 21 (1892), 898; Klein and Schütz, *Wiener med. Wochenschr.*, 6 (1898), 238; Drescher, *Sanitätsberichte über die Kgl. Preuss. Armee*, 1898/99, I Teil, C. I. Gruppe 10 Unterabt.

<sup>3</sup> Mannheimer, *J. Infect. Dis.*, July, 1914.

<sup>4</sup> Parks, "Pathologic Bacteria and Protozoa."

<sup>5</sup> Roscau, "Preventive Medicine and Hygiene," p. 83.

<sup>6</sup> Lumsden and Anderson, *Bull. Hyg. Lab.*, U. S. P. H. S., 78 (1911).

<sup>7</sup> Cf. Rettger and Markley, *Eng. News*, 66, 636; Whipple and Bunker, *Munic. J.*, 31, 526.

<sup>8</sup> Klein and Schütz, *Weiner med. Wochenschr.*, 6 (1898), 238.

<sup>9</sup> Mair, *Proc. Roy. Soc. Med.*, 2 (1908-9), Pt. 2, 227.

<sup>10</sup> Baginsky, *Hyg. Rundschau*, 6 (1896), 597.

<sup>11</sup> *Loc. cit.*

<sup>12</sup> Fehr, *Berlin klin. Wochenschr.*, 37 (1900), No. 1.

<sup>13</sup> Burrage, *Proc. Ind. Acad. of Science*, 1909; cf. *Eng. News*, 63 [25], 740.

sore throats and colds at the Purdue gymnasium pool. The author<sup>1</sup> "noted a prevalence of colds, sore throats and some cases of la grippe and pneumonia, rather strikingly restricted to the users of the swimming tank in Northwestern gymnasium." That was, however, before chemical sterilization was introduced and it is only fair to state that since that time, during which period the water has been carefully watched and treated with hypochlorite, no infection of any kind has been traceable to the pool.

Bunker<sup>2</sup> states that at Brown University no epidemics of any sort could be directly attributed to the pool, but affections of the nose and ear were occasionally found among members of the swimming team. Whipple<sup>3</sup> notes the occurrence of similar mild infections from the Brooklyn Polytechnic swimming pool. Tully<sup>4</sup> concludes that the "Wisconsin University pools are kept in excellent sanitary condition and there is little danger of disease transmission." Levine<sup>5</sup> states that: "During the two years' service of the tank at the Iowa State College, there has been no epidemic of any kind traceable to the pool, but there have been sporadic complaints of colds and sore throats. The danger of infection in pools has probably been overemphasized."

Dr. Cobb<sup>6</sup> says he has had occasion to treat "quite a number of cases of ethmoiditis and acute otitis media which apparently were caused by diving in a swimming tank." He states that a swimming tank can not be kept sterile. "Even if we succeeded in sterilizing it, the first person who entered would contaminate the water anew." Dr. Cobb objects to diving especially and states that people do this "because they are deceived by the ostentatious methods which are employed and believe the water is clean." One of his cases, H. J., 17 years old, made five visits to a swimming tank and returned with acute ethmoiditis. The disease disappeared when the patient refrained from diving. Two other cases, one sub-acute otitis media, the other otitis media, arose from a lake boy's camp. J. S., aged 14, had double ethmoiditis. The author concludes: "These cases are selected out of a large number of similar cases of infection acquired in this way. The danger is a very real one and it would seem that the sooner those who patronize these swimming tanks realize the danger of it, the better it would be for the health of their upper respiratory tract."

In the absence of statements as to the hygienic precautions taken at these particular tanks, charged with having produced ear and nose infections, it would not seem warrantable to assume that they were typical and that, therefore, these are results to be expected from any swimming tank. Definite proof as to the origin of the infection, as well as the meagerness of the data, would not warrant any sweeping generalizations such as that with which the author concludes. Moreover, it is hardly fair to accuse those in charge

of swimming tanks with having invited a false sense of security through "ostentatious methods" of keeping the water clean. Finally, the article was written in 1908 and cannot consider the great progress made in swimming tank hygiene during the past eight years. The article was quoted as one of a few going directly on record in the matter of swimming pool epidemiology.

Danger from gonorrheal infection through swimming pools seems least probable as the specific organism is very short-lived in water. No cases of such infection are on record although the possibilities under careless tank control are evidenced in the articles of Hertzka,<sup>1</sup> Steiker,<sup>2</sup> Skutsch,<sup>3</sup> and Bending.<sup>4</sup>

Turning now to the means of safeguarding the swimming pool, the following items are in point: (1) construction and equipment, (2) disinfection, (3) suits, (4) the preliminary shower, (5) inspection and exclusion, (6) sanitary education of pool users, (7) bacteriological control.

POOL CONSTRUCTION is now fairly well standardized. All pools should have smooth walls and bottoms and be free from all obstructions. The maximum of air, light and ventilation should be provided. It is unfortunate that custom and plumbing exigencies have too often relegated the swimming pool to the basement. There should be a raised, broad flat ledge about the pool to protect it from floor drainage. There should also be a combined life rail and overflow gutter, sometimes called a scum gutter. Among other things, such a device protects the wall from discoloration by lapping water. Vacuum cleaning should be provided for the removal of the mixture of hair, lint, rust and coagulum that accumulates in every tank. While not a menace to the health of the swimmers, this material should be removed for aesthetic reasons at least.

Under the heading of construction and equipment comes the question of intermittent cleansing and filling *vs.* continuous re-filtration with complete cleansing and refilling only at wide intervals.

At first thought, a tank cleansed and re-filled weekly or bi-weekly would seem to offer a safer water than that in which the same water has been rotated several weeks. As will be shown later, however, there is no direct relation between the number of pool fillings per week and the sanitary condition of the water.<sup>5</sup> A pool is contaminated very quickly and normally; the contamination, as indexed in the bacterial count, increases until the third day when it falls somewhat.<sup>5</sup> On the other hand, if the pool water is being filtered continuously while being used and a certain amount of fresh water added every day, other things being equal, it will not reach the same degree of pollution as in the intermittent system. The latter system also saves heat and water and maintains the pool at a more uniform temperature. As a matter of fact, neither system is adequate without daily sterilization.

<sup>1</sup> Hertzka, *Monatsschr. f. Geburt u. Gynäkologie*, **16** (1902), 3.

<sup>2</sup> Stieker, *Z. Geb. u. Gyn.*, **45** (1901), 510.

<sup>3</sup> Skutsch, *Cent. f. Bact.*, **12** (1892), 309.

<sup>4</sup> Bending, *Munch. Med. Wochschr.*, **56** (1909), 1864.

<sup>5</sup> Hesse, *Z. Hyg.*, **25** (1897), 482; Selter, *Hyg. Rundschau*, **18** (1908), 1381; Hilsun, *Cent. Bakt.*, 1 Abt., **27** (1900), 661; Lewis, *Eng. News*, **65** (1911), 689.

<sup>1</sup> Lewis, *Eng. News*, June 8, **65** (1911) [23], 689.

<sup>2</sup> Bunker, *Am. J. Pub. Hyg.*, N. S., **6** (1910), 810.

<sup>3</sup> Whipple, *Munic. J. Engr.*, **30** (1911), 577.

<sup>4</sup> Tully, *Am. J. Pub. Health*, March, **1912**.

<sup>5</sup> Levine, *J. Infect. Dis.*, **18** (1916), 3, 293.

<sup>6</sup> Cobb, *Boston Med. and Surg. J.*, **159** (1908), 9.



Most continuous filters are faulty in not providing a device for the addition of the alum quantitatively or under exactly controlled conditions.

There should also be provided as an adjunct to the filter, a sedimentation or coagulation basin of such size in relation to the filter capacity as to permit the storage of the water at least a half hour after the addition of the alum. This permits complete reaction and coagulation of the alum and saves the filter. As much as 80 per cent purification may take place in such a preliminary basin through settling. Any other arrangements may result in carrying some alum into the tank, especially during periods of rapid filtration or after the water has been refiltered for some time and its natural alkalinity much reduced by repeated treatment with alum. This alum may later react in the pool, making the water irritating and murky.

DISINFECTION is not a substitute for refiltration or intermittent filling, but a daily necessity under either system. Commercial hypochlorite of lime seems to have won its place as an agent, though liquid chlorine is used successfully and eventually ultra-violet light, now being used in a few instances, may supplant chemicals for this purpose.

The amount and method of adding hypochlorite must vary with the nature of the water and with the usage. As a rough criterion, a tank of 60,000 to 70,000 gal. capacity needs 1 lb. per day. The chemical should be supplied in pound cans only, as it rapidly deteriorates. The system of adding in solution by means of a synchronous pump working with the circulative pump in the continuous filtration system, has the advantage of mechanical control and uniformity of feed. I am yet to be convinced, however, of its advantage over the simple expedient of adding the chemical by hand at the end of the day's usage. When added gradually during refiltration, the concentration is never so high as when the whole amount is put in at once. The germicidal action is, therefore, not so great. Moreover, when added continuously, the swimmers are in contact with the fresh solution and may complain of odor and tastes. If added at night it has fully reacted and by morning is fully dissipated leaving a sterile, wholesome water with which to start the day. An effective and simple method of adding hypochlorite is to transfer the chemical to a thoroughly perforated can and drag it by means of a wire and a pole over the surface of the pool until it has gone into solution. Clark and Gage<sup>1</sup> in tests upon the Andover pool obtained more satisfactory results by the periodic application of bleach directly to the tank. The continuous addition of 0.3 part per 1,000,000 available chlorine to the water passing through the filters, resulted in a purification of only 68 per cent. Tests made by the author upon the water of the pool at the New Trier high school, which is equipped with a continuous filter and synchronous pump for adding hypochlorite of lime, showed the water to run high in bacteria with 7 to 8 tubes fermenting out of 10 when inoculated with 1 cc. quantities of water. A change

to the system of adding the chemical in 1-lb. quantities at night, conditions otherwise remaining the same, showed marked and immediate improvement.

The preliminary shower with soap should be rigidly enforced. It must be remembered that most of the contamination comes from the buttocks and perineum. As a matter of fact a sitz bath with a perforated ring device, working automatically while the bather sits on it, would be desirable. The average individual gives the matter little thought and few really understand the purpose of the preliminary shower. Women are the worst offenders, neglecting the requirements through indifference or false modesty. Checking up the conditions at Northwestern, we found the women were mostly taking the shower with their suits on. The swimming instructor should educate such persons to the idea that a swimming pool is not a place for cleansing the person, but a kind of gymnasium for a special sort of exercise shared by many as a means of recreation and instruction in life-saving.

SUITS are, of course, no problem with men, but it is a very serious problem where women share the pool, on account of contamination and discoloration of the water through fading. In general, fast black cotton or wool suits which have been previously soaked in salt solution give the best results. It would be desirable to sterilize these in some manner each time after use.

After these preliminary precautions have been taken, a rigid inspection of those using the pool should be exercised, and all those excluded showing signs of infection. This should apply not only to the grosser skin and venereal diseases, but to coughs, colds, sore throats, running noses, etc. The principle of inspection and exclusion is being applied to schools as a supplement to all other hygienic precautions. In the more progressive schools for young children, especially, not only symptoms of the recognized diseases such as scarlet fever, mumps, whooping cough, etc., are grounds for exclusion, but simple colds as well. A running nose is one of the earliest symptoms of a large number of contagions.

Much can be accomplished in pool management by educational efforts designed to create a knowledge of proper sanitary conduct, and a sense of responsibility for the wholesomeness of the pool. Floor talks or instruction sheets and placards should be employed showing the reasons for the requirements, the danger from expectorating in the pool, the need of the thorough soap shower, the desirability of emptying the bladder before entering the pool, etc.

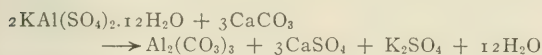
Finally, every director of a swimming pool should, as one of his personal rights, insist on the aid of bacteriological tests in determining the efficiency of his methods. The appearance of a pool is not in the slightest sense any criterion as to its safety. Bacteriological tests alone can tell this. Chemical tests are of little value as the contamination with organic matter from bathers makes interpretation difficult. Even the bacteriologist has difficulty as the subject is new and there is an absence of standards. The

<sup>1</sup> Clark and Gage, *Ann. Rep. Mass. State Bd. of Health*, 1912, p. 347.

author's opinion is that a swimming pool can, and should be, maintained up to the standards of a drinking water. Certainly it should be kept free at all times from colon bacilli.

**ALKALINITY IN THE ROTATING SYSTEM**—As is well known, the reaction of alum when added to water for purposes of producing a "floc," depends upon alkaline salts in the water. Practically all natural waters contain alkaline salts as carbonates and bicarbonates of the alkaline earths, less frequently of the alkali metals. The amount of such alkalinity, however, varies, from which it is apparent that the amount of alum that various waters may convert into "floc," as well as the speed of the reaction, will also vary.

The reaction of alum with the native salts in a water results in the conversion of alkaline calcium carbonate into its equivalent of neutral calcium sulfate as shown by the following equation:



The aluminum sulfate immediately undergoes hydrolysis. Therefore, when a water has reacted with alum, its alkalinity is reduced to a corresponding extent, while its hardness remains unchanged. It is plain, therefore, that if the water in a swimming pool were rotated through a filter, and treated with alum each time without adding fresh water or alkaline chemicals, there would come a time when a "floc" would form so slowly that the reaction might not take place between the alum chamber and the filter bed. Eventually, with complete exhaustion of the native alkalinity, no reaction whatever would occur. The matter of the speed of the reaction is of special importance in swimming pool filtration as the type of filter used does not permit a fore-period for "floc" formation such as the coagulating and settling basins supply in large filtration plants. Moreover, the turbidity of the re-filtered water in a swimming pool is never high, and turbidity aids flocculation.

Applying these considerations to Lake Michigan water and the Evanston Y. M. C. A. pool, the water showed a methyl orange alkalinity of 118.3 parts per 1,000,000 as it entered the system after having been filtered at the city filtration plant. Normal carbonate alkalinity was absent.

The above equation shows that 948 parts of potassium alum (the kind in use at the time these observations were made) will require 300 parts of calcium carbonate for complete reaction. In order to determine how many rotations of the water in the pool this alkalinity would permit, it was necessary to know how much alum was added per gallon to the water being filtered. Since the filter used supplied the alum from an alum chamber attached to the filter inlet pipe and the amount is regulated by the operator according to the appearance of the water, there was no direct method of determining the amount of alum being used. Observations over several weeks showed that the filter was run on an average of 11 hours per day at a capacity of 5000 gal. per hour. By weighing the alum placed

in the chamber during the same period it was found to average 5 lbs. per day, or 0.64 grain per gal. As the capacity of the tank is 65,000 gal., the equivalent in volume of the pool's capacity would be re-filtered every 13 hrs. Each refiltration would require 0.2025 grain per gal. of alkalinity expressed as  $\text{CaCO}_3$ , this being the equivalent of 0.64 grain of potassium alum. Since the water contains originally 6.902 grains of alkalinity per gal. expressed as  $\text{CaCO}_3$  it is apparent that theoretically 34.0 complete rotations would be possible, or in other words the same water could be used under the rotating system 6.7 weeks.

In practice, however, the conditions vary from the above in the following respects. Twice a week the sediment in the bottom of the tank is removed by a suction hose attached to a special return pipe of the pump. This necessarily removes considerable water. Furthermore, there is loss from sloppage and evaporation. Fresh water is added twice a week to restore the level in the pool. Careful observations over a period of time established that the amount of fresh water added to supply this loss from these various sources averaged 7,220 gal. per week. In other words, a volume of fresh water equivalent to the capacity of the pool was added every nine weeks. The extent to which this addition of fresh water would increase the number of possible rotations through displacing water of lowered alkalinity by an equal volume of fresh water of original alkalinity may be figured as follows: There would be added each  $3\frac{1}{2}$ -day period 3,610 gal. of fresh water of an alkalinity of 6.902 grains per gal.:  $3\frac{1}{2}$  days would represent 38.5 hrs. of refiltration and since the 65,000 gal. of water in the tank are rotated every 13 hrs. this would correspond to 2.9 complete rotations. The alkalinity would be reduced by 0.5872 grain per gal. for each such period.

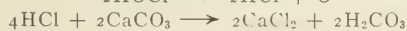
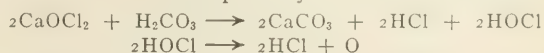
Furthermore, there was added to this pool each night, Sunday excepted, 1 lb. of hypochlorite of lime. Lunge gives the following typical analysis (percentages) of commercial chloride of lime:

Available chlorine.....	37.00	38.30
Chlorine as chlorides.....	0.35	0.59
Chlorine as chlorates.....	0.25	0.08
Lime.....	44.49	43.34
Iron oxide.....	0.05	0.04
Magnesia.....	0.40	0.31
Alumina.....	0.43	0.41
Carbon dioxide.....	0.18	0.31
Silica, etc.....	0.40	0.30
Water and loss (by difference)...	16.45	16.33

Hooker in his "Chloride of Lime in Sanitation" states that from these analyses the following approximate formula may be assumed:

4CaOCl <sub>2</sub> ·2Ca(OH) <sub>2</sub> ·15H <sub>2</sub> O, analyzing			
45.1% CaO	68.00%	CaOCl <sub>2</sub>	
16.85 H <sub>2</sub> O	20.00	Ca(OH) <sub>2</sub>	
38.05 Cl	12.00	H <sub>2</sub> O	
100.00	100.00		

The CaOCl<sub>2</sub> functions through interaction with the free carbonic acid and probably bicarbonates as follows:



from which it is apparent that the alkalinity of the



water is neither increased nor decreased by this component of the "bleach."

While hypochlorite is soluble in about twenty times its weight of water, leaving a small residue, mostly  $\text{Ca}(\text{OH})_2$ , it would be completely soluble under the conditions. Thus the alkalinity of 65,000 gal. of water gains daily by the addition of 0.2 lb. of calcium hydroxide, corresponding to 0.0290 grain per gal. expressed as calcium carbonate. The alkalinity per gallon at the end of the first half week would then be determined as follows:

$$\frac{(61,390 \times 6.3157) + (3,610 \times 6.9029) + (65,000 \times 0.0870)}{65,000} = 6.4353$$

The alkalinity at the end of the second half-week period would be calculated in the same manner save that the residual 61,390 gal. would have an alkalinity of 6.4353 — 0.5872 grains per gal. This method leads to the following series of values for the alkalinity per gallon at the end of successive periods.

(1) 6.4353	(7) 4.1271	(13) 2.4885	(19) 1.3259
(2) 5.9936	(8) 3.8136	(14) 2.2660	(20) 1.1680
(3) 5.5765	(9) 3.6175	(15) 2.0559	(21) 1.0189
(4) 5.1825	(10) 3.2375	(16) 1.8575	(22) 0.8781
(5) 4.8104	(11) 2.9734	(17) 1.6701	(23) 0.7451
(6) 4.4590	(12) 2.7240	(18) 1.4931	(24) 0.6194
			(25) 0.5007

Summarizing, it appears that a pool of the capacity of 65,000 gal. filled with water of an original alkalinity of 6.902 grains per gal. and treated with 0.64 grain of alum, if filtered at such a rate as would permit a complete rotation of the water every 1.2 days, could be rotated 6.7 weeks so far as its ability to react with alum is concerned. If fresh water is added twice a week in amounts sufficient to displace the original 65,000 gal. in 9 weeks, and "bleach" added in 1-lb. quantities 6 days a week, the alkaline life of the pool would be extended to  $12\frac{1}{2}$  weeks. These conclusions do not take into consideration the obvious fact that before the alkalinity became zero the reduced concentration would so lessen the speed of "floc" formation as to shorten the above periods in actual practice.

In these calculations a perfect mixing of the water is assumed and the effect of water lost by evaporation is not distinguished from that of water lost by sloppage or in cleaning the pool by the suction method. The first assumption is probably not far from the fact as the swimmers and the refiltration keep the pool water rather thoroughly mixed. Water lost by evaporation would not cause a loss of alkalinity but would concentrate the salts. It would, however, be an involved problem to disentangle this factor, and the error in disregarding it is probably well within the limit of error of the methods employed in the entire calculations. As a matter of fact, the water lost by vacuum cleaning was observed to be the principal source of loss. In a pool provided with a side wall gutter near the surface, the sloppage loss would be greater than in the case studied.

A series of six weekly alkalinity determinations on the pool water gave the following results: 5.8649, 5.5507, 5.3280, 5.0517, 4.5066, 4.2996 gr. per gal. as  $\text{CaCO}_3$ . In another series of daily determinations the following results were obtained: 5.538, 5.352,

5.124, 4.985, 4.950, 4.732, 4.623, 4.490, 4.445, 4.525, 4.249, 4.734. These results show the fall in alkalinity according to the theory. The departure from the theory in the rate of decrease results from the fact that the amount of alum added and the amount of water displaced in cleaning has varied from the quantities used in the calculations.

After swimming meets, when the water was unusually turbid and the sediment greater, the amount of alum, fresh water, and the period of filtration have been increased.

If free chlorine were used as a sterilizing agent, it is obvious that instead of contributing to the alkaline life of the pool this would shorten it by converting an equivalent of alkalinity into neutral chloride.

Sterilization by the electrolysis of sodium chloride would present certain advantages of economy and would supply a needed source of alkalinity as a by-product. A method of saving alum and conserving the alkaline life of the pool has been practised in some cases by feeding alum rather freely for an hour at the beginning of the filtration, then shutting it off during the remainder of the filtration.

#### HARDNESS IN THE ROTATING SYSTEM

From the fact that the addition of alum to a water does not affect its hardness since calcium is merely changed from a carbonate to a sulfate, it follows that under the rotating system the hardness of the pool water would increase by the amount of calcium in the added chemical. Expressed in terms of  $\text{CaCO}_3$  this is equivalent to about 80.5 per cent of the total weight of hypochlorite. Added daily at the rate of 1 lb. to 65,000 gal., this would amount to increasing the hardness by 0.0863 grain per gal. With an original hardness of 6.2964 grains per gal. expressed as  $\text{CaCO}_3$ , and with three additions of 1 lb. of hypochlorite the hardness of the pool water in grains per gal. at the end of the first half-week would be calculated as follows:

$$\frac{(61,390 \times 6.555) + (3,610 \times 6.2964)}{65,000} = 6.540$$

The hardness at the end of the second half-week would be calculated in the same manner save that the hardness of the residual water would be  $(6.540 + 0.2589)$ .

The values for successive half-week periods are:

6.296	7.174	7.908	8.477
6.540	7.388	8.063	8.600
6.770	7.571	8.209	8.716
6.988	7.744	8.347	

The rotation of Lake Michigan water, under the above conditions, would in three months produce an appreciably hard water through the cumulative effect of the added "bleach."

In a series of hardness determinations commencing the sixth week, the following results were obtained: 8.745, 9.390, 10.332, 10.000, 10.062, 10.228, 10.359, 10.768, 11.188 grains per gallon.

#### THE SANITARY CHEMICAL ANALYSIS IN SWIMMING POOL CONTROL

It is apparent from the principles of interpreting a sanitary-chemical water analysis that this method has little or no place in studying the sanitary condition of

swimming pool water.<sup>1</sup> The small amounts of organic matter, ammonia, chlorides, etc., determined in such an analysis are harmless in themselves, but are taken as an index to the bacterial process by which nitrogenous organic matter is oxidized ultimately to nitrates. In a swimming pool, these same substances may come in various forms from the bodies of the swimmers and so would not correctly index the bacterial process occurring. By the same principle, the author has noted heavy indol tests on swimming tank water unrelated to changing bacterial counts.

A series of 6 daily analyses of the tank water at the Northwestern pool gave the following results, expressed in parts per million:

	Mon.	Tues.	Wed.	Thurs.	Fri.	Sat.
Total solids.....	134.8	152.4	176.0	133.2	132.0	179.2
Volatile matter.....	13.6	18.0	24.0	20.0	28.4	15.6
Chlorine.....	9.809	9.809	8.583	9.809	11.079	12.262
Nitrites.....	None	Trace	Trace	Trace	Trace	Trace
Nitrates.....	0.116	..	..	0.120	0.112	0.116
Free NH <sub>3</sub> .....	0.030	0.019	0.052	0.075	0.098	0.091
Albuminoid NH <sub>3</sub> .....	0.042	0.060	0.071	0.074	0.087	1.228

The pool, at the time of these analyses, was emptied, cleaned and refilled each Saturday. It was being used each week by an average of about 500 persons, one-fifth of whom were women.

A fairly consistent rise in chlorides, volatile solids, "free" and "albuminoid" ammonia is noticeable.

The following table gives an analysis of the Evanston Y. M. C. A. tank-water after six weeks of rotation, together with a typical analysis of Evanston city water for comparison. The latter is filtered at the municipal plant and is very pure at all times.

	Tank Water	City Water
Albuminoid ammonia.....	0.087	0.047
Free ammonia.....	0.011	0.015
Nitrites.....	0.026	0.000
Nitrates.....	1.64	0.08
Chlorides.....	12.5	5.00
Alkalinity.....	82.0	118.0
Hardness.....	149.0	108.0
Total solids.....	206.0	147.0

The decrease in alkalinity, increase in hardness, chlorides, total solids and nitrogen forms is such as one would expect, but affords no information as to the sanitary state of the pool at the time, since most of these variations from the original water, with which the pool was filled, have a purely chemical origin.

#### A COMPARISON OF THE EFFICIENCY OF THE ROTATING AND THE INTERMITTENT SYSTEMS<sup>2</sup>

The two Evanston pools offered opportunity for a comparative study of the bacterial efficiency of the two prevailing systems used in swimming tanks, the rotating or continuous filtration and the intermittent. The Northwestern pool is emptied, cleaned and refilled once a week during the winter and twice a week during the more intensive summer use. The Y. M. C. A. pool is used the year round by a larger number of persons, but the Northwestern pool is also used by women, who are harder on a pool than men. On the other hand, more young boys patronize the Y. M. C. A. pool, and these are not so controllable in the matter of precautionary measures as older persons. The factor of patronage, therefore, in the two cases, might be con-

<sup>1</sup> Atkin, *Proc. Ill. Water Supply Assoc.*, 1911, 3, 73; Mannheimer, *Am. Phys. Ed. Rev.*, 17 (1912), 669.

<sup>2</sup> Angel, *Proc. Incorp. Assn. Munic. & Co. Engin.*, 34 (1908); Bunker, *Am. J. Pub. Hyg.*, 20 (1910), No. 4.

sidered balanced. Both pools are of modern construction, have the same capacity, the water is maintained at the same temperature, and each receives 1 lb. of hypochlorite at night. Each pool is in charge of a competent swimming instructor. Preliminary soap showers are enforced in both cases and exclusion in the case of persons obviously affected with coughs or colds. It is believed, therefore, that differences in the bacterial condition of the water may fairly be attributed to differences in the two systems employed, the rotating and the intermittent. Over 200 analyses have been made on each pool and the rotating system has consistently shown a better condition of the water. Below are summarized the results of 22 analyses made upon each pool during the summer of 1915, each pair of samples being taken upon the same day. The samples were taken from the spring board in each case, and about 6 in. under the surface. This uniform method of sampling was adopted after failure through repeated tests to detect any consistent variation in bacterial content at different points in the same pool. Atkins' remarks this same lack in data collected by him on the Chicago pool. Levine<sup>2</sup> states that samples taken from different parts of the tank showed some differences in bacterial content, but these variations were not of sufficient magnitude to be of any sanitary significance. He remarks that in the Iowa pool, stratification of the water might result with the cooler and purer filtered water at the bottom of the pool. However, this pool was idle 20-22 hrs. each day.

The samples taken were, in all respects, handled in the same manner. Various dilutions were made and the samples plated upon plain agar with 4 days' incubation at 20° C., and litmus lactose agar with 2 days' incubation at 37.5° C. For the gas production test 1 cc. of the undiluted sample was placed in each of 10 fermentation tubes of lactose broth and incubated 2 days at 37.5° C. Transfers from tubes showing over 20 per cent gas produced gas in lactose bile in over 90 per cent of the cases.

TABLE I.—RESULTS OBTAINED IN 22 ANALYSES EACH UPON NORTHWESTERN GYMNASIUM POOL WATER (INTERMITTENT FILLING) AND EVANSTON Y. M. C. A. POOL WATER (CONTINUOUS FILTRATION)

No. of Tests and Per cent of Tests Falling within Limits Indicated									
Bacteria per Cc.	4 days P. A. at 20° C.				2 days L. A. at 37.5° C.				
	Y. M. C. A.	No.	%	N'w.	Y. M. C. A.	No.	%	N'w.	%
0-100	10	45	..	..	19	86	2	9	..
101-500	3	14	1	5	1	5	2	9	..
501-1000	3	14	..	9	..	..	2	9	..
1,001-5000	3	14	2	9	1	5	4	18	..
5,001-10,000	..	..	3	14	..	..	6	27	..
10,001-100,000	..	..	7	32	..	..	5	23	..
100,001-500,000	1	5	5	23	1	..	1	..	..
500,001-over	..	..	1	5	..	..	..	..	..
Lost	2	..	3	..	..	..	..	..	..
Gas Producers									
Red Colonies 2 days L. A. at 37.5° C.	Y. M. C. A.				N'w.				
	No.	%	No.	%	No.	%	No.	%	
0	22	100	10	45	0	17	77	11	50
0-50	..	..	6	27	0 to 2	..	..	2	9
51-100	..	..	..	..	2 to 4	1	5	1	5
101-1000	..	..	2	9	4 to 6	1	5	1	5
Lost	..	..	..	..	6 to 8	..	..	1	5
					8 to 10	3	14	6	27

In respect to the relative cost of rotating the water for a period of 3 months and the intermittent system, filling the pool afresh each week, the saving under the former system was found to be 51.7 per cent at the

<sup>1</sup> Atkins, *Proc. Ill. Water Supply Assn.*, 1911.

<sup>2</sup> Levine, *J. Infec. Dis.*, 18 (1916).



Evanston Y. M. C. A. There is a saving in the cost of water and of heating, which is reduced somewhat by the extra cost for alum and power.

#### HYPOCHLORITE VS. COPPER SULFATE AS A STERILIZING AGENT IN SWIMMING POOLS

Copper sulfate has recently been recommended, and in a number of instances adopted, as a substitute for "bleach" in swimming tank sterilization. It has the advantage of economy and ease of addition. Copper sulfate has long held a place in drinking water purification as an agaeicide, but its bactericidal powers in safe amounts have never been urged. Stokes<sup>1</sup> obtained satisfactory results in swimming tank disinfection with copper sulfate in a dilution of 1 in 100,000. Mannheimer<sup>2</sup> notes its use in three New York pools studied by him. Rettger<sup>3</sup> abandoned sulfate of copper because of the hardness of the resulting water. Thomas<sup>4</sup> found 0.4 part per million of copper sulfate more efficient than 2.5 parts per million hypochlorite. Levine<sup>5</sup> obtained very satisfactory results with copper sulfate in amounts of 1.5 to 3 parts per million added intermittently. He considers it preferable to "bleach," to which he attributes an irritating effect upon the eyes and possible harmful influence on the teeth. The last objection seems to the author rather strained.

In Table II appears the result of analyses made upon the water of the Evanston Y. M. C. A. pool for a typical one-week period followed by a 15-day copper sulfate treatment. One pound of hypochlorite was added each night in the usual manner, while the copper sulfate was used in the proportion of 0.4 part per million. During the hypochlorite régime there was an average of 106 persons using the tank per day, while during the copper sulfate treatment the average was 125. There was some complaint during the latter period of the irritating effect of the water upon the eyes. This latter was noted also in a series of experiments upon the Northwestern pool water where 0.5 to 0.6 part per million of copper sulfate was used. If copper sulfate in these quantities is irritating, it is obvious that its use in the rotating system is questionable, owing to the cumulative effect.

TABLE II—RESULTS OBTAINED UPON EVANSTON Y. M. C. A. POOL WATER DURING A HYPOCHLORITE TREATMENT FOLLOWED BY COPPER SULFATE TREATMENT

Bacteria per Cc	Per cent of Tests Falling within the Limits Indicated					
	4 day P. A. at 20° C.	Hypo.	2 day L. L. A. at 37.5° C.	CuSO <sub>4</sub>	Hypo.	2 day L. L. A. at 37.5° C.
	0.4 pt.	1.9 pts.		0.4 pt.	1.9 pts.	
0-100	6	...	...	66.6	83.3	...
101-500	6.6	...	...	6.6	16.6	...
501-1000	...	...	...	6.6	...	...
1,001-5,000	...	50	...	6.6	...	...
5,001-10,000	...	16.6	...	13.3	...	...
10,001-100,000	53.3	33.3	...	...	...	...
100,001-500,000	26.6	...	...	...	...	...
500,001-over	6.6	...	...	...	...	...
Red Colonies	CuSO <sub>4</sub>	Hypo.	Gas	CuSO <sub>4</sub>	Hypo.	
2-day L. L. A. at 37.5° C.	0.4 P. p. m.	1.9 P. p. m.	Producers in 10 cc.	0.4 P. p. m.	1.9 P. p. m.	
0	100	66.6	0	73.3	83.3	
0-50	...	33.3	0 to 2	26.6	16.6	

In both series of experiments with copper sulfate its effectiveness in removing gas producers and red colonies was noticeable. During a period of 22 days at the

Northwestern pool gas producers were noted only on 6 days, which in this respect is a better showing than under the hypochlorite administration.

In a series of bottle experiments upon pool water using copper sulfate in a dilution of 0.5 part per million and 33 per cent hypochlorite in a dilution of 1.9 parts per million, the author's results were conflicting. In the main the "bleach" gave better count. A typical result in this series is given in Table III.

TABLE III—RESULTS OF BOTTLE EXPERIMENTS UPON A SAMPLE OF NORTHWESTERN POOL WATER

	Control	"Bleach" 1.9 per million	Copper Sulfate 0.04 P. p. m.
BACTERIA PER Cc.			
Plain agar, 4 days, 20° C. ....	27,750	900	26,250
L. L. agar, 2 days, 37.5° C. ....	35.0	11	20
RED COLONIES: L. L. agar. ....	0.0	0	0
GAS PRODUCERS:			
1 cc. each of 10 tubes (no. fermenting) .....	6	0	7

Five cc. of sample in a fermenting tube showed 40 per cent of gas in the control and copper sulfate-treated sample and none in the sample receiving "bleach."

Transfers from the fermented tubes fermented lactose bile vigorously.

Some 8 liters of pool water were taken in the evening just before the addition of "bleach." Control tests were run at once upon the untreated water from which two 4-liter portions were then taken, treated respectively with the agents in the above amounts, well shaken and allowed to stand over night.

The author's confidence in the advisability of applying conclusions deduced from bottle experiments on water sterilization to large scale conditions, has, however, been somewhat shaken by similar attempts in connection with city filtration plant control.<sup>1</sup> It is obvious, from the conflicting opinions on this point of the relative value of copper sulfate and hypochlorite in swimming tank sterilization, that more experimental results by different workers are greatly needed. No doubt the varying alkalinity of pool water would be a modifying factor in copper sulfate efficiency.

As pointed out by Levine<sup>2</sup> standard methods of pool analyses looking toward proper bacterial standards are greatly needed in the whole field of swimming pool sanitation.

#### SAFETY OF SWIMMING POOLS

The question is often asked, "Is a certain pool absolutely safe?" There is but one answer: "No, nor can it be made absolutely safe." There is no practical environment wherein an individual is "absolutely safe." In recognition of this, a certain firm recently devised a necktie attachment which automatically sprayed formaldehyde in front of the wearer's visage, truly a "*reductio ad absurdum*" of germaphobia.

It is probably not desirable that an individual should live in an absolutely aseptic or antiseptic environment. It is very reasonable to suppose that the personal equipment which we call individual resistance to disease is acquired in part through repeated exposure to different mild contagions resulting in slow body immunization.

This possibility of infection is always greater in crowds and greater in winter when the population

<sup>1</sup> Stokes, *Am. Med.*, **10** (1905), 1075.

<sup>2</sup> Mannheimer, *J. Infect. Dis.*, **15** (1914), 159.

<sup>3</sup> Rettger, *Eng. News*, **66** (1911), 636.

<sup>4</sup> Thomas, *This Journal*, **7** (1915), 496; *Jour. A. M. A.*, **65**, 1104.

<sup>5</sup> Levine *J. Infect. Dis.*, **18** (1916), 3, 293.

<sup>1</sup> Lewis, *Proc. Ill. Water Supply Assn.*, **1912**.

<sup>2</sup> Levine, *J. Infect. Dis.*, **18** (1916), 3, 293.

congregates in schools, theatres and assemblies of various kinds. The statistics of every health department bear this out. The crowd-contagion danger is undoubtedly greater in a swimming pool than under ordinary conditions for two reasons: *first*, water is a better transfer medium for bacteria and infectious material than air; *second*, in swimming pools there is coughing, clearing of nostrils, sometimes spitting, together with the probability that some one will snuff the water or even swallow it. There is no system of filtration or sterilization yet known that will absolutely safeguard this contingency. Infectious matter from the mouth or nostrils might be passed between adjacent swimmers even if the water were a dilute solution of disinfectant.

Is this a serious indictment against the swimming pool? I believe not, for the reason that sick people do not visit swimming pools as often as they might mingle in crowds, for example. Furthermore, those using swimming pools are usually athletically inclined and not easily susceptible to infection. No doubt the exhilaration, quickened circulation, etc., incident to such exercise makes for special resistance at the time. The possibility of "disease carriers" innocently mingling with those using such pools must be conceded. Certainly it is the duty of those having charge of indoor swimming pools to take every precaution to protect their patrons. Refiltration and sterilization, together with the strict enforcement of the preliminary shower with soap, are the accepted primary measures. In addition, the tank room should be kept scrupulously clean and well ventilated. There should be sufficient equipment for expectoration, and floor talks should be frequently given, explaining the necessity of co-operating in keeping the pool clean and wholesome. The dangers of carelessness should be pointed out and a group consciousness on the matter of thorough preliminary showers and the proper use of cuspidors should be created. When all this has been done, there should be established a strict inspection and exclusion régime. Every cough or skin infection should be forbidden entry to the tank.

With these precautions, conscientiously enforced, the swimming pool is certainly as safe as any other feature of gymnastic or athletic activity. If the records prove anything, indoor swimming compares most favorably in the matter of injury and mortality statistics with such accepted sports as football, hunting, boating, etc.

Acknowledgment is herewith made to Mr. A. F. Whipple, former graduate student at Northwestern University, for part of the analytical data used in this paper.

EVANSTON, ILLINOIS

### EXTENDING THE USEFULNESS OF A SHAKING MACHINE<sup>1</sup>

By ROBERT M. CHAPIN AND JACOB M. SCHAFER

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A shaking machine, if not a necessity, is at times a great convenience in any laboratory. But the purchasable types of machines are in general each adapted to only a single kind of work, so that a complete equip-

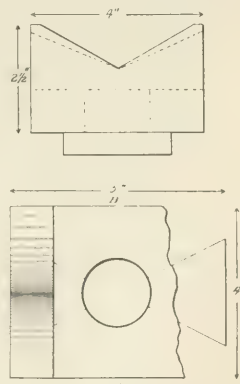
ment demands two or more different machines, which may easily deter one from the purchase of any. The purpose of this paper is to describe simple attachments whereby one machine may have its usefulness at least doubled.

The machine referred<sup>a</sup> to is of a well-known type,<sup>1</sup> in which an oscillating platform is driven by a vertical bent axle, the platform being prevented from rotating by cogs in its sleeve meshing with cogs fixed to the frame. The platform is constructed to carry 6 flasks, the necks of which are held in 6 spring clamps radiating from a central collar about the sleeve.

The first discovered extension in the possibilities of this machine was its use as a sieve shaker. The collar holding the spring clamps is raised and fastened so that the plane of the radiating limbs of the clamps is slightly above the end of the sleeve. Upon the center of this skeleton platform is placed the charged sieve or sieves, with cover and receiver. In the sieve itself must be placed a couple of pebbles or balls of flint, iron or porcelain, the motion of which will prevent clogging. But slight ingenuity is then needed to lash the whole down with cord, or with what is much better, a length of  $\frac{1}{4}$  in. rawhide belt-lacing.

From satisfactory results as a sieve shaker, the use of the machine as a shaker for liquids naturally developed. A cradle must be constructed of appropriate form for the work in view. The one illustrated in the figure, made of hard wood and faced with leather, will carry separatory funnels or bottles up to 2 liters capacity. When the cradle is set on the radiating clamps, the collar carrying the latter being fastened in its lowest possible position, the projecting end of the sleeve enters the hole in the center of the base of the cradle, while the two trapezia beneath the base fit between adjacent clamps. Then pass a bight at the middle of a length of rawhide belt-lacing under the clamp projecting at either A or B, carry the doubled lacing over the base of the cradle, once or twice around the opposite clamp, pass between the spring leaves of the clamp, and draw tight. Now place in position the bottle or separatory funnel, and pass the lacing back and forth over it and around the two clamps, finally securing the ends as before. If the container is a globular separatory funnel the lacing is best passed over the neck and the throat just above the stop-cock.

The idea is the important thing here presented, and hence the simplest possible type of fittings has been described. One may elaborate on the idea as much as circumstances warrant. In this laboratory the cradle now in use has the large hole in the base bored only about half way through from the bottom, where it is met by a  $\frac{1}{4}$  in.-hole, bored on the same cen-



<sup>1</sup> It is contrary to the policy of the Department of Agriculture under such circumstances to refer to a proprietary article by name.

<sup>1</sup> Published by permission of the Secretary of Agriculture.



ter. Through the latter hole passes a wing headed screw bolt which enters a female screw threaded into the oil hole found at the upper end of the sleeve. The head of the bolt plays on a countersunk iron washer. The container to be shaken is secured in place by a leather band and clamp permanently attached to the cradle.

With proper speed adjustment the shaking is thoroughly effective, while either form of cradle is quickly demountable if the machine is wanted for its originally intended use as a flask-shaker.

A minor drawback to this type of machine is a tendency to pound sometimes under an imperfectly balanced heavy load. It would seem that this might be overcome by better designing of the cogs. Meanwhile the pounding may be considerably lessened if a cup made from a pipe cap is fitted around the lower cogs, and filled with grease mixed with sawdust or granulated cork. In extreme cases a clamp or other weight may be fastened to the light side of the platform.

BIOCHEMICAL DIVISION, BUREAU OF ANIMAL INDUSTRY,  
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## ADDRESSES

### ACID-RESISTING ALLOYS<sup>1</sup>

By W. C. CARNELL

Received June 19, 1916

The development and progress of the Chemical Industry is vitally dependent on the development of materials out of which the plant equipment may be constructed. A process that is a success in the laboratory will be a success in the factory, if conditions are duplicated. Platinum and glass are available in the laboratory, but may be prohibitive in the factory. Platinum at \$30.00 per Troy oz. was used for the manufacture of concentrating stills for sulfuric acid; platinum at \$95.00 per oz. cannot be considered. Glass has its place, but at best is unsafe for extensive processes.

The branch of the chemical industry that suffered most for materials out of which to construct apparatus was the mineral acids division.

For many years various metals and alloys were offered for which more or less acid-resisting properties were claimed. They had their uses but as complete acid-resisting materials they were not successful. With the advent of fused silica a decided advance was made, and it successfully replaced platinum in a number of processes.

In 1911 a basin of fused silica was tried out at the factory with which the writer was connected; so successful were the results that a 10-ton cascade concentrating plant for sulfuric acid was erected to replace a platinum outfit. The results were all that could be desired. The acid made was even better than that made in platinum. Fused silica is brittle and costly and must be handled with as much care as glass.

In 1913 a material under the trade name of "Feralun" was tried out. This was a mixture of cast iron and an abrasive, the abrasive being an alloy of aluminum and silicon. The surface of the iron was covered with the abrasive. The abrasive was acid-resisting, but the acid soon destroyed the iron, leaving a porous mass. However, we found "Feralun" useful for nipples on acid tank cars.

**FUSED SILICON**—Silicon has acid-resisting properties that are all that could be desired for sulfuric acid, but it is more brittle than fused silica, and its use has not been very extensive.

**"FERRO CHROME"**—This alloy is made by the Electro Metallurgical Co. of Niagara Falls, and is a very promising product. Glacial acetic acid does not attack it; 56 and 28 per cent acetic acid attacked it slightly. Strong and weak nitric and sulfuric acids have practically no effect on the alloy. Hydrochloric acid attacked it readily. The experiments were carried out in a bowl 18 in. in diameter and 6 in. deep.

**SILICON AND IRON ALLOY**—The materials thus far mentioned are valuable for specific purposes. The real dawn of acid-resisting alloy came with the use of "silicon iron" alloy. The beginning of the use of this alloy was about 6 yrs. ago. The

first advertisement the writer observed of this alloy was in the *Journal of the Society of Chemical Industry*, January 15, 1912. This was of a silicon iron alloy, "tantiron," put out by the Lennox Foundry Co., Ltd., of London, England.

In May, 1912, after a year of experimenting, the first silicon iron alloy in the United States was put on the market under the name of "Duriron," by the Duriron Castings Co. of Dayton, Ohio. In 1913 the American rights for "Tantiron" were taken over by the Bethlehem Foundry and Machine Co., of South Bethlehem, Pa.

"Ironac" is another trade name for a silicon iron alloy made by the Houghton Co., Ltd., of London, England. While these are all alloys of iron and silicon, their composition is not the same.

Silicon iron alloy as put out under the above names is very resistant to all strengths of sulfuric acid, and apparatus made of this alloy is used in all forms of concentrating vessels and cooling devices for the concentration of sulfuric acid. By the use of the so-called "cascade basins" set in a proper furnace, full strength oil of vitriol is made from 50° Bé. acid. If all the fittings and coolers are made from this alloy the resulting oil of vitriol is practically free of iron after the plant has been in operation a few weeks. Where brimstone acid is used the resulting oil of vitriol should not contain over 0.0002 per cent iron. For sulfuric acid concentration, the alloy is durable and the breakage is very small. A plant properly handled will run for months without a shut-down. The success of the modern tower system for concentrating sulfuric acid has been due largely to the use of pipes and fittings made of this alloy.

Silicon iron alloy castings have extensively replaced stoneware parts for the manufacture of nitric acid. Early in 1916 the demand for nitric acid increased to enormous proportions; extensions to old nitric acid plants and the erections of new and larger plants was immediately demanded. The capacities of the stoneware factories of the country were soon taxed to their limit. Deliveries could not be made under 6 months, if at all. Had the production of nitric acid been dependent upon stoneware as it was a few years previous, the production of nitric acid would have been greatly curtailed and the story of the World's War would probably be different.

The silicon iron alloy is resistant to nitric acid of various strengths. It can be cast into all the various forms required for nitric acid apparatus. Castings can be made as readily and as quickly as can those made of cast iron. Here was the ideal substitute for stoneware. Necessity compelled its use and to-day it has largely superseded stoneware for nitric acid production.

A large nitric acid plant equipped entirely with this alloy in the form of "Duriron" was in service for 8 mo. and the alloy showed no indications of corrosion or deterioration. There was practically no breakage. Fire destroyed the building housing the plant and most of the supports for the apparatus. The fire did not harm the castings, though they were exposed to intense

<sup>1</sup> Read before the Eighth Semi Annual Meeting, American Institute of Chemical Engineers, Cleveland, June 16, 1916.

heat. Eighty per cent of the castings were recovered and put into service and are in use at the present time. Ninety per cent nitric acid made in a plant equipped with "Duriron" castings showed an average iron content of 0.0014 per cent iron while 36 B $\acute{e}$ . nitric acid (52.30 per cent) showed 0.0042 per cent iron.

The silicon iron alloy was developed to resist acid. It not only resists acid, but it is resistant to erosion and to rust. Ground surfaces, representing the true alloy, are practically immune from rust. The rough casting may show some rust on exposure, but this is due to impurities in the surface caused by contact of the alloy with the molding sand; this is a surface rust only and will not penetrate. The alloy is also heat-resisting, when made of suitable design. For very high temperatures, the walls must not be too thick. Castings do not distort on heating but hold their form up to the melting point.

The following data are given for "Duriron":

TABLE I—ANALYSIS (APPROXIMATE) OF DURIRON

Per cent			
Silicon	14.00 to 14.50	Melting point	2500° to 2550° F.
Manganese	0.25 to 0.35	Specific gravity	7.00
Total carbon	0.20 to 0.60	Compression strength	70,000 lbs. per sq. in.
Phosphorus	0.16 to 0.20	Tensile strength	25 per cent less than cast iron
Sulfur	Under 0.05		

A bar of "Duriron" was compared with a bar of equal size of the best grade of chemical pottery, under equal conditions; the earthenware test bar broke so quickly that the testing machine gauge did not record any pressure. The "Duriron" bar broke under a load of 1000 lbs. By using a suspended vessel on an earthenware bar and gradually loading it with small pieces of metal and sand, a breaking test of 100 lbs. was obtained for the earthenware bar.

TANTIRON—Tantiron was first produced by Mr. Robert W. Lennox of the Lennox Foundry Co., of London, England, about 1908. In 1913 the rights for the use of this alloy in the United States, Canada and Mexico were acquired by the Bethlehem Foundry and Machine Co. of South Bethlehem, Pa.

TABLE II—ANALYSIS (APPROXIMATE) OF TANTIRON

Per cent			
Silicon	14.00 to 15.00	Melting point about	2550° F.
Sulfur	0.05 to 0.15	Specific gravity	6.8
Phosphorus	0.05 to 0.10	Tensile strength	6 to 7 tons per sq. in.
Manganese	2.00 to 2.50		
Carbon (graphite)	0.75 to 1.25		

The alloy is not suitable for apparatus in which high internal pressures are to be used, unless it is strengthened by a protecting jacket. Forty to fifty lbs. is given as the maximum working pressure for an autoclave made of Tantiron.

In general, silicon iron alloy cannot be cast in rectangular shapes or flat surfaces. The chemical engineer should collaborate with the foundryman in order to design shapes which can be produced in the foundry, and still serve the purpose of the operating conditions required.

#### CONCLUSION

While there is still opportunity for improvement and while there is much more to be desired in an acid-resisting material out of which to construct apparatus for the acid industry, yet, the silicon iron alloy or silicide of iron, as it has been called, has proven a boon to the acid industry; without it many things could not have been accomplished. It is more efficient than stoneware. At best, chemical stoneware if made properly should take 10 to 12 weeks for its production. Castings of this alloy can be made and delivered in the same time it takes to make castings out of cast iron. The limitation to castings made of this alloy are those of shop and foundry alone. One company has a foundry with a furnace capacity of 72 tons per day. Today thousands of tons of castings made of this alloy are in use. It is finding its way in all branches of chemical industry. Since its introduction new chemical processes have been started which were impossible before, because of lack of suitable apparatus.

Silicon iron alloy is being improved upon rapidly and the time does not seem far distant when all sorts of vessels will be made of this or a similar alloy that will give to the chemical industry the ideal non-corrosive material that may be fabricated into all the shapes peculiar to the needs of the industry.

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#### COKE-OVEN AMMONIA FOR MUNITIONS

By J. W. TORRENTINE

It is a very healthful reconnaissance that the nation is now making of its resources and industries in relation to national preparedness for defense. For the first time it has become recognized in this country that successful wars are to be fought as much with mine, factory and skilled labor as with gun, battleship and armies. The nation finds itself peculiarly independent of foreign sources of materials essential to a state of preparedness: of food materials, the metals, fuels, fabrics and—we hope to show—explosives.

Since for the manufacture of the various explosives for munitions purposes we have been using nitric acid obtained exclusively from sodium nitrate imported from Chile, the impression has come to prevail that we have no domestic source of nitric acid, and, therefore, that in case of war with a nation of sufficient maritime strength to enforce a blockade, we would be seriously embarrassed.

Upon investigation it develops that we have a domestic source of raw materials from which nitric acid may be prepared; that this source is now large and rapidly growing, and that it is susceptible of a practically unlimited development should necessity or public exigency demand. The source meant is the ammonia recovered as a by-product in the distillation of coal for the production of coke and gas. That it has not become more generally recognized as a source of nitric acid is because it has found a ready market in that other great industry dependent on cheap nitrogen compounds, the fertilizer industry, to which it contributes about 40 per cent of the nitrogen now consumed therein, and because commercial methods of converting ammonia into nitric acid are new and imperfectly understood. The explosives industry has been content with its abundant and convenient supply of raw materials obtainable from Chile and, therefore, has not demanded the development of an additional supply. The question has never before arisen in a popular way; hence, the popular misconception.

In time of blockade, with Chilean nitrate no longer available, ammonium sulfate would be the main nitrogenous compound available in this country for munitions and fertilizer purposes. To what extent would this be adequate to meet the demands of the country in such an emergency?

#### PRESENT DOMESTIC PRODUCTION OF AMMONIA

The present production of ammonia in this country is from two main sources: (1) By-product coke ovens, and (2) coal-gas and bone carbonizing works. The production of by-product ammonia has developed from an output of 13,800 tons in 1900 to 153,000 tons in 1913. The details of the record are set forth in Table I; likewise are presented, figures showing the production of ammonia from coal-gas and bone-carbonizing works. From these figures it is evident that the by-product oven is not only the chief source of domestic ammonia, but that it is rapidly overshadowing the other two sources.

Bituminous coal contains 1.2 to 1.34 per cent combined nitrogen. By ordinary methods of coking and from the average coal, a yield of 20 lbs. ammonium sulfate is expected per ton of coal. This is realized when the coking is done in the so-called by-products oven, that type of oven which makes possible the recovery and utilization of the surplus gas (*i. e.*, the gas not needed in the process itself to produce the heat for the coking).



TABLE I.—UNITED STATES AMMONIA PRODUCTION, EXPRESSED IN SULFATE EQUIVALENT (TONS OF 2000 LBS.)

Year	By-product Coke Ovens	Coal Gas & Bone Carbonizing Works	Total Production	Per cent from Coke Ovens
1900	13,800	13,800(a)	27,600	50
1901	15,279	14,000(a)	29,279	52
1902	18,483	17,641(a)	36,124	51
1903	24,098	17,775(a)	41,873	57
1904	37,653	22,011(a)	54,664	60
1905	41,864	23,432	65,296	64
1906	..	..	75,000(a)	..
1907	62,700	36,609	99,309	62
1908	50,073	33,327	83,400	60
1909	75,000	31,500(a)	106,500	70
1910	86,000	30,000(a)	116,000	74
1911	95,000	32,000(a)	127,000	75
1912	130,000	35,000	165,000	79
1913	153,000	42,000(a)	195,000	78.5
1914	183,000	..	..	..
1915	220,000	..	..	..
1916	234,000	..	..	..
1917	376,000	..	..	..

(a) Estimates.

The surplus gas amounts to from 4,000 to 6,000 cu. ft. per ton of coal. Most of the coal coked, however, is coked in the so-called beehive ovens, a type of oven which makes no provision for the recovery of the surplus gas or other by-products. The

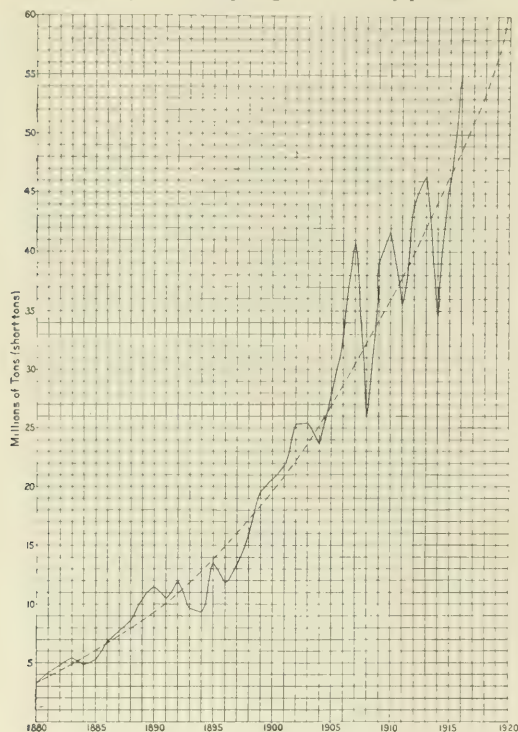


FIG. I.—PRODUCTION OF COKE IN THE UNITED STATES

ammonia produced in the process, in amounts per ton of coal potentially as great as in the by-product recovery process, is evolved with the surplus gas and with that is destroyed. Likewise, other by-products, such as *coal tar*, the source of various substances essential to the modern dye industry, *toluol*, of importance in the explosives industry, and *benzol*, of great value as a substitute for gasoline as a motor fuel and in other ways, are lost. These have a total value of \$1.50 a ton of coal coked. The coke is the only product realized from the coking in beehive ovens. For every ton of coal so coked, then, we may compute the loss as \$1.50.

In the year 1914, approximately 52,000,000 tons of coal were coked in the United States, yielding 35,000,000 tons of coke. Of this coal, 35,000,000 tons, or 68 per cent, were coked in beehive

ovens, while only 17,000,000 tons, or 32 per cent, were coked in by-product ovens. From the latter were obtained as by-products approximately 61,000,000 cu. ft. of surplus gas, valued at \$6,000,000; 110,000,000 gal. of tar, valued at \$3,000,000; ammonia in various forms of a total value of \$7,700,000; and other by-products, principally benzol, valued at \$1,000,000; a total value of \$18,000,000, in amount only 32 per cent of those recoverable from the total coal coked.

These figures show that the by-products recovered in 1914 have a value of \$1.13 per ton of coal. Recent developments in the industry and market have advanced this value to \$1.50 per ton of coal. On the basis of the latter figure, the by-products producible, but lost, from the coal coked in beehive ovens in 1916 will be approximately \$55,000,000. The ratio of value of coke to that of by-products is \$2.37 (the value in 1914 of the coke produced from a ton of coal) to \$1.50 (the value of by-products).

The increase in the amount of coal coked in the by-product ovens is due to two causes: (1) the increase in the total amount of coal coked, and (2) the substitution of the by-products oven for the beehive. The former increase is slower than the latter. It also fluctuates, due to the varying prosperity of the steel and other industries using coke. Its increase, of course, is due to the growth of these, and to the introduction of the use of coke into other industries. In this connection Fig. I shows the rate of increase in production of coke. The estimate for 1916, 55,000,000 tons, indicates that during this year approximately 80,000,000 tons coal will have been coked. The trend of the increase, fluctuations being averaged, is shown by the dotted line. This indicates that by 1920, the production will be 60,000,000 tons of coke, requiring the coking of approximately 90,000,000 tons of coal.

The substitution of the one form for the other is undoubtedly induced by the greater profits to be realized from coking in the by-products oven. Not only is a higher yield of coke realized, but, as has been shown, the by-products represent increased revenue. This transition probably has been gauged to keep pace with the demand for the by-products. Ammonium sulfate, for example, while being produced in increasingly great quantities, has not suffered any marked decrease in price. Coal tar is finding increasingly wide application in road building. The reported development of the American dye industry, if existent, will undoubtedly increase the revenue realized from the sale of coal tar, the source of most of the dyes. The sudden demand for toluol for use in the explosives industry has drawn attention to that valuable product. The high price of gasoline has given impetus to the production of benzol, a product now only partially developed, which can be produced cheaply and which constitutes an ideal motor fuel. From the by-product ovens now in operation 54,000,000 gal. of this commodity could be produced.

The rate of substitution of the by-product for the beehive oven is illustrated by Fig. II. The dotted portion of the line is an extrapolation to show when this substitution will approximate 100 per cent. The present rate of increase indicates that this approximation will be realized in about 5 yrs.

In Table II are set forth figures showing roughly the general development of the coking industry and the output of by-product ammonia in the United States.

TABLE II.—DEVELOPMENT OF THE COKING INDUSTRY AND BY-PRODUCT AMMONIA PRODUCTION (SHORT TONS) IN THE UNITED STATES

Year	Total Coal Coked	Total Coke Produced	Beehive Coke	By-products Coke Tons	Ammonium Sulfate Per cent
1901	33,000,000	21,795,883	20,615,983	1,179,900	5.41
1911	53,278,248	35,551,489	27,703,644	7,847,845	22.07
1913	69,239,190	46,299,530	33,584,830	12,714,700	27.46
1916	80,000,000	55,000,000	37,000,000	18,000,000	32.7
1917	..	..	..	33,000,000	..

Especially notable is the fact that the production capacity of the by-product plants completed and operating on April 1,

1916 is 18,000,000 tons of coke, and those now built, under construction and determined upon, by the close of the year 1917 will produce 33,000,000 tons of coke; correspondingly, the ammonia, reckoned as ammonium sulfate, produced during 1915 was 220,000 short tons;<sup>1</sup> that which can be produced by the by-product ovens completed and operating on April 1, 1916, was 234,000 short tons; and finally, that to be expected by the end of 1917, is 376,000 short tons.

#### THE OUTPUT FOR THE IMMEDIATE FUTURE

The present rapid increase in the rate of transition from the beehive to the by-product coke oven permits no other conclusion than that shortly the transition will have been realized. We can predict, then, with confidence, the amount of combined nitrogen which the immediate future will make available for domestic arts and industries. Already the market exists for the coke, the main product, and undoubtedly the demand for it will continue. If the demand for coke does not increase, we can still confidently expect the recovery of the bulk of the am-

monia to supply the munitions industry, and ammonium sulfate the fertilizer industry. The conversion of ammonia into nitric acid for application to the explosives industry, however, is a distinct possibility of the future, which may result in a keener competition between the two commodities and a reduction in their price to the consumer.

#### OUTPUT POSSIBLE UNDER EMERGENCY CONDITIONS

In time of emergency the bulk of the ammonia produced would be immediately available for conversion into nitric acid for munitions purposes. All of that normally entering the fertilizer trade could be so applied, since, be it remembered, the staple food and forage crops on which a nation depends in times of emergency are produced in this country without the aid of fertilizers. Agricultural production would even be restricted in case of blockade, since we normally produce a great deal more than we consume. Not more than 7 per cent of the ammonia produced now enters the refrigeration industry; this could not be withdrawn entirely without inconvenience, though it could be reduced. To this sum could be added that obtained from the other sources, coal-gas and bone-carbonizing works.

In contrast with the foregoing is the situation in Germany where the normal production of by-product ammonia is 550,000 tons ammonium sulfate (1913). This was applied to agriculture. Conditions made necessary a stimulated agricultural production, instead of a restricted one, so that it was not possible to withdraw the ammonia from agriculture for munitions purposes without impairing an already inadequate food supply. Therefore, extreme measures had to be adopted to increase the supply of ammonia.

By methods to be described later, whereby ammonia is converted into nitric acid, one part ammonium sulfate would produce nitric acid equivalent to 1.16 parts of sodium nitrate, from which it follows that the ammonium sulfate produced at the normal rate of output obtaining on April 1, 1916 (234,000 tons) would yield nitric acid equivalent to 271,000 tons sodium nitrate; that estimated for 1917 (376,000 tons ammonium sulfate), 436,000 tons sodium nitrate.

The importations of sodium nitrate during the year 1911 were 547,000 tons, and during 1915 were 577,000 tons. Normally, it is estimated that 40 per cent of the amount imported enters the explosives industry of the country; that would be about 220,000 tons sodium nitrate, an amount decidedly less than that which could be produced from our present output of by-product ammonia.

If the above quantities of ammonia were not adequate, the first step would be to replace all beehive ovens with the by-product form, whereby the ammonia now lost from these would be saved. This would be effecting at once (by the Government) that which is now being accomplished more slowly by the industry itself. Since the ammonia so produced could be regarded as a by-product, its cost would be negligible, the sale of the other products being at such a price as to cover all costs of operation. The size of the investment required, then, would have no significance, since ample interest could be assured.

To erect by-product ovens requires not more than \$1,500 per daily ton coal capacity. Operating 360 days per year, the yearly capacity would be 360 tons coal. The proceeds from the sale of the products would be \$540 for the by-products and \$850 for the coke, from which must be deducted, of course, the cost of the coal, operating expenses and overhead charges.

One of the by-products obtained from the proposed by-product ovens would be combustible gas, about 5,000 cu. ft. per ton of coal coked. If so desired, and if additional ammonia were required, this gas could be used with gas engines to generate electrical energy for the electrical fixation of atmospheric nitrogen by any approved method. The surplus gas from a ton of coal, when so used, generates electrical energy equivalent to

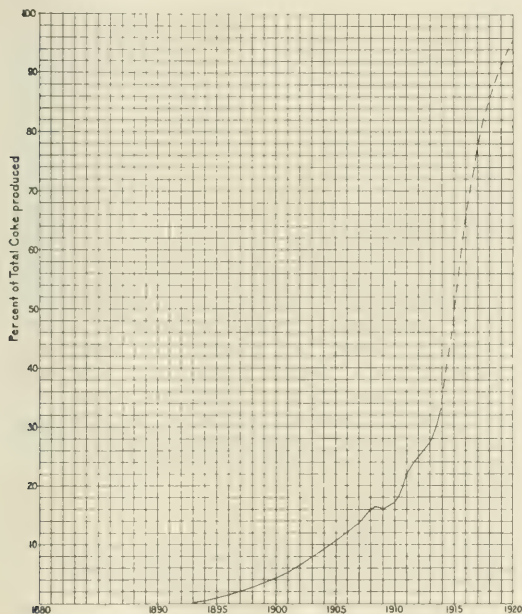


FIG. II.—SUBSTITUTION OF BY-PRODUCT COKE IN THE UNITED STATES

monia now liberated in the coking industry. On the basis of figures obtaining in 1914, that would bring the total production of by-product ammonia to 520,000 tons ammonium sulfate; and on the basis of the estimate for 1916 (80,000,000 tons of coal), the total would be 800,000 tons ammonium sulfate. This will be realizable by the by-product oven alone. In addition there will be a further amount of ammonia from coal-gas and bone-carbonizing works, certainly an increased amount over present production.

This, then, is the production of ammonia which we may look forward to with confidence. This is the development which is taking place normally, in response to ordinary economic and business laws, without apparent stimulation or artificiality. This is what we have available for normal conditions. This is supplemented, it must be remembered, by Chilean nitrate. The supply appears entirely adequate for any development now contemplated. It is probable that Chilean nitrate will continue

<sup>1</sup> This represents approximately 85 per cent of the total production of ammonium sulfate of the country, the remaining 15 per cent, or 40,000 tons, coming from coal-gas and bone-carbonizing works.



160 kilowatt hours; the gas produced from coking 35,000,000 tons coal (1914) would yield over 800,000 continuous horse power, which would be sufficient for the fixation of an amount of nitrogen equivalent to an additional 1,400,000 tons ammonium sulfate. The gas, being a by-product, is produced at slight cost and the installation for the development of the power is limited to comparatively inexpensive gas engines.

As a concrete proposition, in case the normal production of by-product ammonia was not sufficient for the emergency at hand, it would be possible for the Government to install by-product ovens and use the gas for the generation of electrical energy for the fixation of nitrogen. This could be put into operation quickly and at a comparatively small cost. Ammonia would be produced as a by-product at the same time, and use could be made of the coke and other products.

Were the emergency postponed to a time when all the coke was produced in by-product ovens and a market had been found for the gas, use could be made of the enormous quantities of waste and low-grade coals, the lignites and even the peats available, all of which on distillation yield ammonia and combustible gas suitable for use in gas engines. Or should it be desired to effect a permanent and large production of ammonium sulfate, the use of coke could be encouraged by restricting the use of bituminous coal where coke can be used as advantageously. The Government itself could produce coke and sell it at the same price as coal, reserving to itself the ammonia and other by-products. Not only would by-products worth \$1.50 per ton of coal be conserved, but an increase of about 20 per cent in the efficiency of the coal as a producer of power would be effected. Likewise, the smoke nuisance would be abated. It is reported that such a restriction has been in effect in Germany since 1914. This is a measure which would have to be inaugurated by the people, for the producer of coal is interested in the use of more coal, not in its more economical use; and the producer of coke is more interested in the maintenance of good prices for by-products than a larger production. It is a suggestion which is deserving of very careful consideration, for, with the coal now wastefully used, is lost enormous quantities of ammonia and benzol (and power). This rigid conservation would afford agriculture the best of fertilizers and the public as a whole an excellent motor fuel, at a fraction of their present cost.

The basis of practically all explosives is nitric acid. This, usually, is prepared from sodium nitrate. It may be prepared

also from ammonia. When ammonia gas and air, mixed in the proper proportions, are allowed to flow through platinum gauze or other suitable materials, known as catalytic agents, heated to the proper temperature, the ammonia is converted into nitric acid. While the chemical reaction involved has long been understood, its recent modifications and commercial application have come to be known as the Ostwald process for manufacturing nitric acid.

It is reported that this process is in successful operation both in England and Germany; that in the latter country all the nitric acid being produced is obtained by means of it. If, in our country, it could be developed to a degree of efficiency where nitric acid obtained by means of it from by-product ammonia could be made to compete so successfully with Chilean nitrate as to exclude it from American industries, the large sum now annually expended for that commodity in a foreign market could be retained for the domestic market.

Obviously the Ostwald process is of prime importance. Steps should be taken at once to determine all the conditions surrounding its best performance. It is claimed that already it has been developed to the stage where 53 per cent nitric acid can be produced by means of it at a cost of \$0.03 per lb., inclusive of cost of the ammonia. It should be investigated thoroughly in order to establish the best technique of the operation, to further reduce the operating cost, to further increase the yields, to develop new and cheaper catalytic agents and to make such modifications as would render the people free of patent restrictions.

By way of summary it should be added that for times of peace America has a supply of nitrogen compounds adequate for both fertilizer and munitions purposes. This supply includes imported nitrate which is adequate for the munitions industry, and domestic by-product ammonia which contributes to the fertilizer industry. In time of emergency, should importation be prohibited, the by-product ammonia could be withdrawn at once from the fertilizer industry and applied to the munitions industry. This source, by normal processes, is being developed to a degree where no longer will any doubt remain as to its entire adequacy for all emergencies. Accompanying this development a conservation is taking place worth many millions annually to the American people.

DEPARTMENT OF AGRICULTURE  
WASHINGTON

## THE CHEMIST IN RELATION TO FOOD CONTROL

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### THE CHEMIST IN FOOD CONTROL AS RELATING TO THE ENFORCEMENT OF LAW

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The work of the chemist in food control, in so far as it relates to the enforcement of regulatory laws, is largely the obtaining of scientific evidence which may be of value in detecting the adulteration or misbranding of food products. He must not, however, be limited to the use of chemistry in obtaining this evidence, but will find that chemistry is only one of the many tools that he must use and his effectiveness and the value of his evidence will be very much restricted unless he brings to bear upon the question the assistance of bacteriology, botany, physics, and other of the sciences and arts.

The adulteration of food products, in a general way, consists in the debasing or imitation of recognized food products, and the Food and Drugs Act defines these various forms of adulteration as follows:

"The mixing of any substance, which reduces or injuriously affects the quality or strength of the article; such as the addition of water in milk.

"The substitution of foreign material, in whole or in part; such as the mixing of distilled vinegar with cider vinegar.

"The removal of any valuable constituent of the article, in whole or in part; such as extracting the essential flavoring oil from cloves.

"The coloring of an article, so as to conceal its inferiority; such as coloring noodles yellow so as to imitate the color of eggs and conceal the fact that there is a lack of this material.

"The addition of a deleterious or poisonous substance; such as the addition of salicylic acid to preserves in such quantities as might render the article injurious to health.

"The using of spoiled or decomposed products; such as moldy tomatoes in catsup."

All of these forms of adulteration above enumerated assume the existence of an unadulterated or genuine product, and the basis of most of the work in the obtaining of evidence of such adulteration depends largely on comparison of the genuine with the adulterated article. The greatest difficulty in the work is to get an accurate standard with which we can compare or measure the article under examination. It is comparatively easy to detect and measure adulteration if we have the article before it is adulterated to compare exactly with the article after

it has been adulterated. For instance, if we have a pure cider vinegar, before its mixing with distilled vinegar, to compare with the mixture, we can tell with accuracy and measure almost exactly the amount and kind of the adulteration.

If we have a sample of the cloves before the extraction has been made, to compare with the extracted product, we can measure accurately the amount of oil that has been removed. If we have a sample of the milk before it is watered, to compare with the watered sample, the detection of the adulteration is simple and conclusive; and so on through the various forms of adulteration.

The best and most accurate standard or measuring rod is the product itself before it has been adulterated. Such standards, however, are not always, or often, available for the food chemist. In fact, his chief work might be said to be to obtain the best possible standard to use as a measuring rod, and he should bear in mind that the farther he departs from the thing itself the more subject to criticism becomes his evidence.

In general, there are several kinds of standards or measuring rods which are employed, and I am giving them in the order of their value as it seems to me:

- (1) The product itself, before adulteration.
- (2) Records of analyses of similar products, as nearly as possible representative of the thing itself.
- (3) The general literature on the class of products and compilations of data.

The chemist finds, when he starts to use any of the other standards than the product itself, that there is such a natural variation in products that his standard of comparison must become either a maximum, minimum, or average, so that, while he may be able to prove that the product is adulterated, the accuracy of his estimation of the amount of the adulteration is very much diminished. If he is compelled to use only the data published in the books and literature as to the composition of the product under consideration, he will find that there is probably such a wide variation as to the composition of the product that his accuracy of measurement is very slight. He also finds this condition to exist—that records have been made of many samples regarding which there must be doubt as to their genuineness and of which there is little information as to their exact kind.

#### STEPS IN ANALYSIS OF A FOOD

The skill of the food chemist, therefore, depends largely on his ability to classify the article under examination, and then to obtain a proper standard of comparison, and, finally, to make an accurate comparison. Assume, for instance, that the problem presented to the chemist is a sample of ground black pepper which the inspector has collected and which, for reasons he has obtained from the trade and from a general knowledge of the situation, he believes has been mixed with some material whereby its price has been reduced. The chemist takes the sample and examines it for clues, and his first work should be to classify the article as closely as possible. In order to do this, he must first know who is the manufacturer, where the product is produced, and, if possible, from what it was produced. At least these should be the lines of thought toward which he should direct his attention. Then he should consider the product itself, as to its color and appearance in comparison with samples of known origin and of the various kinds, since this color or appearance may be sufficiently decisive to give an indication as to the variety of pepper used in its manufacture or as to the presence of probable adulterants. After he has very carefully considered the article itself from the standpoint of appearance, taste, smell, and character, he should then make his analysis, and, after this has been completed, we may be able to say that the product has the appearance of a black pepper, that the microscope does not show any foreign material, that the product has an abnormally high ash and crude

fiber, and is somewhat peculiar in color and appearance; but we must still further classify the product we are working with before we can obtain a proper measuring rod with which to compare.

We know that there are on the market at the present time at least four kinds of black pepper used commercially, and this product may be made from any one or from a mixture. If by any means we can show that it is made from one special variety, we have classified the product to a very considerable extent, so that we can eliminate from comparison the data, analyses and information regarding the other three varieties. For, if we go to the published results of analyses, we find that there is a wide variation in the compositions of these four varieties of pepper commercially on the market. We also find that, unless by some means we can exclude from consideration at least one of these varieties, we will not be able to show that the product is adulterated, for we find that the data on Acheen peppers show an especially high crude fiber and ash, and, in all probability, we will find analyses of supposedly genuine products which will have a higher ash and higher crude fiber than the sample under consideration. On the other hand, if we can exclude this grade of pepper from consideration by some means, we find that the other peppers vary only within rather narrow limits, and we will have a fairly satisfactory standard or measuring rod with which to compare our sample under consideration, and from which comparison we will probably be able to prove the adulteration. If we now compare our analysis with the data on Singapore, Alleppey and Tellicherry peppers, we find the crude fiber and ash in our sample are excessive, probably due to the admixture of pepper shells on account of the fact that no foreign ingredients were found. In order, however, to further limit our standard, and in order to be able to estimate approximately the amount of adulteration, which is a very desirable thing to do, we must develop if possible a still more accurate standard of comparison. This we may be able to do if we can limit our standard to a single variety. In order, however, to get such a standard, it is necessary for us now to go back to a consideration of the manufacturer, what we know of him or of the raw materials he is using, what peppers he has on hand, and whether or not he has purchased or has in his possession pepper shells.

In order to get such information, we have to depend on other methods than pure chemistry, and work with the inspectors, without whom our work would be exceedingly difficult. If then we can find that a certain grade or kind of pepper is exclusively used and that this manufacturer has purchased pepper shells from time to time and samples of these can be obtained, we have a possibility of preparing a standard for measuring our product which will give us a very much greater accuracy, especially in a quantitative idea. If we had been compelled to depend upon the literature as a standard, or upon our knowledge of the composition of various kinds of peppers, or practical standards adopted by regulation or law, we would have been very much in the dark in regard to what our results meant, but, by classifying our product and eliminating from our standard everything except what is truly comparable, we are able not only to show that adulteration has taken place but approximately the quantity.

After we have reached our conclusion and go back over the evidence, we find that we have used the eye, the taste, the microscope, knowledge of trade conditions, and study of factory methods combined together with a little chemistry.

#### ADVANTAGES OF INDIVIDUAL STANDARDS

The chemist in reality might be considered as a scientific detective who must follow every clue until he makes out his case and obtains a true and correct standard with which he can compare the unknown. The possibilities of this method of



making an individual standard for each case are much greater, I think, than most food chemists have realized or have used. Take, for instance, the question of watering and skimming of milk. If our analytical data indicates the possibility of the addition of water and we turn to the literature for information, we find a most confusing condition. Thousands and thousands of analyses of milk, widely varying, have been published, and it is doubtful if any of the mixing would be detected if these records were permitted to be used as a standard, but it is recognized that different breeds of cows give milk of entirely different composition, so that the first thing that should occur to us is to determine from what breed of cattle the milk which we have analyzed comes. Then it is possible for us to eliminate from our comparison all of the data which has been published or recorded on cows of other breeds, but it is almost always a practicable and feasible proposition to get a sample of the milk under consideration before it has been adulterated. By going out to the farm, we can find out the kind of cattle which are being milked, we can stay there during the milking periods and obtain samples of the milk under our personal supervision in such a way that water could not be added. When we have obtained an average sample of the milk of the night and morning and have obtained the analysis, we then have an accurate standard with which to compare the product under consideration. If it is not possible to get such a sample, we can at least narrow our standard down to determining the breed of cattle. If it is necessary for the chemist to take a sample of milk and analyze it without any information as to its source and he is unable to obtain any information as to its source, we have a very unsatisfactory and inaccurate standard or method of proving adulteration. We must then take into consideration the wide variations recorded in the literature, and our final conclusion must be a more or less accurate guess.

It would be possible to go on and outline a number of other cases where it is possible and feasible practically to obtain the product itself before adulteration as a standard for comparison, but I think these two illustrate a general principle toward which the intelligent and thoughtful man must work in every case. We know from our experience that the composition of natural products varies from time to time, from season to season, and from location to location. The article now on the market may not have existed a year or ten years ago.

Take, for instance, the grapes of a certain section, which are peculiar in that they have certain qualities, and a grape juice made from them has certain peculiar characteristics as to acid, sugar, and color. The grape juice made from the same variety of grapes, grown in another section, might be materially different, so that, in our classification and comparison of grape juices, we must try to eliminate from consideration grape juices which were not made under the same conditions and in the same location.

The first thing the analyst should do in examining grape juice is to determine, by taste and appearance if possible, the kind of grapes from which manufactured, and, if possible, the place of production. Then he is in a fairly good position to eliminate from consideration the analyses and data which have been published on other varieties.

It has seemed to me, during the consideration of this paper, that some results published in the past have been of comparative little value, because exact detailed descriptions of the samples are not given. It seems to me that data, in order to have the greatest value as a standard for comparison, must describe exactly in minutest detail the kind, place of production, and every other factor which would have an effect upon the composition of the product.

The idea was spread abroad some years ago that it was impossible to determine by an analysis whether American beers were made from malt or malt substitutes, because the recorded

analyses of foreign beers made from a certain kind of malt were similar in analyses to American beers made from malt and malt substitutes. Of course it was impossible to determine, by analyses of American beers and comparing them with data on German beers, that there was any substitution for malt, but why should we do so unscientific and inaccurate a thing as to permit ourselves to use for a standard for comparison a product which is not a true standard? The proper standard for comparison of American beers would be American beers produced from the malt used in this country and under the conditions prevailing in this country. The point that I wish to make, and to reiterate, is that it is not scientific or proper to use, as a basis of comparison, data or records or analyses of products which are not the same as the product with which we desire to make the comparison.

We have in our literature many, many analyses of maple sugars and maple products, and we find that maple products coming from certain sections are quite different in composition from those produced in other parts of the country. It is impossible, in some cases, to reach any conclusion as to whether or not a maple product is adulterated if we must consider in our comparison the wide range of variations which have been found in these products made all over the country, but, if we can limit ourselves to maple products made in Ohio, or maple products made in Vermont, or maple products made in Canada, for the basis of our comparison, if we can classify our unknown sufficiently to eliminate certain kinds of products, we may be able to get a fairly accurate standard or measure. In other words, the first thing to do with an unknown is to classify the product by smell, taste, appearance, analysis, method of manufacture, and knowledge of varieties on the market. Then, when we have classified our product as far as possible, we must limit our standards so that we do not include in them anything but the products properly comparable, and, finally, we must make our comparison as accurately as possible.

It is perfectly obvious, it seems to me, that our measuring rods or standards of comparison must be really measuring rods, and we must not deceive ourselves into thinking that they are real when as a matter of fact they are not.

I recently read an article in which the man's success had depended upon his being able to see things as they were, and to do the obvious thing, but to do the obvious thing requires two things—knowledge of the situation and thought regarding it, and it seems to me that these are the two things which every food chemist should apply to the question of a proper standard of comparison.

CHICAGO

## FOOD CONTROL FROM A STATE VIEWPOINT

By DAVID KLEIN

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The chemical aspect of state food control work is so intimately connected with the inspection and field investigation phases of the problem that it is not possible to limit the province of the chemist and to confine the discussion within such bounds. To be sure, the chemist is supposed to analyze the samples sent in by the inspectors, and to render an opinion upon their compliance with the provisions of the law. But the chemist's greater contribution to food control lies in a field not circumscribed by the walls of a laboratory: his sphere of activity should be co-extensive with the boundaries of the state. I refer to the application of scientific principles in the regulation of food industries, for the method employed in investigating and controlling an industry should differ in no essential from the course pursued in carrying out an investigation of some highly theoretical subject in the university. Just as every research problem has its characteristics to which the general principles of scientific procedure must be adapted, so has each state its characteristics which must be taken into consideration. Among these may be

mentioned geographical features (size, climate, location, topography), population and food productivity (kinds and amount), and transportation facilities.

The distribution of population is an important item. The problems of controlling the food supply increase in more than a direct ratio to the population gathered into cities. The larger the city, the greater the need for vigorous supervision. It may be argued that the control of city food supplies should be performed by municipal officers. Theoretically, this condition may be the most desirable. Practically, the plan has not been generally successful. The larger cities are bending their efforts towards controlling milk and a few other foods. The smaller communities as a class have not been sufficiently impressed with the need for local food control. Lack of funds, inefficient health departments, indifferent public opinion and local politics are the common causes for failure to supervise the food supply of the municipality. Under such conditions, the state food commissions have a splendid opportunity for municipal surveys, having for their object the educating of the community in matters pertaining to the food supply.

Work of this character was attempted last year by the Illinois Food Department, upon the question of small municipality milk supplies. In a temporary laboratory established in the town to be surveyed, chemical and bacteriological analyses were made of the milk in various stages of its progress from the cow to the consumer. *First*, the milk was examined as delivered by the dealer to the housewife. Then samples were obtained as served at the restaurants and cafeterias, and as sold by grocers. The condition of the milk as received by the city dairies or as delivered by the railroads was also investigated. Finally, inspections were made of the farms at milking time, where samples of milk from the individual cows were obtained, as well as composite tests. In several instances, the pasteurization process was studied in detail, in order to point out to the owner the causes of the very unsatisfactory product that he was offering under the label "pasteurized milk." Throughout the work, the findings were not based on a single sample; *second*, and often, more samples were obtained upon which to base our conclusions. Thus the survey was a more or less complete picture of the condition of the municipal milk from the time of milking to the consumer.

The purpose of the survey was not solely regulatory: the educational aspect was not neglected. The conditions surrounding the milk production on the farm were carefully noted, especially of the sources that cause the greatest contamination. The essentials of cleanliness and cold were continually impressed upon the farmers, with surprising improvement of the milk—at least as long as the survey lasted. In many instances, where pasteurization was practiced by the dealer, the milk was worse after pasteurization than before. Bacteriological investigation easily detected the cause, with the gratifying result that the milk was properly pasteurized.

Surveys such as outlined above are expensive financially, and extremely arduous to the men doing the field work. The results were commensurate with the efforts expended on the work. Public sentiment is of slow growth, and official reform is often slower. Hence, a single survey could not be expected to be productive of great improvements. This much has been achieved. One city established a well equipped laboratory to continue the work. Another city is agitating a new milk ordinance, of a very comprehensive nature. A third city is conducting a survey of its own. In most cases, much public interest was evinced, which only requires further stimulus to assume tangible form. Requests for similar surveys have been made by other cities.

I have dwelt at some length upon this work because it emphasizes a method of state food control tending towards the permanent improvement of the food supply in the large cities

along scientific lines. With the knowledge acquired from the data, it was possible to fix the responsibility of each person who had to do with the milk. Contrast such a plan with one where a few samples of unknown history picked up at random are sent to a laboratory several hundred miles away, for examination. Not only is it difficult to form correct judgments, but the results of such efforts make little impression. The law of mass action is just as applicable in improving food conditions as in making reactions go in the laboratory.

Another example of intensive control may be found in the almost revolutionary changes in the egg industry. A detailed historical development of the situation would be too time-consuming. Beginning with an investigation of the traffic in rotten eggs among unscrupulous bakers in Chicago, the scope of the inquiry inevitably widened to include the entire method of handling eggs, down to the farm house. Then it passed state bounds and became national, so that to-day the permanent improvement of the egg industry is more than a dream of the conservationist. This again is merely a case of finding the cause, for the observed effect; of getting to the real source of the evil and beginning the correcting there.

In the past, much of the efforts of state officials has been devoted to the regulation of the food entering the state from another state or even a foreign country. Where the product is not of local origin, the securing of the necessary evidence, other than analytical information, is very difficult, if not impossible. The attempt of a state official to regulate, at long range, a food-stuff whose production is entirely beyond his jurisdiction, often results in embarrassment to the official and discredit to food control work. More profitable would be the intensive surveys of home industries. There would be the opportunity to study intimately the various steps in the preparation of the product; to detect intentional or accidental adulteration or manipulation; to determine to what extent deviations from analytical standards are inherent in the process; to investigate seasonal variations in natural products. Such a study could easily lead to improved sanitary handling of the food and to utilization of wasted material. Home industry would be fostered and developed, with the result that the products would enter interstate commerce in better condition, with practically no supervision by the officials of the states in which the product is to be sold. It would place the food official in an authoritative position with respect to the foods produced in his state. Control at the source would become a reality.

The place of the chemist in such a scheme would be one of importance. The present very vexing question of the interpretation of analytical results would be answered with much more assurance and accuracy. Factory practice would be combined with laboratory examination. In formulating rules for sanitary equipment and conduct of an industry, there would be a solid basis of fact for each regulation, with a clear distinction between essentials and non-essentials. In every industry there are many who have developed the sales end of the business with practically no regard to the manufacturing side. There are many who have but little knowledge of the nature of the products dealt in, or of the sources of contamination, much less any idea of control. Here is an opportunity for applied science that the state officials have not utilized to the greatest advantage. The educational phase cannot be disassociated from the law enforcement side of food control work. The educational project must always be augmented by the force of the law. Without it, the whole plan will soon become useless, because of the debasing influence of unfair competition. Education and improvement mean nothing to the unscrupulous food manufacturer. But he thoroughly understands that it is up to him to stay in the procession because the law can compel him to remain there, if he shows a disposition to fall out of line.

In this brief outline I have tried to indicate the possibilities



of chemistry and the allied sciences in the service of food law enforcement and control. A plea is made for the application of the elementary principles of scientific attack to the large complex problems of food production and distribution. The food control chemist is, or should be, something more than a laboratory analyst. His spheres of labor and of usefulness are co-extensive with the food industries of his state.

CHICAGO

## FACTORY CONTROL IN THE MANUFACTURE OF CORN-STARCH AND CORN SYRUP

By A. P. BRYANT

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The number of industries in which a certain amount of chemical control is exercised is constantly increasing, and in those industries which have a more or less elaborate system the nature of this varies with the nature of the manufacturing process and even in the same line there will be considerable variation in its extent and details.

I have been asked to tell you in a few words something about the chemical control in the manufacture of corn-starch and corn syrup, an industry which annually uses over 50,000,000 bushels of shelled corn and produces from it a large variety of products, of which starch and corn syrup are the chief. The object to be obtained in an industry of this sort is the recovery of as much of the starch of the corn as possible and the utilization of the remainder of the grain to the best advantage and with the least possible loss.

The different steps in the process of obtaining the starch separated from the rest of the corn are all mechanical, but the completeness of separation is controlled only by analyses of the materials at different stages, the results of which analyses serve as a guide for factory operations. In fact it may be said that these operations are based almost entirely upon the data furnished by the laboratory. It follows, therefore, that it is necessary to have not only accurate and representative samples, but also quick and accurate methods of analysis.

In different factories the details and extent of control will vary somewhat, but the general character is the same. In what follows I shall attempt to describe very briefly the methods more particularly as practiced in one factory.

The chemical work will naturally fall under four divisions: (1) Examination of supplies and raw products. (2) Control of factory operations. (3) Examination and standardization of finished products. (4) Special and research work.

### EXAMINATION OF SUPPLIES AND RAW PRODUCTS

The extent to which supplies are analyzed and their quality or strength thus controlled will depend upon the extent of laboratory equipment and force; the analyses may be more or less complete and will follow to a considerable extent similar control in other industries. There will be analyses of coal, lubricating oils, and general manufacturing supplies, which in this case include sulfur, soda ash, bone-black, muriatic acid, etc.; and finally the examination of the corn, *i. e.*, the raw product. Each car of corn is carefully sampled and the moisture determined. Also, from time to time, complete analyses are made of average samples of corn to determine the amount of protein, oil, starch, water soluble matter, fiber, and ash present. Upon these determinations are based the comparison of the yields actually obtained with what should have been obtained, as well as the variation in treatment which may be required for most satisfactory operation.

### CONTROL OF FACTORY OPERATIONS

The manufacture of corn-starch and corn syrup may be divided into three parts: the soaking of the corn; the separation of the different parts of the corn kernel (germ and oil, hull,

gluten, and starch) and the manufacture of the finished products from these.

The control in the soaking or steeping process consists in the regulation of the strength of the steep water, *i. e.*, the very weak sulfurous acid obtained, by burning sulfur in a draft of air and dissolving the sulfur dioxide in a large quantity of water. The amount of sulfur dioxide is determined at frequent intervals and the relative amount of sulfur burned and water used regulated according to these tests. Later in the process further tests are made to assure the total elimination of the sulfur dioxide in the finished products. This sulfur water is used to keep the corn sweet during the period of between one and two days, while it is soaking in warm water preliminary to the subsequent operations. These involve first the tearing apart of the soft, soaked corn; then the floating of the germ on a mixture of starch and water and its removal from the rest of the corn; next the grinding of the remaining portion of the corn and the separation of the bran or hull from the starch and gluten by means of silk covered shakers or reels; and finally the settling of the starch from the gluten on starch tables.

These successive steps are all in the wet and are governed by the gravity of the mixture of starch, gluten and water, and controlled by frequent observation. The completeness of each separation is determined by the analyses of samples, either taken automatically and continuously or at frequent intervals by a sample carrier.

As an example of the way the laboratory results are used a few illustrations may be given. The completeness of the separation of the germ from the rest of the corn is determined by taking a measured amount of germ-freed corn and adding it to a mixture of salt and water heavy enough to float any germ which might not have been removed in the factory process. The presence of floating germ indicates that the starch and water was not sufficiently heavy in the factory operations and the gravity is then increased. On the other hand the presence of germ which will not float because it is weighted down with starch and hull indicates that the degerminating mills are not working properly and should be attended to.

Again, a sample of the bran from the shakers or reels is tested for its starch content. This indicates the satisfactory or unsatisfactory operation as a whole. A duplicate sample thoroughly washed over silk bolting-cloth and then tested for starch shows whether any improvement that ought to be obtained should be sought for at the mills by closer grinding, or at the shaker and reels by more thorough washing, or both.

The satisfactory separation of the starch and gluten is tested by determining the protein in the starch on the one hand and the starch left in the gluten on the other. Some light immature starch granules will of necessity be carried away in suspension with the gluten, but this must be reduced to the lowest possible amount.

The starch, which is obtained as the final result of the operations already alluded to, is used for the preparation of the various kinds of starch (such as pearl, lump, powdered, laundry, etc.), for roasting to produce dextrin, or is sent to the refinery to be made into corn syrup, or corn sugar. The gluten and bran are united, filter-pressed and made into gluten feed. The germ is sent to the oil house from whence, after due time, it emerges as corn oil and corn oil cake or corn oil cake meal.

The control work thus far outlined has to do simply with the completeness of the mechanical operations involved in the separation of the different component parts of the corn. In the refinery on the other hand a chemical change is involved in the hydrolysis of the starch under pressure and in the presence of a trace of hydrochloric acid. In the manufacture of corn syrup the hydrolysis is carried only to a point where from 40 to 50 per cent of the starch has been actually hydrolyzed, the remainder being split up into dextrans. There are found both

dextrose and maltose in the hydrolyzed products, but for control work it is sufficient to determine the reducing value of the product and report this as dextrose.

The acidified starch milk of the desired gravity, usually 22° Bé. for syrup conversions, is run into a converter and cooked with live steam until the color reaction of a test sample drawn from the converter coincides with that of a similar sample tested in the laboratory and found of the desired degree of conversion or dextrose ratio. The operations of the converter are thus controlled directly by the laboratory. The charge, once having been brought to the desired test, is released into a neutralizer where sufficient sodium carbonate is added to neutralize exactly the hydrochloric acid in the syrup. The completeness of the neutralization is determined at frequent intervals, but cannot vary one way or the other more than a trifle for this reason: there still remains in the starch a minute amount of gluten after all the previous treatments and this is kept in solution in the hot slightly acid syrup. Once neutrality has been reached, this trace of gluten, carrying with it a trace of oil and pentosans, separates, causing a "break." At this point the liquid can be filter-pressed and this residue removed, but either a trace of acid or of alkali prevents this; consequently, the neutralization in a way is fool-proof although there is a fine point of exact neutrality that can be determined only by laboratory tests.

In the manufacture of corn sugar, the operations are similar to the above excepting that the action is carried further, until from 85 to 95 per cent of the starch has been hydrolyzed, depending upon the kind of sugar. The neutralization and subsequent purification, however, are practically the same as with corn syrup.

The purification of the syrup is obtained by means of charred bone or bone-black and throughout the process until the refined and concentrated liquors are finished and ready for shipment great care must be taken to see that all conditions are the most favorable; that the gravities of the liquors are kept constant; that no contamination by dirt or entrance of wild yeast is allowed; in short, that all conditions are as ideal as possible. This is brought about by means of laboratory tests on average or special samples taken at all stages of the refining and finishing processes. In this way it is possible to detect and remedy trouble or irregularities, which, if allowed to persist, might affect the color or general appearance or even the quality of the finished product. For example, a leaking valve might allow raw starch to escape from the converter before it had had a chance to be hydrolyzed, but a test with iodine would reveal this. Or the sides of some of the tanks might become infected by wild yeast, but as tests would show this long before any real trouble could be experienced, the source of the irregularity is thus discovered and remedied. Thus by constant watchfulness and frequent tests it is possible to maintain uniformity and satisfactory operations in this most important department, but this eternal vigilance must not let up day or night.

The finished corn syrup is concentrated *in vacuo* to a gravity of 42, 43, 44 or 45° Bé. based on a temperature of 100° F. These gravities are taken at the vacuum pans, but samples taken to the laboratory serve as a check and keep the pan man lined up.

The gluten and the bran separated as already outlined are united, the concentrated soluble matter removed from the corn during the steeping added, and in due time we get corn gluten feed. The chief function of the laboratory in connection with this is to determine the moisture in the finished product, and thus keep the product up to standard in this respect.

The germ of the corn, removed in the first mechanical separation, is sent to the oil house where it is dried, ground, cooked and the oil expressed, the residue forming corn oil cake or corn oil cake meal as the case may be. A determination of the oil left in the cake or meal shows the satisfactory or unsatisfactory operation of the hydraulic presses or oil expellers.

In what has been said, account has been taken only of the material actually in process and recovered. It is necessary, however, to look out for losses. These are sought in the sewers. Inasmuch as the milling process requires a great volume of water, it is necessary to get rid of this at various places. Wherever there is an outlet to the sewer a continuous automatic device is or should be placed and the samples tested for solids in suspension and solution. Solids in suspension are unnecessary loss and require immediate steps to remedy or obviate the condition permitting this. Solids in solution may indicate avoidable loss or a loss too small in amount or too diluted in quantity to recover. In the refinery there is possibility of entrainment during boiling in the vacuum pans and the slight amount of syrup which would be carried over can be detected and roughly estimated colorimetrically, if desired, by use of the alpha naphthol test. Leaks in the steam tubes of the vacuum pans which might permit syrup to leak through when the vacuum is broken can be detected by this same test in samples of the condensed steam from the tubes. Similar tests will show whether the filter presses and the bone-black filters have been sweetened off properly before being washed to the sewer.

By making tests of these waters, day and night, a very accurate control is possible of the conditions in the refinery, and, in fact, in the whole plant, which might lead to avoidable losses.

#### SPECIAL METHODS AND TESTS

In order properly to guide factory operations it will be seen that the laboratory must make many tests and that the results must be obtained in the shortest time conducive to a satisfactory degree of accuracy. This means that short-cuts and quick methods are required and that these shall give essential agreement with official methods. A few examples will illustrate:

Moisture determinations may be made in a vacuum bath heated by steam jacket at atmospheric pressure in three hours.

In determining oil in various products carbon tetrachloride may be used as an extractive reagent and the total time of extraction reduced to  $2\frac{1}{2}$  hours, the results agreeing very closely indeed with official results by ether extraction by the official method. This method has been used by the writer for many years and was described in the *Journal of the American Chemical Society*, 26 (1904), 568. Another advantage of this solvent is its freedom from danger of combustion. Starch may be determined indirectly by malting in the usual manner, filtering on weighed filters and determining the loss of weight after thorough drying. This loss of weight corrected for moisture and water-soluble matter in the original material and for insoluble solids in the malt extract used may be taken as starch and is perhaps as accurate as the official determination of starch by the reducing value of hydrolyzed malted extract, and the time consumed is much less.

Reducing value is determined volumetrically by a Fehling solution standardized by C. P. dextrose so that 25 cc. solution is completely reduced by  $12\frac{1}{2}$  cc. of 1 per cent dextrose solution.

Protein is determined by the modified Kjeldahl method using copper sulfate. Where practicable 0.875 g. material is taken and the final titration with N/10 alkali gives percentage directly, 1 cc. being equal to 1 per cent protein in the sample.

The above are the more important control tests, but special tests suggest themselves for special cases. Colorimetry plays an important part in comparing colors of starch, syrup, and other materials with standards. In controlling the strength of the weak sulfuric acid used for soaking the corn and testing for its subsequent removal, considerable amounts of iodine solution are required. Owing to the increasingly high cost of iodine and potassium iodide, the writer has been using for routine work a solution of potassium permanganate standardized through sulfur dioxide against iodine solution. This solution works admirably for control work and yields a marked saving in expense.



The results furnished by the laboratory show what is taking place at different steps of the process through the factory. These results, however, must be coordinated and applied in order to make them of value. From the results of the routine tests the foremen in the different departments of the plant can correct their respective operations so as to improve the results. At other times some unusual condition or combination of conditions may bring about unfavorable results, which will require special tests and analyses and perhaps more or less research work in order to avoid them. Once a certain kind of trouble has been experienced it becomes easy to avoid this a second time, but in the manufacture of corn-starch and corn syrup, as of course, in other industries, it is the unexpected that usually happens. Consequently, the one in charge of operations must not only keep in constant touch with the laboratory results, but carry on such additional tests and experiments as seem necessary in order to obtain the information which will permit getting the most satisfactory results from the plant.

#### EXAMINATION AND STANDARDIZATION OF FINISHED PRODUCTS

A complete analysis of the different finished materials serves as a guide for standardization. For example, the gluten feed and corn oil cake meal must be guaranteed to contain not less than a stated minimum of protein and fat and not more than a stated maximum of fiber. These limits will naturally be put at such values that under the individual factory conditions they can always be attained unless for some very unusual cause. It is the function of the laboratory to prove whether or not these guarantees are met, although for that matter the process control will give a very definite idea as to this. The crude oil is analyzed for its content of free fatty acids: if the oil is refined, a still further control must be exercised, both over process and finished product. The starch is tested for moisture and for impurities, which in this case are the other normal constituents of the corn, *viz.*, protein, oil and fiber, which should be present in the merest trace. Corn syrup will be tested for gravity and perhaps acidity. It is interesting to note that pure corn syrup has a trace of acidity, using phenolphthalein as indicator, due apparently to some slight acidity of the dextrins or other inversion products formed in the hydrolysis of the starch. It also has a trace of alkalinity, using methyl orange as an indicator, due to traces of sodium phosphate present in the ash of the syrup. With rosolic acid as indicator, it is practically neutral. In addition the syrup may be tested for its boiling properties as used with sugar in candy making, and its resistance to discoloration when heated. This latter would be noticeably affected were the refining process insufficient to remove all but the most infinitesimal traces of gluten, etc. In short, it is the duty of the laboratory to devise and execute the most rigid and severe tests in order that the syrup may be brought to the very highest state of purity.

#### SPECIAL AND RESEARCH WORK

No industry is in a really healthy condition unless it is advancing along the lines of improvement of its products or development of new fields for their use. In the starch and corn syrup industry there is still opportunity for abundant research work and there will be found many new uses for the products already made and many new products discovered which can be manufactured from the constituents of the corn kernel. The number of different products is already large, including pearl and powdered starch, various kinds of lump starches, modified starches, soluble starches, dextrins of various kinds, corn syrup, several preparations of corn sugar, refined oil for table uses, rubber substitute, cattle foods and many other products.

As regards improvements in quality, it may be said that the pure food law, which some ten years ago abolished the bleaching of corn syrup with sulfur dioxide, has been most beneficial as it necessitated improvements in the refining process so as to get a

more highly refined product, and to-day corn syrup is whiter even than in the old days of bleaching syrup, and much better. In fact, it is one of the most, if not the most highly purified food product that we have.

In conclusion we may repeat that the manufacture of corn-starch and corn syrup, while almost entirely a mechanical process in its execution, can be guided and controlled intelligently only by the most thorough, rigid and comprehensive system of chemical supervision.

CLINTON, IOWA

### THE CHEMICAL CONTROL OF GELATINE MANUFACTURE

By J. R. POWELL

Chemist, Armour Glue Works

Previous to the present decade, chemical control in the gelatine industry was rather limited. The manufacturer bothered himself chiefly about producing a product that would give a sufficiently strong jelly, and be brilliant enough in appearance to satisfy a trade which was critical about these points only. With the recent awakening to the possibilities of better manufacture and control of all food products, a more exacting chemical control of gelatine manufacture became a commercial necessity. Once this control was established, it became, and still is proving of real assistance to the manufacturer, in addition to developing a product acceptable to the trade. Improved methods introduced have tended to increase yields, improve what is commercially known as test, and conserve by-products, all of which gives the producer greater returns. As a result, what was once looked upon as a necessary nuisance will soon come to be accepted as a necessary source of help.

However, in outlining the precautions taken in this industry, many things will be mentioned under chemical control, that, while properly so designated, are the outgrowth of long practical experience, and cannot be directly credited to the introduction of chemistry. It is remarkable, however, as others have undoubtedly noticed in other industries, how many processes or tests practical men sometimes use, which, on first inspection, seem to be without rhyme or reason, are found to be based on very sound principles, when given a thorough study.

Control work naturally divides itself into three classes: (1) inspection of raw materials and chemicals, (2) control of the manufacturing process, (3) inspection of the finished product.

#### RAW MATERIALS AND CHEMICALS

Raw materials for the manufacture of gelatine, being by-products of other industries, have been far from being standardized, and the quality has been extremely variable. When the supply of materials was great, corresponding to the demand, and as a consequence, the price was correspondingly low, this variation did not worry the manufacturer so much. Margins were great enough that some variation in yield could be overlooked. As the demand for this material comes to exceed the supply, and it becomes necessary to buy on a competitive basis, the possible yield from such material becomes a vital point. As a result, inspection of such material for its actual value to the manufacturer is continually becoming more important. If the stock is to be used only for glue manufacture, examination ends at this point, but that used for the manufacture of gelatine should be examined for impurities that would render it unfit for making an edible product. For instance, arsenic and other heavy metals that are not permissible in the finished gelatine may be present in such quantities that the stock cannot be used, so it must be turned to the manufacture of glue or technical gelatine. Other stock may contain only such impurities as can be removed by proper processing, and subsequent treatment must, at least in part, depend upon the results of the examina-

tion. Still other stock may be found that shows no impurities and may be processed without any such special provisions being made.

In the examination of chemicals, it is such impurities as just mentioned that require the greater attention, as most of these products have been standardized, and variations in quality are limited. It is easy to conceive how acid used in the process may contain objectionable quantities of the tabooed metals. Water is so common that it is not usually considered a chemical, but in certain manufacturing processes would rightly be considered as such. Although at first thought it seems easy to obtain a water supply that is free from objectionable impurities, it would be interesting to consider the effect the total solids in a water of ordinary purity would have on a finished product, when this water is used for boiling out the gelatine. Gelatine liquor leaves the boiling vats at a concentration of from 2 to 3 per cent. If the water in question contained 15 grains of total solids as mineral matter per gallon, this would add about 1 per cent of an ash in the dry gelatine obtained to that extracted from the stock and coming from the other sources.

#### MANUFACTURING PROCESSES

The chemical control of the various processes of manufacturing can be made very elaborate. For the sake of economical and convenient operation, however, this control work usually is, as far as possible, worked out to a system of simple tests that can be made by the operators who handle the routine of the manufacture. These operators may not understand the mechanism of the tests, or know what they are really testing for, but are trained to expect certain reactions, and if they do not obtain them, they know all is not well, and the attention of the proper party may be called to the trouble.

This control of the manufacturing process begins with the first treatment of the raw material, which is usually the so-called liming. As this is usually conducted in a saturated solution of lime-water, the strength of the solution requires no control. On the other hand, the stock must be well watched, as over-liming will reduce the yields very materially, while under-liming will likely leave behind certain impurities that should be removed, and, at the same time, require such drastic treatment in boiling that the test will be decidedly injured.

Following the liming comes the washing, wherein the excesses of alkali must be removed to within certain limits, together with other impurities that the lime has dissolved. As it is usually customary to boil slightly acid, this is usually followed by an acid wash, which neutralizes the residual alkali and gives the required acidity. It can be readily seen that, without some control, large amounts of acid may be wasted, unnecessary time and labor consumed in washing, or impurities left behind that should be removed.

The boiling of the stock follows the proper preparation in the wash-mills. The chemical control here is rather limited, the points of interest being chiefly the reaction and the temperatures. High temperature and excessive acidity or alkalinity rapidly hydrolyze gelatine into products of considerably less value.

From this point on through the process, the chemical control diminishes in importance, unless the liquids are to be clarified, or subjected to some other treatment for removal of impurities. However, as the importance of this control decreases, the importance of bacteriological control increases. This is another type of control which will be but mentioned here, that offers a very wide field of application to all points in the manufacture of gelatine, and the possibilities of value are just beginning to appreciate. But it is especially while gelatine is in these comparatively dilute solutions, and varying in temperature from boiling through an ideal incubating state to the necessary

refrigeration required for its congealing, it becomes an ideal breeding place for bacteria. Hence all possible precautions must be taken to prevent infection and get the material past the danger stage as rapidly as possible.

Another item of importance is the air used in the drying of the gelatine. This is especially so where the air must be drawn from the badly polluted atmosphere of our larger cities. Impure air offers three possibilities: *First*, the dirt that may be collected, giving a gelatine that will dissolve with great turbidity; *second*, infections are frequently picked up in the drying alleys, from this dirt, although the product may have entered them practically sterile; *third*, the chemical contamination due to the absorption of chemical fumes in the air.

As has been mentioned, one of the points that must be carefully watched is the reaction of the material throughout the process; and to see how far-reaching the effects of any one factor might be, we will consider this more in detail.

The well-known influence of acidity on the swelling of gelatine and like colloids points to the importance of such control. The points of maximum and minimum swelling of the stock must be definitely related to the extraction of the gelatine and the properties of the resulting product. The fact that salts again modify this action of acidity only adds other complicating factors. The possible detrimental hydrolyzing action of acid or alkali has already been mentioned. Although the process of boiling out of the gelatine is most probably one of hydrolysis, it must be done under such control as will insure the action going only so far, or the product is deteriorated.

Likewise the wonderful probabilities for the formation of undesirable precipitates must be considered. We may have almost any combination of acid, or alkaline albuminates, mucins, and such substances, together with the inorganic compounds, especially the uncertain phosphates. There are conditions where a very slight change in acidity may bring down any one of these, or more likely, a combination of several. Much work has been done on the preparation of colloidal precipitates along other lines, and the operators have gone to great pains and trouble to obtain such precipitates. Here the conditions are somewhat reversed, and great care must be taken to avoid the formation of precipitates in the colloidal state. One of the great factors in this is that gelatine is a protective colloid, and the tendency is for all precipitates to separate in the colloidal form. This is the case even when precipitation is intentionally produced under careful control, for purification or clarification, making it easier, in most cases, to keep impurities out, rather than to attempt to remove them.

Besides the principal product, gelatine, the by-products must also be considered, and given their proper attention. There may be, depending upon the nature of the stock, a recovery of more or less fat, which is to be properly collected and graded. There will be the residual tankage which has its definite value as fertilizer, which valuation must be made on suitable analysis.

#### THE FINISHED PRODUCT

Any control work done on the finished product simply amounts to such analytical work as is necessary to check up the work previously done during the process of manufacturing. Physical tests such as the rigidity of jelly, the viscosity of a solution, together with the appearance of the product gives data upon which the commercial value is fixed. Besides this, of course, the impurities must be checked up to show its suitability for edible purposes. Frequently, other special tests are demanded, depending upon the use to which the gelatine is to be put, but each case of this sort is a law unto itself, these tests being the outgrowth of some special demand made by the consumer.



## FLOUR MILLING PROBLEMS

By HARRY SNYDER

Chemist, Russell-Miller Milling Company

In responding to the request to present a paper on "Flour Milling Problems," at this meeting of the American Chemical Society, I shall discuss briefly some of the problems with which the flour manufacturer has to deal, what is being done to solve them, the aid Chemistry renders in their solution, and the direction wheat and flour investigations should take in order to be of the most use to all concerned: the producer, the manufacturer and the consumer. By flour I mean the fine bolted product of wheat—as this is what is usually understood by the term when one purchases flour in the market.

The flour milling industry is of large proportions. The U. S. Census numbers the mills by the thousands. Although many of those included are old grist mills, by force of circumstances idle, it is estimated that the total number of flour mills either in active operation or capable of being operated is approximately 7,500, with a total daily capacity of about 1,000,000 barrels. The industry is widely distributed, no one state having over 15 per cent of the total flour-making capacity of the country, and no one manufacturer over 4 per cent.

## WHEAT

The United States produces annually from 600,000,000 to 1,000,000,000 bushels of wheat, from 50 to 70 per cent being raised in the winter wheat states, the balance being spring wheat. The wheat yield in the United States fluctuates from 12.3 to 16.6 bu. per acre, the average for the past 17 years being about 14.2 bu. The yield per acre compared by 10-year periods does not appear to be decreasing. There has been a tendency for a decrease in wheat acreage (if we omit the past two years which have stimulated wheat production). The average consumption of wheat in this country is about 5.3 bu. per capita.

The United States is a wheat-exporting country, but how long she will continue to be so no one can accurately predict. While no large areas of virgin land remain to be brought under wheat culture, it is estimated that nearly one-fifth of the land area of this country now classed as "non-tilled agricultural" is suitable for agriculture.

With the application of improved methods of farming the wheat yield could easily be increased 20 per cent or more. Speaking of the agricultural phase of the wheat-supply question as it deeply concerns the miller, I believe we are reaching a point in our agriculture where wheat must be raised as a regular farm crop under good systems of rotation rather than be produced as a virgin soil crop. If the United States is to maintain her prestige for wheat production, it must be through a continuance, or even an improvement, in the production of the best types of wheat for flour and bread-making purposes. The miller occupies an intermediate position between the producer and the consumer. He buys the wheat, makes the flour, sells it to the distributor or consumer and has to shoulder any responsibility as to lack of quality.

There are a number of flour milling problems which are interesting, but of which only brief mention will be made, as variations in the character of wheat from year to year, due to climatic conditions. Some years the miller has to use wheat which contains 14 to 16 per cent of moisture and this results in heavy losses in milling; then again the wheat is dry and more normal conditions prevail. Weeds have become very prevalent, causing much trouble in cleaning the wheat. Smut and fungus diseases, some of which can be largely prevented by proper treatment of the seed wheat, present difficult milling problems. Rust is a factor that some years must be reckoned with. The tendency of wheats at times to become starchy as in yellow berry, the influence of storage upon the quality of the grain and the effect of different methods of storage are other problems

with which the miller must be more or less conversant. Many of these problems are worthy of the best attention of our National and State Departments of Agriculture and Experiment Stations.

The miller, as a manufacturer, has entirely different conditions to contend with than the manufacturer where the raw material is absolutely uniform from year to year and where only the process of manufacture needs to be considered in order to make a uniform product. At times, if he secures his raw material at not prohibitive cost, he must obtain it from different states or localities. This he is privileged to do, as is right, provided he maintains his flour qualities and makes no deceptive claims as to the origin of the wheat used. During the past year the very wet harvest time spoiled more or less of the wheat in some of the southwestern states. As a result an appreciable volume of strong wheat has been shipped from the northwest to the southwest, and consequently flour qualities were maintained. In other years, with reverse conditions, the hard southwestern wheats find their way to northwestern points. This is regulated largely by transportation charges and local conditions. Many small mills, too, in the eastern and central states, find it advantageous to use some northwestern and southwestern wheat to blend with their local wheat. In other countries the blending of wheats is more extensively practiced than in the United States, particularly where there is but little home-grown wheat and the country is dependent upon the surplus of other countries.

## PROCESS OF MANUFACTURE

Flour milling is distinctly a mechanical industry, the object being to remove from the wheat berry the outer coat or wheat bran and the other offal, and to reduce the wheat to a fine state of division, thereby making a product that is in a better physical condition for bread-making and also in a form that is more completely digested and absorbed by the body.

Since the advent of the bleaching processes, suggestions have been made that flour milling is both a mechanical and a chemical industry, but this is not a correct view, because flour milling is in no way primarily dependent upon bleaching processes no matter what the status of bleaching may prove to be. There are no chemical processes involved in the separation of the bran and the wheat offals and in the reduction of the flour, nor are there chemical reagents of any kind employed; hence the problems which arise are necessarily different from those in a manufacturing plant where chemical reagents are used and where a series of chemical changes occur.

The principal features of the milling process are cleaning the wheat, removing the offal, and then the gradual reduction of the stock into flour. By means of "break rolls" the wheat kernels are partially flattened and crushed, making a mechanical mixture of various sized particles: a little break flour, intermediate particles (called Flour Middlings), and larger sized crushed or flattened portions of wheat kernels. All of these particles are separated by means of sieves of different sizes ranging from fine silk with 15,000 or more meshes per sq. in. to coarse wire cloth. The middlings are conveyed to the middlings purifying machines and the coarser stock to another break roll. The purified middlings are in turn gradually reduced to flour by means of smooth rolls. There is no sharp line of division between the flours obtained at the break and the middlings rolls. Some of the middlings are no more free from fiber and debris particles than the best of the break flours. Much depends upon the system of milling employed and the skill of the miller in making the mechanical separations. The break and reduction rolls and the middlings purifier are among the essential features of the gradual reduction process. If a short break system of milling is employed with a minimum of purification, the flour is not so free from dust, fiber, and debris particles. In general, the cleaner and purer the flour, the better its baking qualities.

## APPLICATION OF CHEMICAL TESTS

The task of distinguishing between flours of various degrees of commercial quality is complicated by three sets of factors: (1) Variations in wheat qualities not susceptible to chemical determinations, (2) lack of uniformity as to milling processes, and (3) lack of sufficiently refined methods to distinguish differences in proportion to commercial values.

One of the methods proposed for determining the mechanical grade of a flour is from the ash content. So far as I am aware I was the first to propose this method, about 25 years ago. I, therefore, feel at liberty to discuss the subject fully. As I have published a number of articles relative to the ash content and the grade of a flour, there is but little to add at this time other than to say that my view now is substantially the same as expressed in my writings.<sup>1</sup>

"Flour made from fully matured wheat has the minimum ash content because high maturity is usually accompanied by low ash. The ash determination, alone, cannot be used to establish the comparative value of two samples of flour containing, respectively, 0.36 and 0.40 per cent ash; the one with the lower per cent ash is not necessarily the better flour. If, however, two samples of flour contain 0.42 and 0.55 per cent ash, respectively, the former is a patent and the latter a straight grade flour. When making comparisons, however, too strict an application of the results is not admissible, particularly when the ash determinations are made in different laboratories and by different analysts, as the results then are not always strictly comparable. When the ash determinations are made under similar conditions the results are of much value in determining the grade of a flour." (Minn. Expt. Sta., *Bull.* 85, p. 192.)

In my published works I have placed the ash content of patents as ranging from 0.35 to 0.48 per cent, straight grade from 0.48 to 0.55 and clears from 0.60 to 1.80 per cent. In my "Human Foods," p. 145, I state:

"Patent grades of flour rarely contain more than 0.55 per cent ash, the better grades less than 0.5 per cent. The more completely the bran and offals are removed during the process of milling, the lower the per cent of ash. The ash content, however, cannot be taken as an absolute guide in all cases as noticeable variations occur in the amount of mineral matter or ash in different wheats. Starchy wheats that have reached full maturity often contain less than hard wheats grown upon rich soils where the growing season has been short, and from such wheat a soft, straight flour may have as low a per cent of ash as a hard first patent flour. When only straight or standard patent flour is manufactured by a mill, all the flour is included which would otherwise be designated as first and second patents and first clear."

As these quotations are from my published works of years ago, and prior to my becoming a miller, or identified with the milling industry, any similar statements that I may now make concerning the application of ash tests in determining the grade of flours can not be regarded as biased. As previously stated, ash determinations made in different laboratories and by different analysts are not always comparable.

•To what extent do variations in the ash content of a flour occur when the same sample is tested in different laboratories and by different analysts? Such a test was made by the Association of Official Agricultural Chemists and is reported in Bureau of Chemistry *Bulletin* 152 (*Proc. 29th Annual Convention, Ass'n of Agr. Chemists*, p. 107). "Sample A was a straight flour from Fife wheat." The wheat was stored and milled at "the mill at the North Dakota Agricultural Experiment Station."

Analysts	PERCENTAGES ASH: METHOD A	METHOD B	METHOD C
	Electric Muffle	Muffle Furnace	Addition Calcium Acetate
Leila Dunton, Manhattan, Kans. ....	0.708	0.706	0.647
F. M. Thomas, Ag. Col., N. D. ....	0.72	0.695	0.695
H. L. Wessling, Chicago, Ill. ....	0.70	0.695	0.695
B. R. Jacobs, Washington, D. C. ....	0.71	0.673	0.663
R. B. Beard, Ag. Col., N. D. ....	0.678	0.673	0.663
H. L. White, Ag. Col., N. D. ....	0.678	0.673	0.663
C. K. Glycott, St. Paul, Minn. ....	0.678	0.673	0.663

<sup>1</sup> Early reports Minnesota Experiment Station; also *Bull.* 101, O. E. S., U. S. Dept. of Agr.

In commenting upon the tests, Mr. A. S. Mitchell, then in charge of the St. Paul Laboratory of the U. S. Department of Agriculture, aptly states: "Since A and B give practically the same results, there seems to be no necessity for distinguishing between a method in which an ordinary muffle is used and one where an electric muffle is used."

As all of these methods are used by chemists it is fair to draw conclusions as to the variations which may occur when a number of chemists test the same sample of flour. The maximum result is 0.72, the minimum 0.663 per cent. Hence it would seem fair to say that in well controlled analytical work variations of 0.05 to 0.06 per cent in the ash content of a flour may occur between the results of different analysts. These extremes were found respectively in the Chicago and St. Paul Laboratories of the U. S. Department of Agriculture. With less experienced analysts the differences undoubtedly would be even greater. Since we must allow at least 0.06 per cent tolerance in an ash test of flour for uncontrollable analytical errors, serious difficulties may arise in the practical application of the results.

Suppose a miller sells to a flour dealer 100,000 bbls. of flour, not an unusual order. It was agreed that the flour should contain a certain percentage of ash. Suppose the flour declined \$0.50 or \$1.00 per bbl., as has been the case the past year, and the purchaser was facing a loss of \$50,000 or \$100,000. Now if the flour was received and a sample was tested by another chemist and found to have 0.04 or 0.06 per cent more ash than was agreed, the purchaser could claim that he had received a poorer grade of flour than the contract specified. If there really was an actual difference of 0.05 per cent ash, the flour shipped would be worth from 30 to 40 cents a barrel less than the contract grade. On the basis of a difference of 0.05 per cent ash a claim for \$30,000 to \$40,000 could be made for damages by the purchaser and there would be an excuse for litigation, when, in fact, there is no basis for any dispute because the 0.05 per cent difference in ash is within the limits of error when flour is tested in separate laboratories by different chemists.

Reverse the conditions—suppose the flour advanced in price. If the miller wished to take advantage of the facts, knowing that two chemists would differ by 0.06 per cent in ash, and knowing that such a factor of tolerance must be allowed, there would be nothing to prevent the order being filled with an inferior flour that would pass the ash test and would not be the quality that the purchaser supposed he was getting.

## FLOUR GRADES

The sample tested by the Official Chemists is a straight grade flour milled at the North Dakota Agricultural Experiment Station, and contains 0.66 to 0.72 per cent ash. It is a type of flour made by what might be termed a mill of very limited or of minimum capacity. How would such a sample compare in ash content with a straight flour made by another mill? That would depend upon the character of the wheat used and the nature of the machinery employed. Dr. Ladd, as chairman of the Flour Standards Committee, Department of Agriculture, proposes "straight flour from hard spring wheat 'contains' not more than 0.52 per cent of ash." If such a standard were adopted Dr. Ladd's flour mill, along with a large number of others, would have to stop making flour, as such a mill's product would be illegal, being a straight flour with 0.66 to 0.72 per cent of ash, determined by two separate U. S. Department of Agriculture Laboratories and with 0.14 to 0.20 per cent excess of ash over and above the limit of 0.52 per cent. On such a basis the flour would be adulterated or misbranded, probably the latter.

Various attempts have been made to define flour grades. What is patent flour? Who can tell? As well try to answer the question: "How old is Ann?" In discussing flour topics in a recent hearing before the Ways and Means Committee of the House of Representatives on the proposed Mixed Flour Law and the



amendments to the Pure Food Law, Dr. Wiley aptly answered the question from a chemical point of view (page 374, H. R. 9409).

MR. RAINEY: "In what way are the different grades of flour designated?"

DR. WILEY: "I am not a miller and I do not know. I know the common names that are applied."

The difficulty is that mills do not have wheat of uniform character from year to year. The wheats differ widely in different parts of the country, and furthermore the equipment in mills is necessarily so varied, in order to mill the different kinds of wheats, that the products designated as patents, straights, or clears are not admissible to classification on a hard and fast basis of ash content, or on the basis of any other constituent or quality.

If these chemical tests are not as yet sufficiently accurate to determine the grade and quality of a flour, are baking or other tests any more accurate and reliable? This question can best be answered by reference to the Association Report previously quoted. The straight flour testing 0.66 to 0.72 per cent ash, as noted, was subjected to baking tests in different State and Government Laboratories. The results showed a range in volume from 1990 to 2520 cc., a difference of 530 cc. The largest loaf volume was 25 per cent more than the smallest loaf. The color values ranged from 90 to 101. The absorption of water for the 340 g. of flour used in baking ranged from 50.2 to 57.3. It would seem then that allowances of 7 per cent in absorption, 25 per cent in volume and 10 points in color and texture must be allowed for differences in the work of individuals, testing flour by baking tests. As to the comparisons of gluten tests, but few figures are available, but they show a range from 33.7 to 37.57 for moist gluten and 13.1 to 13.82 for dry gluten. The total nitrogen content ranged from 2.34 to 2.505, a difference of 0.165 per cent or about 1.0 of protein. In another report (Aug. 15, 1915, *Journal of the Association of Official Agricultural Chemists*), the dry gluten of two analysts working on the same samples ranged from 10.81 to 14.63 per cent on one sample, to 10.95 and 13.32 per cent on another sample.

In interpreting the comparative results of either chemical or bread-making tests of two persons working on the same sample of flour and with the same methods, but in different laboratories, a range of 10 to 25 per cent must be allowed for uncontrollable errors, depending upon the feature under comparison. These differences between the results of investigators are well established by the work of the Association of Official Agricultural Chemists. It is better for chemists frankly to admit these limits of error than to attempt to condone them.

I do not wish to leave the impression that chemical and baking tests of flour are of but little value. Their greatest value comes when the "personal error" is reduced to the minimum by the skilled flour technologist who is making the same tests day after day in the same way, under absolutely uniform conditions and when his results are compared one with another. When millers and bakers get such widely divergent results on the same sample of flour tested by different chemists in different laboratories, they are confused and there naturally arises more or less a feeling of lack of confidence for the whole system of flour testing. I heard one mill manager express himself thus: "If you have a flour tested, be sure and have it tested by a number of chemists so as to have a variety of results to pick from."

A mill owner, Mr. Krafts, of St. Louis, at the hearing before the Flour Standards Committee last June, said in part (p. 168):

"But I don't remember ever having any flour analyzed. Only once I heard of it. Once my partner said to me that somebody said his 95 per cent flour was better than ours, and that he had this thing and that thing in it. I said, 'Maybe it has: What are those things?' I knew we did not put anything like 'em in ours, that's all I knew, and he said, 'Suppose we get some of our samples analyzed, and see.' I said, 'Go ahead, I don't mind,' and so he sent some to some fellow—somebody

told him about—and it came back, and he came in and showed me the returns from the doctor. And he said: 'What's this mean—do you know?' and I said: 'Chris, look at that, will you! Look what you have got in the flour.' I knew we hadn't put anything like that in there and that's all I knew. I said: 'What are all these things anyhow?' They didn't convey to my mind anything at all. I rolled it up and threw it in the waste basket, and that's how I know we had it analyzed once."

Another method occasionally employed by practical millers to determine the value of chemical or baking tests is to send separate portions of the same sample of flour, under different names, to the same laboratory for tests. At the hearing to repeal the Mixed Flour Law such an incident is given by Mr. Shoening, a miller of Illinois:

"Now, no man has more respect for a chemist than I have. I have a chemist in my family now. My son is a graduate of the ——— University. He took a special course in chemistry and has a diploma. When he came back I put him to work. I bought him a pair of overalls and made a practical miller out of him. He wanted to run the mill. This is his hobby. Then he began to analyze the flour as he made it. I knew that the flour was uniform, but he got a different result every time he made an analytical test." Then Mr. Shoening tells how he took a sample of flour, divided it into three parts, sent the samples from different express offices to the same laboratory. "Well, sir, when those reports came back—and I have the documentary evidence now in my desk at Columbia, although I have never said anything about it—they were such that if those laboratory tests would govern the price of flour, I would have to sell the same flour, made out of the same wheat—90 cents a barrel less for one sample than I would have to take for the other."

These quotations are not given with any view of discouraging flour testing by chemical or baking methods, but rather to show how many millers actually regard such tests. The fact is, millers in general do not consider flour-testing, as it is ordinarily practiced, of any great value. I think much of this view is due to the chemist not perfecting his methods of investigation, not thoroughly studying the questions involved and attempting to draw definite conclusions on insufficient data. In the case of the ash test, too much is left to the individual judgment of the chemist as to just how far the refining process should be carried so as to secure an ash of definite characteristics. The old distinction between crude ash and pure ash seems to have been discarded. In discussing the ash content of cereals and flours, the Chemical Division of the U. S. Dept. of Agriculture, years ago,<sup>1</sup> stated some general principles which are particularly applicable to the question. At that time the Official Method was

"The charring of the material at a low temperature, the extraction of the char with hot, distilled water to remove the soluble ash therein and the final combustion of the carbonaceous residue at as low a temperature as possible until an ash fairly free of carbon is secured. While this method can be applied with a fair degree of success to small quantities of cereal flours, and for the purpose of determining simply the percentage of ash therein, the attempt to apply it to considerable quantities for the purpose of securing an amount of ash for the complete analysis is attended with difficulties."

These difficulties are enumerated under four headings, showing whereby excessive temperatures may bring about losses and unbalanced combinations of the ash constituents, and incomplete oxidation on the other hand may leave a considerable amount of carbon. "At best the ashes are of a light gray color and in some cases, owing to the excess of carbon, inclined to be black. The application of sufficiently high temperature to secure complete oxidation produces serious changes in the composition of the ash, rendering complete oxidation difficult."

A crude ash determination cannot be left to the novice. The ash should be granular, and as free from carbon as possible. If fused, a glassy coat of phosphates may be formed causing a dark ash due to occlusion of carbon. Constant weight is not necessarily a criterion of an accurate ash test. Many flour ashes apparently pure are found upon examination with a low-power microscope to contain innumerable unburned carbon

<sup>1</sup> Bull. 13, Part 9, p. 1210.

particles, appearing like unburned coal in coal ashes. Particularly is the ash rich in carbon if too much flour has been burned, say over 2 g., in a dish that is not sufficiently exposed to the air, and where the ash forms an appreciable layer. The best ash results are obtained by long combustion at a low temperature to insure reasonable oxidation of carbon. Such an ash can at the close of the operation be fused, if desired, without loss of weight, provided the temperature is not raised much above 675° C. An ordinary set of analytical weights of the first class when checked against special standardized weights of the Bureau of Standards may show variations sufficient to cause a difference of nearly 0.02 per cent in an ash test. When we consider all of the possible sources of error in an ash test, it is not surprising that two analysts may show a difference of 0.06 of a per cent when testing the same sample of flour. Errors in drawing samples also occur; these I have discussed in a previous paper and will not consider at this time.<sup>1</sup>

#### NEW ACIDITY TESTS

In considering acidity, difficulties arise which are very confusing. The per cent of acid obtained from a sample of flour varies directly with the time of extraction and the temperature employed; hence it is essential that these two factors be uniformly maintained to secure concordant results. The acidity is a measure of a number of things—soluble proteins, certain soluble ash constituents and any free lactic and similar acids that may be present. In the Official Tests as previously mentioned, a variation of 0.10 per cent may occur between the results of different investigators working on the same sample (see page 108 for results: 0.29, 0.275, 0.258, 0.198 and 246 per cent acid obtained by different official workers).

Last year or the year previous the Association of Official Agricultural Chemists adopted as a provisional method a temperature of 40° C. and a time limit of one hour(?). This method, until further tests are made, should be considered no more than provisional, as it appears to have been tried by only two co-operating chemists although with quite satisfactory results. This method gives somewhat higher figures than obtained formerly where 17° C. was the temperature employed for extraction. A flour with 0.09 per cent acidity by former tests may show 0.11 per cent or so by the present provisional method with a higher temperature for extraction, and hence this year where millers and bakers have had acidity tests made and higher results reported, some have been unnecessarily alarmed, fearing that the excess of acid indicated unsoundness of the flour, when in fact the higher acidity is not due to unsoundness but to changes in methods of analysis. This is confusing to the layman and difficult to explain to him.

#### FLOUR BLEACHING

I am not discussing the color of flour, or flour bleaching in this paper, because this matter is still in litigation and its discussion now would be inopportune. There are certain general facts, however, which appear to be established by the U. S. Supreme Court decision in directing a retrial of the case.

"If it cannot by any possibility, when the facts are reasonably considered, injure the health of any consumer, such flour, though having a small addition of poisonous or deleterious ingredients may not be condemned under the act," and "It is not required that the article of food containing added poisonous or other added deleterious ingredients must affect the public health, and it is not incumbent upon the Government in order to make out a case to establish this fact." \* \* "the added poisonous or deleterious substance must be such as may render such article injurious to health. If the testimony introduced on the part of the respondent was believed by the jury they must necessarily have found that the added ingredient, nitrites of a poisonous character, did not have the effect to make the consumption of the flour by any possibility injurious to the health of the consumer."<sup>2</sup>

Hence it would appear that the question as to possibility of

injury to the health of the consumer by the use of bleached flour has been disposed of by the Supreme Court decision. This would leave, however, other phases of the question unsettled. It would seem then that bleaching of flour is not to be prohibitive on the basis of any possible injury to health, but if anything is to be done it will be of a regulatory nature. In considering flour bleaching, each method of bleaching, nitrogen peroxide, chlorine, etc., should be considered upon its own merits or demerits as the case may be. The full legal status of flour bleaching should be settled for the general good of the flour trade, and a uniform practice be followed in all parts of the United States.

As a rule, flour made by mechanical processes is not subject to adulteration. The Mixed Flour Law passed by Congress in 1898, put a stop by regulatory measures to indiscriminate mixing of corn and wheat flours and introducing into flour corn-starch and other materials, which practice at that time was quite threatening to the flour industry. During the past year it has been proposed to repeal this law and amend the present National Pure Food Law, so as to permit the blending of corn-starch and wheat flour without the present regulatory measures—the mixture to be sold under the name of flour. It is a measure which the flour industry opposes practically as a unit.

Unless the miller makes some misstatement in labeling his packages of flour, he has but little to do with food laws, as the fine bolted material made from wheat is flour and there is no possibility for adulteration to occur. In the case of the feeds and wheat offals, a statement of protein content, crude fat and crude fiber is generally given on the package, also a statement as to any screenings present, as most states have laws calling for this data. Usually the labeling of his feeds gives the miller but little trouble, as he generally aims to make the guarantee low enough to cover ordinary fluctuations. However, errors in sampling and analysis arise and sometimes the same goods made from identical wheat on the same day will be tested and reported on favorably by one state inspection and reproved by another as deficient in some constituents, and the miller is warned. This brings up the question as to how much tolerance should be allowed for uncontrollable errors in analysis of a sample of feed. If, say a dozen or more state chemists were all working upon the same sample, to what extent would their results vary? Such tests have been made by the Association of Official Agricultural Chemists.

An interesting report on coöperative total nitrogen tests upon which protein content is calculated is recorded in *Jour. Assn. Official Agricultural Chemists* (Nov. 15, 1915), p. 380. Sixteen Official Chemists took part in the work, all testing the same sample for total nitrogen. The Associate Referee who conducted this comparative work remarked: "The figures for total nitrogen are, with the exception of one result, quite satisfactory." Omitting this high result the difference between the lowest and highest nitrogen tests (2.46–2.76) is 0.3 per cent nitrogen, which calculated into protein is equivalent to 1.87 per cent. On the basis of the lowest test 15.37 per cent protein was found, and on the highest 17.25 per cent.

Some state chemists frankly admit that at least 1.0 per cent or more can be allowed in a protein test for uncontrollable errors. Other state chemists will not admit any tolerance and stand ready to consider mill feeds below the guarantee if they fall short of 0.50 per cent. There should be a uniform practice followed in all states, and a fair tolerance allowed as chemical analyses of feeds have by no means reached a position where the results of one chemist can be absolutely duplicated by another.

#### FUNCTION OF THE CHEMIST IN A FLOUR MILL

A small or medium-sized mill cannot afford to employ a chemist regularly. A flour technologist, a person familiar with the manufacture of flour from the mechanical or milling point of

<sup>1</sup> 8th Intern. Congr. Appl. Chem., 18, p. 323.

<sup>2</sup> U. S. Supreme Court Decision No. 548, October Term, 1913.



view, will be of the most service in such mills. Such a person must have a practical knowledge of bread-making and of the general working qualities of flour. In a large flour mill organization there is a place for the chemist provided he is properly equipped for the position. He must have a fair knowledge of flour milling from the mechanical side, and also a thorough knowledge of technical bread-making, along with his chemical training. The broader his chemical training the better equipped he is for his work. There are many chemical engineering problems in a mill to investigate, as cost of fuel, reduction of boiler scale, lubricants, strength of cloth used for flour containers, etc. If the chemist can help reduce the cost of a barrel of flour even a fraction of a cent, he is assisting materially in the general economy of production.

#### FLOUR RESEARCH

The main part of the chemist's work should be research. Many of the possible problems are of such a character as to escape entirely the notice of chemists not intimately connected with a flour milling plant. Such a problem is wheat storage in its relation to flour qualities. The wheat kernel undergoes a cycle of interesting changes from the time of harvest until it reaches what might be termed its old age. These are largely cell respiration changes. The activity of the germ and the products which it forms are interesting questions. Our ordinary methods of analyses are not sufficiently refined to investigate many of the problems. Some of the methods employed in measuring changes in physical chemistry are promising. A slight increase in soluble constituents, as changes preceding germination, are reflected in the conductivity. The chemist and flour technologist can closely cooperate in the study of many questions, but the chemist must not get the mistaken idea that his analyses will point the way to the solution of all of a mill's problems. He must cooperate with all departments. If, along with the necessary equipment for his position, he has a fair business knowledge, he may occasionally make suggestions that will be of some value. A little of the time of the chemist will necessarily be given to routine work, but this he can well afford to reduce to the minimum as the flour technologist can generally give more and better information than can the chemist from the chemical analysis alone. A good flour technologist often makes a poor chemist, and a good chemist often proves a poor technologist. Chemical and technical knowledge are sometimes possessed by the same individual to a fair degree.

Many of the problems in connection with wheat and flour are of a biochemical nature. I use this term advisedly as it is becoming such a popular one that there is a tendency to use it indiscriminately, and I fear some of the courses of instruction in biochemistry that have sprung into existence "over night," as it were, will need to be greatly strengthened in order to prove satisfactory.

It is as difficult in wheat and flour work to measure life processes by chemical analysis as it is elsewhere in the animal and vegetable world. Two flours may have practically the same percentage composition in protein, starch, and other constituents and yet have widely different values for bread-making purposes. It is not possible to take a flour of high protein content, dilute it with starch from any cereal so that it will show the same amount of protein or crude gluten as some other flour and have the two alike in their bread-making qualities. There is an individuality to wheats and flours which is not as yet susceptible to exact measurements by chemical methods. It is not only a question of the per cent of constituents in a flour, but also of their interrelationship and the way in which the flour responds in bread-making. Some of the factors which impart quality to flour for bread-making purposes are well known, others are not; some even impart a negative value. It is the sum or total of all of the factors, positive and negative, which must be considered in reaching a conclusion, rather than any one factor.

Since the modern reduction process of flour milling is of such recent development, much of the literature and the traditions of flour making apply to the old mill-stone days when a less refined product was made. There are some who still argue with vehemence that the old grist mill and millstone flour is superior to the modern product. A few facts will, I believe, help to place before you the difference between the two flours so that comparisons can be made. In the old gristmill days little or no attention was paid to the cleaning of the wheat, and in the milling process some of the bran and fiber were reduced with the flour, and the flour middlings were not completely removed from the bran and offal. The flour was dark in color, mainly on account of its dirt content, and if used at once made very good bread, but soon developed a so-called "nutty flavor." The flour had poor keeping qualities because it was poorly milled and was not made from thoroughly cleaned wheat. The nutty flavor was due to the first stages of butyric acid fermentation, the ferments being associated with the dirt and impurities in the flour. Modern, well-milled flour has good keeping qualities; in fact, it gradually improves with moderate age. In modern flour there is a larger percentage of the total wheat kernel present, although somewhat less of the dirt, bran and fiber. This is due to improvements in the milling system. Modern flour is much cleaner and contains less impurities than the old gristmill product and from a sanitary point of view is a better food product.

The flour chemist must be familiar with nutrition investigations as problems relating to the nutritive value of flour are continually arising. The general public is not well informed upon the nutritive value of foods and frequently is imposed upon by the statements of the uninformed or those who wish to be pecuniarily benefited by the promulgation of such ideas as that ordinary white flour and the bread made from it are deficient in nourishment. Graham Lusk<sup>1</sup> briefly notes this lack of knowledge as to the value of foods: "Even among educated persons one may hear the grossest error of judgment regarding the nutritive value of a hen's egg, and few of those who eat in restaurants realize that the greatest quota of nourishment which is brought to them lies not in the specific dish served, but in the bread and butter which ostensibly is presented as a gift."

The miller is sometimes violently censured for removing the bran from his flour. It is said that he robs the flour, takes out the most valuable and nourishing part and sells a depleted article to the public. It would be made to appear that the miller was doing this for his own profit. What are the facts? The bran and wheat offals sell for  $1\frac{1}{4}$  to  $1\frac{1}{2}$  cents per lb., while his flour sells for  $2\frac{1}{2}$ -3 cents per lb. It certainly would be financially to the benefit of the miller to sell bran at flour prices. Where, then, is there any gain to the miller for the so-called robbing of the flour of its most nutritious part? The general public do not want and will not buy flour containing bran, and the public cannot be coerced in matters concerning food any more than they can in religion or politics. Then, too, there is sound reason in the public demand for white flour bread in preference to bread with bran. The extensive experiments conducted by the U. S. Department of Agriculture, covering a series of years, have plainly demonstrated that the flours with the larger particles containing the bran are not so completely digested and absorbed by the body as the fine flours containing no bran. The bran lowers the digestibility and the availability of the nutrients in the bread. There are cases where this may be an advantage, but not in the case of normal persons as the average mechanic or laborer. There are also individuals who are benefited by the mechanical action of the bran during digestion, but these cases form no valid basis for reasoning that all persons of normal digestion should eat only bread containing the bran.

England, a short time ago, was violently agitated by the Bread Reform League's advocacy of standard bread, bread made

<sup>1</sup> "The Fundamental Basis of Nutrition," p. 1.

from standard flour containing bran. A Commission of Parliament finally had to investigate the subject and wisely reported that what was most important was increasing the protein content of wheats and encouraging the use of flours with the maximum of gluten or protein.

Another accusation occasionally made against bread is that it is deficient in phosphates and mineral matter. The chief function of flour is to furnish protein and carbohydrates cheaply and in liberal and well proportioned amounts, but it furnishes also liberal amounts of mineral matter. In a study of the question some years ago, Dr. H. W. Wiley<sup>1</sup> in discussing the mineral matter of flours says: "Enough is left, however, not only to supply the need of the body for mineral constituents, but also for the condimentary purposes mentioned above." Graham Lusk says: "However, those who live on the usual mixed diet rarely suffer salt hunger." The term salt being used in the broad sense to indicate mineral matter. "Salts, therefore, scarcely enter into the food as an economic question." The layman fails to appreciate that phosphates are included in the mineral matter and "salts" along with inorganic or ash constituents as a group.

#### PROTEINS IN FLOUR

The more recent investigations of the proteins, particularly of their derivative and component parts, show that not all proteins have the same nutritive value. Some contain a larger number of typical substances necessary for growth and muscular construction and others are deficient even in certain derivative products. To call a substance a protein does not necessarily signify its absolute food value. This brings up the question: What of the proteins of flour? Generally speaking, a flour with 12 per cent protein has about 5 per cent each of gliadin and glutenin, and about 2 per cent collectively of a number of other proteins, albumins, globulins and proteoses. The gliadin is the glue-like body particularly characteristic of wheat and which serves as the "binder" of the gluten. The glutenin has all the essential components for purposes of nutrition, and ranks equally with any protein as casein, or meat proteins, or ovalbumin for "all sufficient sources of protein supply."<sup>2</sup> There is present in flour approximately 6 per cent of these proteins of the A or highest grade, which is twice as much as is found in milk, and besides these there are 6 per cent more of gliadin and similar proteins to serve for general conservation purposes. The proteins of corn, the zeins, are not the equals of the wheat proteins, as the zeins do not contain in their make-up certain component substances necessary for growth. Recent investigations and the views advanced in regard to the nutritive value of the proteins in no way affect the high position which flour and bread occupy in the dietary, because flour contains so much of the growth promoting proteins combined with the conservation proteins.

There are other substances, such as vitamins, which are receiving deserved attention in the study of foods. These protein derivative substances, the products of cell activities of both plant and animal substances, take a very important part in nutrition since in their absence neurotic conditions arise from malnutrition. The vitamin bodies are particularly lacking in such foods as rice and corn which are deficient in protein. Beriberi and pellagra are diseases caused by the use of large amounts of foods which are deficient in protein and vitamins. Pellagra occurs mainly in those localities of the United States where the average consumption of wheat per capita falls below 4.6 bu., and not in the states consuming the average of 5.3 or more. According to statistics pellagra is practically absent where a liberal diet is used in which bread forms an essential part.

In this connection it is interesting to note that vitamins are produced from the activity of the yeast plant, and hence bread

made with yeast contains not only the vitamins of the flour but also that made by the action of the yeast plant during bread-making. In fact, Funk of the Lister Institute in the study of beriberi and its cure obtained the vitamin principle from yeast. Whether the temperature in baking is sufficient to destroy completely vitamin products has not been demonstrated, but it would appear that it is not, as the interior of the moist loaf in baking does not reach a particularly high temperature. In the case of polished and unpolished rice in the pellagra question, no study appears to have been made of the vitamin products contributed by the wild yeast present on the surface of the rice and a constituent of the rice polish.

#### VITAMINE CONTENT OF OLD AND MODERN FLOURS

Illogical comparisons are sometimes attempted as to the vitamin content of old millstone and modern flour. It is asserted that the old flour contained the vitamins in abundance while the modern flour contains none. What are the facts? In the absence of exact quantitative methods for determining vitamins, indirect means are employed. It is argued that as more of the bran and fiber are removed from the modern flour it must of necessity contain less vitamins. But here is one fallacy of argument; bolting-cloths and sieves were used in making the old flour long before the advent of modern milling. The difference in bran content between the two is altogether too slight to ascribe special vitamin virtues to the one and not the other. Furthermore, in modern milling the flour layers supposedly richest in vitamins are now more completely recovered than in the old gristmill product when much of these flours went with the feeds. Now in the end the two flours, old and new, stand on the same basis as to vitamin content.

Bread enters into the dietary to a greater extent than would appear from a superficial view of the subject and is justly designated "the staff of life." The Eastern, Northern, Central and Western States all consume more flour than the Southern States. The U. S. Department of Agriculture estimates the consumption of wheat per capita as ranging from 4 to 4½ bu. in Georgia, Florida, North and South Carolina, Alabama, Mississippi, Kentucky and Tennessee, and from 6 to 7.2 bu. per capita in all of the states west of the Rockies except California, also in Minnesota, the Dakotas, Colorado, Wyoming and Oklahoma. The remaining states consume from 4½ to 6 bu. per capita, the general average being 5.3. Assuming the wheat to weigh 60 lbs. per bu. and to yield 72 per cent of flour, it would be equivalent to 240 lbs. of flour consumed per capita in the United States.

It is interesting to look at the economic aspect of the question. A family of five persons, two adults and three others, either children or elderly persons, consuming respectively 0.27, 0.24, 0.19, 0.12, 0.10 lb. of protein per day in accord with our dietary standards, would require a total of 0.92 lb. of protein. This family of five consuming the average of 240 lbs. per capita of flour would use 1200 lbs. of flour per year. Assuming this average flour (the total flour from the wheat) to contain 11.50 per cent protein, the 1200 lbs. of flour would, therefore, contain about 138 lbs. of protein. The average dietary of the family called for 0.92 lb. of protein per day, or 336 lbs. per year; that is to say, over 40 per cent of the most expensive and most important nutrient in the daily dietary of the average individual of the United States is supplied in the flour. In the states consuming 6 bu. and more per capita of wheat, 45 per cent or more is thus supplied. Calculations made by the writer a few years ago and based upon the amounts of foodstuffs consumed by the average family, according to statistics of the U. S. Bureau of Labor, show that flour costs about one-tenth as much as all other foods combined, although it furnishes over 40 per cent of the total protein and over 50 per cent of the energy of the daily ration.

The per capita consumption of flour in the United States is not as large as in some countries where cheap foods are neces-

<sup>1</sup> "Food and Food Adulterants," *Bull.* 13, Part 9, p. 1217.

<sup>2</sup> G. Lusk, p. 22.



sary. A barrel of the best flour rarely retails for upwards of \$8.50. During the past twenty years it has been much below this figure. Even if flour should be sold at retail in small lots at 5 cents per pound it would still be the cheapest and best food to form the basis of a dietary.

There are other economic phases of the flour question that deserve brief mention. There are upwards of 66,000 persons engaged in various ways in the milling industry, over 40,000 as daily wage earners, 11,000 clerks and salaried officers and about 15,000 proprietors and firm members. The total pay-roll is over \$35,000,000 annually. The flour mills represent a capital investment of over \$400,000,000, pay over \$2,000,000 in taxes, and manufacture nearly a billion dollars' worth of products in a year, and over 95 per cent of this sum is paid out for raw material and cost of manufacture and sales. This and similar data previously given are taken from U. S. Census Reports, abstracted and compiled in the *Millers' Almanac*, 1916, published by the Northwestern Miller, Minneapolis, Minn.

It is very essential that the export flour market be kept open, otherwise many flour mills will be idle. If all the flour mills of the country were operated to full capacity for a little over three months (100 days), they would make enough flour for home consumption. There is no industry in which there is fiercer competition for trade—both domestic and foreign—than in flour milling, and it is safe to say that the average profits per year are materially less than 10 cents per barrel. A number of years ago my attention was called to the singular fact that a company was saved from having a deficit by using a barrel containing two less hoops than formerly. It is right that the chief food of a nation should be made not only as cheaply as possible, but also as good as possible.

What is most needed at the present time is that more attention be paid to the production of good wheats, particularly those of high protein content. Since flour enters so largely into the dietary it cannot be made too good. Professor Mendel<sup>1</sup> aptly says: "Of all the food stuffs the proteins offer the most serious problem. They represent the indispensable staple for tissue construction; they are produced at the greatest expense." While in the case of some persons too much protein may be consumed, as when meats are used to excess, any trouble would be obviated and a better balanced and cheaper ration secured by the use of more bread and less meat. It is not intended to convey the idea that one "should live on bread alone," any more than that we should live on any single food material, but if a person had to live on any one food, bread would be the best to use. Any attempt to lessen the protein content of flour and increase its starch or carbohydrate content must be regarded as a serious menace to the nutritive value of our chief article of diet. Professor Mendel<sup>2</sup> notes a tendency for a bread and potato diet to be deficient in protein. In speaking of the industrial workers coming from the country to the city, he says: "They cannot well get along with their former simple diet, because the cheap food materials which one easily obtains, as bread and potatoes, contain too little protein. They undoubtedly need an increase of protein material." There is certainly no need for any increase in starchy materials to combine with bread.

#### BREAD-MAKING

Another important need is a better understanding of the principles of bread-making, and a wider diffusion of our present knowledge of the subject. There is too much poor bread and this is due to a lack of knowledge. Bread-making is an art founded upon scientific principles. Rule-of-thumb methods for bread-making should give way in our Domestic Science Courses to a study of principles, so that the manipulator will vary the method of procedure and the amount of ingredients to conform to the character of the flour used. It is just as neces-

sary to make slight variations in the process of bread-making as it is to make slight changes in butter-making.

Generally the quantity of bread consumed is regulated by its quality. Good bread is eaten with a relish, poor bread with indifference or not at all. If it is desired to economize in the cost of living, the amount of bread used in the dietary must be increased, because there is no food at ordinary market prices that furnishes such a large amount of valuable nutrients in a balanced form and at such a low cost as flour. Hence it is economy to encourage in every way a wider use of bread and flour in the dietary. There are other gains beside economy. Mendel<sup>3</sup> quotes Rubner as saying: "Long ago the medical profession started an opposition to the exaggerated meat diet, long before the vegetarian propaganda was started. It was maintained that flour-foods, vegetables and fruit should be eaten in place of the over-large quantities of meat."

Flour milling problems and nutrition questions are closely related and demand the best thought and attention that science can give. These questions must be approached in a broad way and in the right spirit. They are not questions for the charlatan, or the zealot food reformer to toy with. They are of such importance that they are destined to be studied until correct scientific conclusions are obtained. Science cannot be fooled permanently. Adulterated science has been attempted, but like other forms of adulteration it is detectable. Chemists must keep up the ethics of their profession. There should be but one scientific standard for all things. Any business or practice which is not right, or which will not stand the closest scrutiny has no claim to continue its existence.

It is to be regretted that occasionally men possessing some scientific knowledge are willing to use it for selfish ends. Such persons cannot be called scientists, because true science will not be polluted. Scientists may, and often do, differ, but when a person will distort facts, disregard the welfare or general good of the public, or by stealth or cunning injure an industry and knowingly commit unethical acts, such a person rightfully forfeits the respect of scientists. Both government experts and those employed by manufacturers should be above such practices. They should leave those who wish to follow such lines, in the language of Kipling:—..... "Sweating and stealing a year and a half behind."

MINNEAPOLIS, MINNESOTA

#### MANUFACTURED FEEDS FOR LIVE STOCK

By C. S. MINER

Manufactured feeds for live stock are known in the trade by a variety of names, *viz.*, Horse, Dairy, Stock, Horse and Mule, Hen, Chick, and Scratch Feeds and usually are composed of mixtures of by-products, mixtures of grains, or mixtures of grains with by-products. The industry is one whose growth has been so recent and so rapid that most of us neither appreciate its magnitude nor realize the part which chemists have come to play in its control. The annual output of manufactured feeds has grown steadily until now it is measured in millions of tons and since practically all of it must be produced under chemical supervision this industry is an important one from the standpoint of the chemist.

The question of chemical control, as it happens, is by no means optional with the manufacturer. In the feed industry in its early days there were many abuses of public confidence. The use of improper ingredients, deceptive labeling, and other fraudulent practices indulged in by the unscrupulous resulted in the passing of State Feed Control Laws designed to protect not only the consumer but the honest manufacturer as well. There are now laws of this sort in over forty states—which means in all the states where there is any market for manufactured feeds—and the large majority of them are ably and energetically administered. Although the variations in the details of these

<sup>1</sup> "Changes in the Food Supply and Their Relation to Nutrition,"

p. 20.

<sup>2</sup> *Loc. cit.*, p. 25.

<sup>3</sup> *Loc. cit.*, p. 24.

laws are such as to constitute a source of considerable annoyance to manufacturers the essential requirements in all of them are substantially the same. They require that each bag of feed shall be labeled to show the ingredients of which it is composed and the minimum per cent of crude protein, crude fat, and maximum per cent of crude fiber which it is guaranteed to contain. A very few states require the label to show the guaranteed per cent of carbohydrates and there are isolated cases where guarantees of nitrogen-free extract or starch and sugar are required. In consequence it has become the almost universal custom of manufacturers to stamp on their bags the per cent of crude protein, crude fat, crude fiber, and carbohydrates and the list of ingredients. This is done in order to be able to use one bag for all states. It may seem to some of you that the determination of carbohydrates presents so many difficulties as to make it practically impossible as a routine determination. This difficulty is avoided by a ruling of the Department of Agriculture which permits the sum of the crude fiber and nitrogen-free extract to be considered as carbohydrates for the purpose of the guarantee. That this saves work for the chemist and worry for the manufacturer is true—but it is equally true that it is highly inaccurate from a chemical standpoint. Since the literature previously recognized the term "nitrogen-free extract," which is at least definite in its meaning, and covers the same constituents with the exception of crude fiber as are now permitted by this rule to be called carbohydrates, the recognition of this inaccurate use of the term carbohydrates appears ill-advised at least.

In this connection it is of interest to note how the Federal authorities have acquired jurisdiction over the feed guarantees. The Federal Food and Drug Act does not require any more of an animal feed than of human food, merely that both shall be truthfully labeled and free from poisonous or deleterious ingredients. It does not require any statement of chemical composition or list of ingredients. The State Laws do and the manufacturer must label his feed to conform to their requirements. Consequently he becomes responsible under the Federal Food and Drug Act for the truthfulness of this label the instant his product is shipped across a State line. Since most of his shipments are interstate, the result is substantially the same as though the requirements of the State Laws had been written into the Federal law and the weight of Federal authority is added to that of the States to compel the manufacturer of feeds to maintain the standard which he sets for himself by his label. It will be evident from the foregoing that the chemist's position in the feed industry is the consequence of laws which practically make it obligatory upon the manufacturer to utilize his services. Competition forces him to make high guarantees for his feeds and the laws compel him to keep them always up to these guarantees. Since the standard is a chemical one, the chemist's services are indispensable. The problem of the feed chemist is, therefore, so to control the manufacturing process as to keep the finished feeds invariably above guarantee and yet not so far above as to make the cost prohibitive from the standpoint of competition. To do this there must be accurate analyses of all the raw materials going into the feed and of all the finished feeds. The problem consequently resolves itself into the production of the largest possible number of accurate determinations of crude protein, crude fat, and crude fiber, in the shortest possible space of time and to accomplish this the routine of the laboratory must be worked out with the same regard for efficiency that obtains in a well regulated factory, for the laboratory where thousands of samples are analyzed annually does in fact become a factory for the manufacture of analyses.

Fortunately, since the whole question is one of routine analysis, there are available the methods of the A. O. A. C. which are accepted and used by practically all chemists connected with the industry and where these methods are rigidly adhered to there is surprisingly little variation in the results obtained by different laboratories. There are, of course, exceptions to this condition

but most of them are due to the apparently inevitable book-keeping errors which occur where thousands of similar samples are analyzed, and to differences in the samples for which the chemist is not responsible. The A. O. A. C. methods are on the whole excellent but they are not fool-proof, especially when applied to a wide range of materials on which they were not tested before being made official.<sup>1</sup> By simple expedients, however, it is possible to apply the official methods satisfactorily to all of the very numerous materials which are used for the manufacture of feeds.

Since the manufacturer must guarantee not only crude protein, crude fat, and crude fiber, but also ingredients, the feed chemist is expected to be something of a microscopist, but in actual practice it is only the official chemist who examines large numbers of feeds microscopically. The manufacturer's chemist knows what goes into the feed and it is not necessary for him to examine it. He should, however, make certain that the raw materials are true to name and while normally this is the case there are plenty of instances where materials purchased by manufacturers in good faith have been used in manufactured feeds and later found by state officials to have been adulterated. Screenings in malt sprouts, bran, or linseed meal constitute one of the commonest examples of such a possibility. Since screenings are almost invariably present in such products the question of determining whether to accept or reject a shipment oftentimes becomes a difficult one especially because of the lack of quantitative methods of microscopic analysis. This situation is a typical one and the result is that in most cases the chemist makes very little effort to control the raw materials by other than chemical means or visual examination, and adulteration unless gross is therefore not likely to be detected.

You may have judged from what I have said that the feed industry demands only routine work of its chemists. I do not want to leave that impression. In this industry as in others routine analysts are valuable as a class. As individuals they are readily replaceable and not highly valued. What is highly valued here as elsewhere is the ability to apply specialized training and experience to the solution of practical problems and the chemist who can do this will find himself very soon occupying the position, not of routine analyst, but of chemical director to his company. He will be consulted on all chemical phases of the business just as the attorney is consulted on all legal phases. He will pass upon the scientific accuracy of the advertising matter, upon the wording of contracts for raw materials, upon the value of new raw materials, and he will be expected to evolve new formulas or pass judgment upon those suggested. In fact it will be his business to give an expert judgment upon every problem involving chemistry which arises in connection with the manufacture and marketing of feeds.

The future of this industry holds even greater possibilities for chemists. Our rapidly increasing fund of information concerning the factors involved in nutrition and growth, such as the amino acids, the mineral constituents of foods, and the accessory diet factors—vitamins and the like—is certain to be applied in the development of the feed industry with the result that a much more complete and accurate form of chemical control will become necessary. And not only routine control but research as well, for the feed manufacturer will not always be content to depend upon State institutions for research as at present. The industry, therefore, both for its present and future possibilities is one which I can conscientiously recommend to the consideration of the young chemist looking for his place in technical chemistry.

CHICAGO, ILLINOIS

<sup>1</sup> To cite a single example we have found that peat or feeds containing considerable percentages of it give erratic results for crude fiber because of the slow filtration. By the simple expedient of centrifuging, decanting, or otherwise partially separating the dissolved from the suspended matter before filtration and passing the nearly clear liquor through the filter before the suspended matter is added, satisfactory results are obtainable.



## CURRENT INDUSTRIAL NEWS

### LEATHER TRADE IN NIGERIA

The demand for leather in Nigeria, says the *Leather World*, 8 (1916), 388, is limited to the varieties used for slippers and saddlery. The southern districts are not so well adapted for tanning materials but in the marshes along the coast there is an abundance of mangrove and its exploitation would, it seems, be remunerative, considering that labor is cheap. The natives work well in their way for 12 to 24 cents per day, but resent being ordered about too much. The population of Nigeria is about 6,000,000.—A. McMILLAN.

### NEW INSTITUTION

According to *Engineer*, 122 (1916), 33, what is described as an "experimental workshop and industrial laboratory," has been established by the recently founded Aeronautical Institute of Great Britain. The laboratory is situated at 45 Horseferry Road, Westminster, and according to information received concerning it, is intended to form a link between "an invention in its primitive stage and its scientific application and commercial development." It has, further, been gathered that its work will not possess the minute accuracy of exact scientific investigation but will aim simply at ascertaining whether any practical purpose would be served by submitting a new device to systematic and frequently delicate and costly scientific research. In short, the laboratory, it is claimed, will afford means of producing and testing under good conditions, new ideas, and of quickly obtaining results which can give reliable indications as to the practicability of the proposed devices. It will specialize on aeronautical work but will be open to deal with inventions outside this sphere.—M.

### VEGETABLE DYES

Samples of dyes have been received at the Board of Trade, London, from the Consul at Szechuan, as follows:

RED: *Lithospermum officiale* L; *Rubia cordifolia* L; and *Carthamus tinctorius* L. (Safflower).

BLUE: *Strobilanthes flaccidifolia*; Nees (Indigo).

GREEN: *Polygonum orientale*.

YELLOW: *Curcuma longa* L (turmeric); *Sophora Japonica*; and *Gardenia florida* L.

BLACK: *Rhus Semialata* Murr; *Quercus, Mongolica* or *Sinensis* (silkworm or chestnut oak) and *Stillingia sebifera* (tallow tree).

Information regarding preparation and employment of above may be obtained at Board of Trade Offices, London.—M.

### PARAFFIN AS A PETROL SUBSTITUTE

In view of the abnormally high price of petrol and the difficulty of obtaining it, an article in *Engineer*, 122, No. 3158, will be read with interest. A description is given of the Binks vaporizer and carbureter, by the use of which paraffin may be substituted for petrol in motor-driven vehicles. A small tank is fitted for the supply of petrol for starting the engine and paraffin is used after the vaporizer has become sufficiently hot. The carbureter has two float chambers, one for petrol and the other for paraffin and has a main jet and two pilot jets. The sprayed paraffin enters the vaporizer which consists of two concentric tubes, between which the exhaust gases from the engine pass and thus heat the walls of the inner tube. The latter tube contains a worm which causes the mixed air and paraffin to whirl as the mixture transverse the inner tube. There is thus a tendency to throw any unvaporized paraffin into contact with the hot walls where vaporization is completed. With present prices, application of this and similar devices may reduce the cost of fuel for motor engines by 50 per cent.—M.

### SWISS DYE INDUSTRY

A report has been issued by the Basle Chamber of Commerce dealing briefly with the position of the dye manufacturing industry in Switzerland. It seems that all the firms formerly engaged in the production of coal-tar dyes have had to enlarge their plant in order to manufacture the intermediate products used in the industry, most of which had previously been imported from Germany. The supply of raw material seems to be the chief cause of anxiety, but reference is made to the assistance given by the British Board of Trade in facilitating the transport of crude tar products from that country to Switzerland. The various color makers are making negotiations with a view to erecting a large plant for the production of mineral acids. The report further states that synthetic indigo has been produced on a small scale only, owing to the difficulty of obtaining raw materials, but it has been found possible, notwithstanding, not only to supply the demands of the Swiss market but also to export a moderate amount. Owing to complaints raised by Swiss dyers that they were not receiving a fair share of the output, the dyestuff manufacture has been placed under the control of the government to some extent and export licenses are now necessary. These are granted only to countries which are supplying raw material to Switzerland and the amount of color exported is in proportion to the amount of raw material supplied. At the present time and under these conditions, England is the only country receiving dyes in any quantity.—M.

### LAC EXPORTS FROM BRITISH INDIA

The *Indian Trade Journal* of May 19 contains a communique, issued by the Commerce Department of India, which states that the Collectors of Customs have been instructed to permit exports of lac to all allied countries under license. Permission has also been granted, under license, for the exportation of lac in normal quantities to the usual consignees in neutral countries outside Europe. Applications to export to neutral countries in Europe should be submitted to the Government of India through the Collector of Customs at the port of shipment.—M.

### JAPANESE CHEMICAL PRODUCTION

Official returns of the production of chemicals in Japan during 1915 contain the following figures (lbs.):

Benzol.....	128,000	Naphthalene.....	1,170,000
Ether.....	549,000	Alcohol.....	7,600,000
Aspirin.....	50,000	Hydrochloric acid.....	4,819,000
Sulfuric acid.....	153,420,000	Acetic acid.....	723,000
Caustic soda.....	240,000		

The exports of camphor last year amounted to 5,044,000 lbs. valued at \$1,737,500 and showing a steady increase.—M.

### COPPER INDUSTRY IN AUSTRALIA

Considerable interest, says *Engineering*, 102 (1916), 104, is attached to the recent developments in the copper industry in Australia. The Hampden Cloncurry copper mines instead of sending metal overseas for conversion into the pure metal as heretofore, now sends the whole of its output to be refined at the works of the Electrolytic Refining and Smelting Co. of Australia at Port Kembla. The refinery is not yet able to refine the whole of the company's output electrolytically and the excess is pre-refined and is being disposed of at satisfactory prices. A company has also been formed to manufacture all classes of copper wire, copper tubes, sheets, etc., with works adjoining the electrolytic works at Port Kembla. The consumption of manufactured copper goods is a growing one and after exhaustive investigation and on assurances of support from the commonwealth authorities, its inauguration seems to be commercially justified. The capital of the Company is \$1,000,000.—M.

# SCIENTIFIC SOCIETIES

## FIFTY-THIRD MEETING AMERICAN CHEMICAL SOCIETY NEW YORK, SEPTEMBER 25 TO 30, 1916 PROGRAM OF PAPERS

### PUBLIC MEETINGS

Addresses of Welcome. DR. HADEN EMERSON, Health Commissioner of New York City, and NICHOLAS M. BUTLER, President of Columbia University.

Response. CHARLES H. HERTY, President of American Chemical Society.

Outline of Colloid Chemistry. W. D. BANCROFT.

Coal and Coke By-Products as a Source of Fixed Nitrogen (Illustrated). H. C. PORTER.

Chemistry and the National Welfare. GEN. WILLIAM CROZIER, Chief of Ordnance, War Department.

Chemistry and Banking. J. E. GARDIN, Vice-President of National City Bank.

Chemistry and Conservation. GIFFORD PINCHOT, President of National Conservation Association.

Expanding Relations of Chemistry in America. CHARLES H. HERTY.

### INDUSTRIAL CONFERENCES

Electric Furnace Steels and Alloy Steels. J. A. MATHEWS, Chairman. American Dyestuff Manufacture. C. H. HERTY, Chairman.

American-Made Chemical Glass and Porcelain. A. H. THOMAS, Chairman.

Industrial Alcohol, Acetone, and Acetic Acid. ARTHUR D. LITTLE, Chairman.

Manufacture of Paper Pulp and By-Products. R. B. WOLF, Chairman. Medicinal Chemicals. HAROLD HIBBERT, Chairman.

Miscellaneous Chemical Industries: Convertibility of Plant. W. H. GROSVENOR, Chairman.

Oils and Motor Fuels. R. F. BACON, Chairman.

### AGRICULTURAL AND FOOD CHEMISTRY DIVISION

L. M. TOLMAN, *Chairman* G. F. MASON, *Secretary*

1. Chemical Factors in the Deterioration of Raw Sugars. C. A. BROWN.

2. Maple Products, IX: On the Composition of the Soluble and Insoluble Portions of the Ash of Maple Syrup. J. T. SNELL and MR. VAN ZOEREN.

3. An Increase in the Sucrose Content of Sugar-Beets after Their Removal from the Soil. DR. F. G. WIECHMANN.

4. Determination of Minute Quantities of Metal in Organic Substances with Special Reference to Lead in Urine. HALSEY DURAND. Determination of Added Water in Milk.

5. The Relation of the Fat in Milk to the Solids-not-Fat. LUCIUS P. BROWN and CLARENCE V. ERKROTH.

6. Chemical Quality of New York City Milk. LUCIUS P. BROWN and CLARENCE V. ERKROTH.

7. The Use of Hard Water for Cannery Purposes. W. D. BIGELOW and F. F. FITZGERALD.

8. Detection of Watered Milk, by Means of Simplified Molecular Concentration Constants. L. W. FERRIS.

9. The Estimation of Total Solids in Evaporated Milk by Means of the Babcock Formula. O. L. EVENSON.

10. Detection of Added Water in Milk by Means of the Freezing Point. J. T. KEISTER.

### BIOLOGICAL CHEMISTRY DIVISION

C. L. ALSBERG, *Chairman* I. K. PHELPS, *Secretary*

#### Part I—Colloid Chemistry Symposium (Theoretical and Applied)

Irreversible Adsorption of Dyes. D. B. LAKE.

Phase Relations in Biological Systems. G. H. A. CLOWES.

Displacement of Equilibrium by Catalytic Agents. W. D. BANCROFT.

Stabilization. E. F. FARNAU.

Shower Proofing. E. L. MACK.

Selective Adsorption and Differential Diffusion. J. ALEXANDER.

The Photographic Developer. J. M. BALL.

Structure of Liquids with Particular Reference to Surface Tension. I. LANGMUIR.

Electrical Endosmose. T. R. BRIGGS.

The Reaction between Potassium Permanganate and Ferrous Chloride. A New Method for Preparing Colloidal Hydrous Ferric Oxide. MARKS NEIDLE and JOHN H. CROMBIE.

Studies in Dialysis. II. The Dialysis of the Chlorides of Iron, Chromium and Aluminum, Particularly in the Hot. MARKS NEIDLE and JACOB BARAB.

The Colloid Material of Clay. GUY C. GIVEN.

Terminology in Colloid Chemistry. A. W. THOMAS.

Refining of Oils. C. BASKERVILLE.

Relation between Chemical Composition and Electrical Resistance.

C. G. FINK.

Paints. T. R. BRIGGS.

Yellow Bricks. L. A. KEANE.

Vulcanization of Rubber. D. SPENCE.

The Splitting of Fats. W. D. RICHARDSON.

Adsorption of Chromium by Hide Powder. A. W. DAVISON.

Asphalt. C. RICHARDSON.

Plaster of Paris. L. A. KEANE.

Emulsions and Suspensions with Molten Metals. H. W. GILLET.

The Purification of Kaolin. C. L. PARSONS.

Colloids in Glass. ALEXANDER SILVERMAN.

Fritting and Fusing. W. D. BANCROFT.

#### Part II—Additional Papers Not Read in Symposium

1. Carbon Monoxide, Occurrence Free in Kelp (*Neurocystis Leutkeana*). S. C. LANGDON.

2. The Oxidation of Sulfur by Micro-organisms. J. G. LIPMAN.

3. A Comparison of Barbituric Acid, Thiobarbituric Acid and Malonylguanidine as Quantitative Precipitants for Furfural. A. W. DOX and G. P. PLAISANCE.

4. An Accurate Aeration Method for the Determination of Alcohol in Fermentation Mixtures. A. W. DOX and A. R. LAMB.

5. A Direct Reading Potentiometer for Measuring Hydrogen Ion Concentrations. F. E. BARTEL.

6. The Separation and Estimation of Butyric Acid in Biological Products. I. K. PHELPS and H. E. PALMER.

7. Investigations of the Kjeldahl Method for Determining Nitrogen. A Qualitative Study of the Hydrolysis of Amines. I. K. PHELPS, H. W. DAUDT, C. L. ALSBERG and H. E. WOODWARD.

8. On the Proteins of the Peanut, *Arachis Hypogaea*: 1. The Globulins Arachin and Conarachin. C. O. JOHNS and D. B. JONES.

9. On Kafirin, an Alcohol-Soluble Protein from Kafir, *Andropogon Sorghum*. C. O. JOHNS and J. F. BREWSTER.

10. On a Saponin from *Yucca Filamentosa*. L. H. CHERNOFF, A. VIEHOEVER and C. O. JOHNS.

11. On a Saponin from *Agave Lechiguilla*. C. O. JOHNS, L. H. CHERNOFF and A. VIEHOEVER.

12. On the Chemistry of the Cotton Plant, with Special Reference to the Upland Variety, *Gossypium hirsutum* (First Paper). A. VIEHOEVER, L. H. CHERNOFF and C. O. JOHNS.

13. Urease of the Soy Bean and of the Jack Bean. I. F. HARRIS.

14. Needs and Requirements of Modern Toxicology. E. E. BUTTERFIELD.

15. A Rapid Method for the Removal of Organic Matter in Blood, Feces, Tissue and Foods. H. H. WILLARD and C. H. LAWS.

16. The Availability of the Insoluble Calcium Phosphates when Present as a Constituent of Infant's Food. A. W. BOSWORTH.

17. The Chemical Changes Produced by the Addition of Lime Water to Milk. A. W. BOSWORTH.

18. Chemistry of the Liver in Acute Yellow Atrophy. M. KAHN and V. L. ANDREWS.

19. A Method of Testing the Function of the Liver by Means of Sulfo-Conjugation of Thymol. M. KAHN and C. S. FOSTER.

20. An Improved Nephelometer-Colorimeter (a demonstration). P. A. KOBER.

21. Improvements in the Copper Method for Estimating Amino Acids (a demonstration). P. A. KOBER.

22. The Efficiency of the Aeration Method for Distilling Ammonia; in Answer to Certain Criticisms (a demonstration). P. A. KOBER.

23. Cholesterol and Cholesterol Esters in Human Blood. W. R. BLOOR and A. KNUDSON.

24. The Formation of a Phenol by *Aspergillus niger*. C. L. ALSBERG and J. F. BREWSTER.

25. A New Reagent for Volatile Amines and a New Reagent for Volatile Tertiary Amines. C. L. ALSBERG and H. E. WOODWARD.

26. Elimination of Malates Following the Subcutaneous Injection of Sodium Malate. L. E. WISE.

27. Isolation of Cyanuric Acid from Soil. L. E. WISE.

28. The Isolation of an Organic Colloid of the Gel Type from a Soil. A Complex Carbohydrate. E. C. LATHROP.

29. The Carbohydrate of Thymus Nucleic Acid. GEORGE PRIRCE.

30. The Inosite-Phosphoric Acids of Cottonseed Meal. J. B. RATHER. (By Title)

31. Gossypol, the Toxic Principle of Cottonseed. W. A. WITHERS and F. E. CARUTH.

32. A Device for Measuring the Reaction of Solutions (Lantern). W. T. BOVIE.



## FERTILIZER CHEMISTRY DIVISION

J. E. BRUCKENRIDGE, *Chairman* F. B. CARPENTER, *Secretary*

1. The Utilization of City Waste for the Manufacture of Fertilizers. J. W. TURRENTINE
2. Variation in the Composition of City Garbage. W. J. O'BRIEN AND JOHN R. LINDMEIER
3. The Availability of Nitrogen in Garbage Tankage. JAMES P. SCHROEDER

4. The Availability of Nitrogen in Fertilizers: Some Modern Lights Thereon. CHARLES B. LIPMAN.

5. Fertilizer Sampling Methods in the United States. F. S. LODGE.
6. Note on the Results of Analysis on Samples Taken with Different Styles of Samplers. F. B. CARPENTER.
7. Results of Further Co-operative Work on the Determination of Sulfur in Pyrites. H. C. MOORE.
8. A Summary of the Potash Situation. H. A. HUSTON
9. Note on the Recovery of Molybdic Acid. PAUL RUDNICK.
10. The Action of Calcium Carbonate on Acid Phosphate. E. W. MAGRUDER
11. The Effect of Changes in Temperature and the Sulfuric Acid Radical on the Pemberton Volumetric Method for Determining Phosphoric Acid. P. MCG. SHURY.
12. The Volumetric Determination of Phosphoric Acid by the Molybdate Cold Precipitation Method. W. P. HEATH.
13. The Preparation of Concentrated Fertilizers. ALBERT R. MERZ AND W. H. ROSS.
14. Results of Recent Investigations with Methods of Analysis on Samples of Commercial Wood Ashes. R. E. ROSS.
15. The Relative Availability of Acid Phosphate and Raw Rock Phosphate in Indiana Field Tests. S. D. CONNER.

## INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS DIVISION

H. E. HOWE, *Chairman* S. H. SALISBURY, JR., *Secretary*

## Part I—Symposium on Occupational Diseases in the Chemical Trades

1. Introduction. PROF. CHAS. BASKERVILLE, Chairman, Committee on Occupational Diseases in the Chemical Trades.
2. The Occupational Hazard in the Chemical Industry; the Need for Prophylaxis. DR. J. W. SCHERESCHESKY, Surgeon, U. S. Marine Hospital Service, Pittsburgh, Pa.
3. Aniline and Other Coal Tar Products. GEORGE P. ADAMSON, Baker & Adamson Chemical Co., Easton, Pa.
4. Some Abnormal Effects on Workmen Engaged in the Manufacture of Port Orford Cedar Lumber. DR. H. K. BENSON, Professor of Chemistry, University of Washington, Seattle, Wash.
5. Bureau of Mines Studies on Occupational Diseases. DR. W. A. LYNOTT, Bureau of Mines, Washington, D. C.
6. Dangers other than Accidents in the Manufacture of Explosives. DR. ALICE HAMILTON, United States Bureau of Labor Statistics, Chicago, Ill.
7. Discussion. DR. W. GILMAN THOMPSON, Professor Physiology, Cornell University Medical College; DR. FREDERICK L. HOFFMAN, Statistician Prudential Insurance Co. of America; MR. JOHN B. ANDREWS, Secretary American Association for Labor Legislation; and others.

## Part II—The Nitrogen Industry

1. Conditions Affecting the Establishment of the Nitrate Industry in the United States. LAWRENCE ADDICKS.
2. By-Product Ammonia for Fertilizers and Munitions. J. W. TURRENTINE.
3. The Oxidation of Ammonia. J. W. TURRENTINE, W. J. O'BRIEN AND HARRY BRYAN.

## Part III—Additional Papers

1. Why the Brewing Industry Demands Recognition by the Universities. CARL A. NOWAK.
2. The Present Status of the Potash-from-Kelp Industry of the Pacific Coast. J. W. TURRENTINE.
3. The Preparation of Oxalic Acid and Citric Acid by Fermentation. JAMES N. CURRIE.
4. The Manufacture of Benzaldehyde and Benzoic Acid. H. D. GIBBS.
5. Noviol, a New Glass for Absorbing Ultraviolet Radiation. W. C. TAYLOR.
6. Single and Multiple Effect Evaporators. OTTO MANTIUS.
7. The Problem of the Cheap Production of Alcohol. ARTHUR N. BRECKLER.
8. The Specific Heat and the Heat of Hydration of Wheat Flour. FARRINGTON DANIELS, B. H. KEPNER AND P. P. MURDICK.
9. The Use of the Cottrell Precipitator in Recovering the Phosphoric Acid Evolved in the Volatilization Method of Treating Phosphate Rock. W. H. ROSS, J. N. CAROTHERS AND A. R. MERZ.
10. The Influence of Moisture on the Yield of Products in the Destructive Distillation of Hardwood. R. C. PALMER AND H. CLOUKEY. (By Title.)
11. The Effect of Incomplete Distillation on the Yield of Products in the Destructive Distillation of Birch. R. C. PALMER. (By Title.)
12. The Effect of Catalysts on the Yield of Products on the Destructive Distillation of Hardwoods. R. C. PALMER. (By Title.)
13. Teased Oil, Properties, Tests, and Possibilities. CHARLES V. BACON
14. Peanut Oil as a Southern Asset. CHARLES V. BACON.
15. The Recracking of a Cracked Oil. GUSTAV EGLOFF AND THOMAS J. TWOMEY.
16. The Effect of Temperature and the Time Factor in the Formation of Gasoline in the Gas Phase at Constant Pressure. GUSTAV EGLOFF, T. J. TWOMEY AND R. J. MOORE.
17. An Experiment in the Training of Chemical Engineers; the 25th Anniversary of the Audubon Sugar School. CHARLES E. COATES.

## ORGANIC DIVISION

C. G. DERICK, *Chairman*H. L. FISHER, *Secretary*

1. The Hydration Diacids. J. R. BAILEY.
2. The Use of Cyanic Acid in Glacial Acetic Acid. J. R. BAILEY.
3. The 5,5-Dimethyl-3-R-2-thiohydantoins. J. R. BAILEY.
4. The Formation of Cyclopentadiopyridazines and Proof of Their Structure. WILLIAM J. HALE.
5. The Formation of Aromatic Hydrocarbons from the Thermal and Pressure Decomposition of Pentanes and Hexanes. GUSTAV EGLOFF.
6. Application of the Nitrometer for the Determination of Constitution and Estimation of Nitrogen in a Class of Nitrocompounds (Nitroamines). W. C. COPE AND J. BARAB.
7. The Preparation and Ionization of the Isomeric Benzenedisulfonic Acids. W. A. DRUSHEL.
8. Carbon Monoxide, Occurrence Free in Kelp (*Nereocystis Luetkeana*). SETH C. LANGDON.
9. Studies on Derivatives of Trihalogen Tertiary Butyl Alcohols.
10. The Acetic Ester of Tribromotertiary Butyl Alcohol or Bromotone Acetic Ester. T. B. ALDRICH AND C. P. BECKWITH.
11. The Constitution of Xanthogallol. F. J. MOORE.
12. Di-*p*-nitro-benzoyl Malonic Ester. C. G. DERICK AND F. C. HAHN.
13. The Scale of Influence of Substitution. The Diad Oxygen Atom. C. G. DERICK, ST. ELMO BRADY AND R. W. HESS.
14. The Scale of Influence of Substitution. The Phenyl Radical. C. G. DERICK AND P. M. DEAN.
15. The Electronic Formula of Benzene and the Molecular Volumes of the Chlorobenzenes. H. S. FRY. (By Title.)
16. A Correlation between the Electronic Formulas of Monosubstituted Derivatives of Benzene and the Quantities of the Isomers Obtained upon Nitration. H. S. FRY. (By Title.)
17. On the Mechanism of Replacement Reactions in the Benzene Nucleus. H. S. FRY. (By Title.)
18. The Preparation of Alkyl Hydroxyurea Chlorides and Their Relation to Esters of Carbon Dioxide Oxime,  $R-O-N=C=O$ . LAUDER W. JONES AND LEONORA NEUFFER. (By Title.)
19. Hydroxamic Acids Related to  $\alpha$ -Hydroxy Acids and to Acrylic Acid and a Study of their Rearrangements. LAUDER W. JONES AND LEONORA NEUFFER. (By Title.)
20. A Study of  $\beta$ -Benzylformhydroxamic Acid and Hydroxamic Acids of Substituted Acetic Acids. LAUDER W. JONES AND M. CANNON SNEED. (By Title.)
21. Unnecessary Use of Potash Compounds in Making Organic Preparations. HERBERT COITH AND JAMES R. WITHROW.
22. The Determination of Small Amounts of Nitrogen and Its Presence in Petroleum. C. F. MABERY.
23. Some Measurements with a New 4-Range Variable Inductance. F. M. BEEGLE, S. F. ACREE AND EDWARD BENNETT.
24. A Correction Formula for Conductivities Measured at Different Frequencies in Cells with Bright Electrodes. H. P. HASTINGS, W. A. TAYLOR, EDWARD BENNETT AND S. F. ACREE.
25. Some Corrections for Conductivity Measurements with Kohlrausch Slide-Wire Bridges. F. M. BEEGLE, EDWARD BENNETT AND S. F. ACREE.
26. Some Spectrophotometric Measurements on Sulfonphthaleins and the Quinone Phenolate Theory of Indicators. J. SAM GUY AND S. F. ACREE.
27. The Influence of the Partial Pressure of Hydrogen on the Potential of the Hydrogen Electrode. N. E. LOOMIS AND S. F. ACREE.
28. A Study of Tipase. HILTON IRA JONES.
29. Identification of Phenols. E. EMMET REID.
30. The Isomeric Octacetates of Gentibiose. C. S. HUDSON AND J. M. JOHNSON.
31. Researches on the Action of Sulfuric Acid on Certain Nitrocarbocyclic Compounds. M. L. CROSSLEY.
32. The Use of General Formulas in Teaching Organic Chemistry. M. L. CROSSLEY.
33. A Hydrate of Anthraquinone 2,7 Sodium Sulfonate. M. L. CROSSLEY.
34. On the Use of the Oscillograph for Measuring the Resistance and Capacity of Conductivity Cells. G. H. GRAY, EDWARD BENNETT AND S. F. ACREE.
35. The Action of Butyl Chloral on Benzene and Its Homologues in the Presence of Aluminum Chloride. G. B. FRANKFORTER AND E. A. DANIELS.

## PHARMACEUTICAL CHEMISTRY DIVISION

JOHN H. LONG, *Chairman*GEO. D. BEAL, *Secretary*

1. Aromatic Sulfuric Acid, U. S. P. W. B. D. PENNIMAN, W. W. RANDALL, C. O. MILLER AND L. H. ENSLOW. (Printed in this issue.)
2. The Registration of Proprietary Remedies. LOUIS HOGREFE.
3. A Bill to Regulate the Use and Registration of Professional Degrees in New York State. LOUIS HOGREFE.
4. Chemicals Admitted into U. S. P., IX. OTTO RAUBENHEIMER.
5. A Demonstration of Standardized Colored Fluids. H. V. ARNY.

## PHYSICAL AND INORGANIC CHEMISTRY DIVISION

IRVING LANGMUIR, *Chairman*JAMES KENDALL, *Secretary*

1. The Calculation of the Vapor Pressure of a Liquid. J. E. MILLS.
2. The Specific Heat of the Elements. J. E. MILLS.
3. The Action of Ammonia on Arsenic Iodide (with Lantern).
- CHARLES H. HERTY AND C. B. CARTER.
4. The Thermodynamic Properties of Silver and Lead Iodides. H. E. TAYLOR.
5. The Inconstancy of the Solubility Product, II. ARTHUR E. HILL.
6. Studies on Catalysis, II. J. E. BOOGE AND JAMES KENDALL.
7. The Catalytic Reduction and Oxidation of Solutions of Iron Sulfate by Colloidal Platinum (with Lantern). FARRINGTON DANIELS AND R. H. KIENLE.
8. The Laws of Plastic Flow (with Lantern). EUGENE C. BINGHAM.
9. Determination of Silver from Cyanide Solutions (with Lantern).
- A. S. MCDANIEL AND L. SCHNEIDER.
10. The Influence of Pressure on Solubility. HERBERT F. SILL.
11. Experimental Physical Chemistry (with demonstration of apparatus in Room 605, Havemeyer Hall, by J. E. Booge, K. P. Monroe and J. C. Andrews). JAMES KENDALL.
12. Emulsions. R. E. OESFEL AND LEO ROON.
13. The Disgregation Constant of Saturated Vapors. F. P. SEIBEL.
14. The Thorium-Mesothorium Ratio. HERBERT N. MCCOY AND H. M. HENDERSON.
15. The Evidence of Physical Properties of Isotopes on the Nature of the Atom. CHARLES WADSWORTH, 3d.
16. The Determination of the Specific Heats of Some Cadmium Salts at Low Temperatures and Their Use in the Calculation of Electromotive Force. F. M. SEIBERT, G. H. HULETT AND H. S. TAYLOR.
17. Inflammability of Carbonaceous Dusts. H. H. BROWN. (By Title.)
18. Inflammability of Carbonaceous Dusts in Atmospheres of Low Oxygen Content. H. H. BROWN AND J. K. CLEMENT. (By Title.)

## RUBBER SECTION

J. E. WEBER, *Chairman*J. B. TUTTLE, *Secretary*

1. A Revision of Wesson's Method for the Direct Determination of Rubber. J. B. TUTTLE AND L. YUROW.
2. Wet Combustion in the Nitrosite Combustion Method for the Direct Determination of Rubber. L. G. WESSON.
3. The Aniline Method for the Determination of Fillers in Rubber Goods. OTTO H. KLEIN.
4. Increase of Resins in the Vulcanization. L. E. WEBER.
5. The Second Report of the Joint Rubber Insulation Committee. WILLIAM E. DEL MAR, *Secretary*.
6. The Rubber Industry. H. C. PEARSON.
7. A symposium on "The Accelerated Life Test of Rubber Compounds." Discussion to be opened by W. C. GEER, with contributions from C. D. YOUNG, C. R. BOGGS, L. E. WEBER, DORRIS WHIPPLE, J. B. TUTTLE, and others.

## WATER, SEWAGE AND SANITATION DIVISION

EDWARD BARTOW, *Chairman*H. P. CORSON, *Secretary*

1. Value of the Sanitary Survey. W. P. MASON.
2. The Present Status of the Mineral Water Industry. (Lantern.) F. L. RECTOR.
3. The Alternate Use of Bleaching Powder and of Copper Sulfate for Sterilizing the Water of Swimming Pools. (Lantern.) FREDERIC BONNET, JR.
4. Storage Reservoirs as a Factor in the Purification of Surface Waters. S. T. POWELL.
5. Reaeration as a Factor in Stream Pollution. EARLE B. PHELPS.
6. The Chemical Composition of the Water of the Yukon River, Alaska. R. B. DOLE AND A. A. CHAMBERS.
7. Thermocline Studies at Kensico Reservoir. FRANK E. HALE AND JOHN E. DOWD.
8. The Relation of Micro-organisms to the Loss of Head in Rapid Sand Filters. J. W. ELLMS AND S. J. HAUSER.
9. The Treatment of Sewage Sludge with Filter Effluent. H. W. CLARK.
10. Is the Recovery of the Nitrogen in Sewage Sludge Practicable? W. R. COPELAND.
11. The Treatment of Residential and Small Community Sewage. L. C. FRANK.
12. Water Meters in Their Sanitary Relations. HENRY LEFFMANN.

13. A Source of Error in the Standard Methods for the Determination of Nitrates in Sewage and Sewage Effluents. STEPHEN DEM. GAGE AND HENRY H. ANDERSON.

14. The Determination of Small Amounts of Methyl Alcohol Vapor in Air. ELIAS ELVOVE.

15. An Experimental Study of Muscicides. A. F. STEVENSON.

16. Some Remarks on the Biochemical Treatment of Sewage, with Especial Reference to the Activated Sludge Method. GEORGE T. HAMMOND.

17. A New Battery Fermentation Tube Holder. W. F. WELLS, U. S. Public Health Service.

AMERICAN ELECTROCHEMICAL SOCIETY, THIRTIETH GENERAL MEETING, NEW YORK CITY  
SEPTEMBER 27 TO 30, 1916

The Thirtieth General Meeting of the American Electrochemical Society was held at New York City, September 27 to 30, 1916, with headquarters at the Hotel Astor. In order that as many members as possible might get together at the Exposition, Wednesday, Sept. 27th, was set aside as Electrochemical Day and the morning session was held at Grand Central Palace. Thursday and Friday mornings the technical sessions were held at the Hotel Astor. About 500 members and guests were registered.

The social features of the meeting held were in conjunction with the American Chemical Society.

## PROGRAM OF PAPERS

The Protection of Iron by Electroplating. O. P. WATTS AND P. L. DEVERTER.

Atmospheric Corrosion of Commercial Sheet Iron. E. A. AND L. T. RICHARDSON.

The Electrolytic Recovery of Lead from Brine Leaches. O. C. RALSTON AND C. E. SIMS.

Electrolytic Zinc Dust. H. J. MORGAN AND O. C. RALSTON.

Electrolysis of Vanadium Salts. S. FISCHER.

The Electro-deposition of Nickel. L. D. HAMMOND.

Current Efficiencies in Nickel Plating Baths with Rotating Cathodes. F. C. MATHERS AND F. G. STURDEVANT.

Deposition of Copper in Electrotype Baths. W. BLUM, H. D. HOLLER AND H. S. RAWDON.

Characteristics of Small Dry Cells. C. F. BURGESS.

Effect of Temperature on the Performance of the Edison Storage Battery. L. C. TURNOCK.

High Temperature Heat Developed during Electrolysis. CARL HERING.

The Possibilities of Developing Super-refractory Materials for Incandescent Lighting. F. A. FAHRENWALD.

Composition of the Ionization Currents Due to Equal Quantities of Radium Emanation. T. H. LEAMING, H. SCHLUNDT AND JULIUS UNDERWOOD.

A New Method for the Study of Silver Peroxynitrate. M. J. BROWN.

The Equilibrium between Bromine and Potassium Bromide Solutions at 0°. GRINNELL JONES AND M. L. HARTMANN.

## THE CHEMICAL SOCIETIES IN NEW YORK CITY

## 1916-1917 SEASON—RUMFORD HALL, THE CHEMISTS' CLUB

October 13—American Chemical Society. Joint Meeting with Society of Chemical Industry and American Electrochemical Society.

November 10—American Chemical Society.

November 24—Society of Chemical Industry.

December 8—American Chemical Society. Joint Meeting with Society of Chemical Industry and American Electrochemical Society.

January 19—Society of Chemical Industry. Perkin Medal Award.

February 9—American Electrochemical Society. Joint Meeting with American Chemical Society and Society of Chemical Industry.

March 9—American Chemical Society. Nichols Medal Award.

March 23—Society of Chemical Industry.

April 20—Society of Chemical Industry.

May 25—Society of Chemical Industry. Joint Meeting with American Chemical Society and American Electrochemical Society.

June 8—American Chemical Society.



## SYMPOSIUM ON OCCUPATIONAL DISEASES IN CHEMICAL TRADES

Abstracts of Papers and Discussions at 53rd Meeting of the American Chemical Society, New York City

**Occupational Diseases in the Chemical Trades.** DR. CHAS. BASKERVILLE, Chairman of the Committee on Occupational Diseases in the Chemical Trades. Dr. Baskerville outlined the work done so far, beginning with the First Congress in Milan in 1906. Great Britain is very much in advance of the U. S. in industrial disease investigations. The A. C. S. Committee has been as active since its appointment as the entire absence of funds would permit. The establishment of a National Museum of Safety in Washington was suggested.

**The Occupational Hazard in the Chemical Industry; The Need for Prophylaxis.** DR. J. W. SCHERESCHESKY, Surgeon, U. S. Marine Hospital Service, Pittsburgh, Pa. The specific hazards provided by the nature of chemical substances add to the complications of the chemical industries. The value of the products of these industries increased 53 per cent in the period from 1909 to 1914. The industry has been little studied in this country from the point of industrial hygiene. The Illinois Commission on Occupational Diseases and the New York State Factory Investigation are notable, however, in the face of discouraging conditions. Some of the ordinary hazards of the industries are classed under superficial poisons, blood poisons and poisons of remote, delayed and cumulative effect. Poisonous fumes and dusts are a danger not to be neglected.

**Aniline and Other Coal Tar Products.** DR. GEORGE P. ADAMSON, General Chemical Co., Easton, Pa. This paper brought out the necessity of handling aniline with unusual precautions since the poison is absorbed through the skin, through open sores and from fumes; even leather shoes permit infection. Absolute cleanliness and special care of the health are essential for those working with it. A weak solution of acetic acid has been found to remove the material from the skin better than any other wash, the oil being almost insoluble in water. Poisoning is ordinarily indicated by a bluish appearance of the mucous membranes but occasionally even this sign is not evident, so that a factory physician and close watch of the employees is absolutely essential. Poisoned patients, if properly cared for, recover in a short time.

**Bureau of Mines Studies on Occupational Diseases.** DR. W. A. LYNOTT, U. S. Bureau of Mines, Washington. This paper was abstracted from recent Bureau of Mines bulletins.

**Dangers Other than Accidents in the Manufacture of Explosives.** DR. ALICE HAMILTON, U. S. Department of Labor, spoke of the extreme lack of statistics concerning the dangers and accidents due to occupational diseases in this country. In her investigations Dr. Hamilton has encountered from 30 to 35 poisonous substances; they include the mineral acids, benzene and toluene and their many derivatives, the aromatic nitro-compounds, phenol and phenolic compounds, nitrophenols, ammonium picrate and a great many of the dye materials. Also quite a number of the explosive materials are dangerous from the poisonous side as well as the explosive. There is an increasing number of deaths from hydrogen sulfide. Deaths from nitrogen oxides are also increasing. The dangers from nitrous fumes is particularly great as they are neither irritating nor corrosive as are other acid fumes, and men may easily obtain fatal poisoning without realizing that anything dangerous is happening. Picric acid as manufactured in this country is particularly dangerous, probably due to the hastily and poorly constructed temporary plants in which the men are working. The symptoms of various poisons were described.

## DISCUSSIONS

DR. W. GILMAN THOMPSON, Professor of Medicine, Cornell University Medical College, New York City, complimented the American Chemical Society on taking up this

question, as it is the first organized scientific body to do so and is only about three years behind the special consideration by even the medical profession for occupational diseases.

DR. F. L. HOFFMAN, Chief Statistician, Prudential Insurance Company of America, Newark, N. J., called attention to the mistakes that can be made by ignorant treatment of the subject of occupational diseases, as is especially illustrated by the findings of the Selby Smelter Commission.

DR. FRANCIS D. PATTERSON, Department of Labor and Industry of the State of Pennsylvania, suggested that much could be brought about at the present time by requiring physicians to report to the state the details of occupational poisonings, which would necessitate, of course, pay for the physicians if the work is to be properly done. In the State of Pennsylvania there are 1000 industrial accidents for every working day.

DR. LESTER L. ROOS, Medical Inspector of the Division of Industrial Hygiene, New York State Industrial Commission. The fallacy of the statement by capitalists that labor is unwilling to use hygienic safety devices is indicated by the fact that cases of poisoning and illness were decidedly cut down when a "comfort house" accommodating 50,000 men was installed in a large white lead plant. The necessity for the study of occupational diseases by physicians was illustrated by cases. An amendment to the labor laws requiring occupational illnesses to be reported by law is now being considered.

MR. NEWELL T. GORDON, Department of Labor of New Jersey (in place of Miss Erskine), plead for frankness between the manufacturer and employees and stated that many manufacturers did not explain the dangers of their industries to employees because they were afraid to do so.

DR. TRACY H. CLARK, Medical Director, The National Union, Chicago, suggested that the American Chemical Society should bring about cooperation between insurance inspectors and plant physicians, as this would be the quickest way to secure results.

MR. MEEKER, U. S. Commission of Labor, called attention to the very limited facilities of his department and prime need for revision of the list of industrial poisons given in Bulletin 101 of the Labor Bureau. All the poisons need to be listed by Industry and Occupation and the cooperation of every physician and chemist in the United States is necessary.

MR. C. I. JOHNSON, Goodyear Tire and Rubber Company, stated that they had changed from a 12- to an 8-hr. day in their aniline manufacture and had found that the health of their employees was greatly improved. Alcoholics are more susceptible to the poisoning than others. The speaker thinks there should be some way to separate the extremely susceptible people from others and put them where there would be less danger of infection.

MR. GOODWIN called attention to the use, suggested by a German, of a few drops of chloroform in a glass of water as an antidote for nitric oxide fumes. He criticized an Italian book for saying that the manufacture of T. N. T. is not dangerous and reported his own experience in being poisoned by working on this. He also called attention to the dangers from nickel carbonyl poisoning.

DR. JOHNSON stated that the poisonings from the aromatic nitro-acids came from the lower nitrated compounds that were formed during the process and were volatile.

MR. WILLIAM P. MASON testified concerning *bona fide* cases of immunity and said they are of no consequence whatever in treatment of the occupational diseases subject.

[A vote of thanks was extended by the Division of Industrial Chemists and Chemical Engineers to Dr. Baskerville for arranging the symposium. The papers of the symposium will appear in full in our next issue.—EDITOR.]

# INDUSTRIAL CONFERENCES

Abstracts of Discussions at the 53rd Meeting of the AMERICAN CHEMICAL SOCIETY, New York City

## ELECTRIC FURNACE STEELS AND ALLOY STEELS

JOHN A. MATHEWS, *Presiding*  
Grand Central Palace, September 27, 1916

THE CHAIRMAN: Dr. Burgess, who is unable to be here today, suggested that this conference state in what way the Bureau of Standards in their metallurgical division can be most useful to the industry and in what line of investigation they would be most likely to get valuable and important results along iron and steel lines.

PROFESSOR RICHARDS: I would suggest first of all that Dr Burgess determine some of the new physical constants of pure iron. They should include not only the mere composition but also the latent heats of fusion, the specific heats in the solid and in the liquid states, so that we may know the heat required for super-fusion, the electrical conductivity in the solid state and in the liquid state and the latent heats of fusion.

THE CHAIRMAN: The Bureau is already working along that line and has made elaborate arrangements for the manufacture of pure iron and the study of its properties. Nevertheless, the industry wants to know a great deal about the properties of alloys, and it will be a long wait for us if we have to determine the properties of pure iron first; it would, perhaps, be better to go along with the investigation of these two matters side by side rather than to wait for the complete information, regarding pure iron.

### RELATIVE QUALITY OF ELECTRIC FURNACES AND THE CRUCIBLE OR OPEN-HEARTH, AND HOT AS COMPARED TO COLD REFINING

PROF. RICHARDS: The electric steel industry has nearly doubled itself within the last two years, and it is probably going to proceed at that rate until the electric furnace steel industry will equal in size some of the other large steel propositions. One serious question is of getting the refractory material best suited for the electric furnace. Those which use the arc are continually troubled with the melting of the roof. Attempts to find more refractory material than silica for the roof are being made in a number of places. Chromium oxide is being tried as substitute for silica, and perhaps other materials. Undoubtedly Dr. Mathews does not agree as to its entirely monopolizing the field for alloy steels, because I have heard him say that some steels can be made better in a crucible than in an electric furnace. My own view is that it is largely a matter of skill in pouring. The difference between the present quality of alloy steel made in the electric furnace and in the crucible is in many cases the result of the pouring of the steel very carefully from the crucible, and not so carefully from a large ladle when it is made in an electric furnace.

Another phase of the question is the use of the liquid metal; because of the usually high cost of power, the use of liquid metal saves an immense amount of the power required to melt the cold charges. The extension of the electric furnace as an adjunct to the Bessemer and open-hearth for the final refining of the liquid metal at a minimum cost is a very rapidly growing use of the electric furnace. Not only will we have the electric furnace used in connection with the Bessemer and open-hearth, but already I believe it is being used in the triple process of first the Bessemer, where the metal is commenced in process, and then the open-hearth, and finally the transferring to the electric furnace, which is known as the triplex process to get the electric furnace to the point where it can be used to the best advantage. The time is probably coming within a not distant future when nearly all the steel made will be put through the electric furnace before it is put into ingots.

PROF. HOWE: I would like to ask you if you think that for

certain purposes crucible steel is still decidedly better than the electric steel because of the higher heat of the crucible method.

THE CHAIRMAN: In the paper already referred to, I say that in the furnace the conditions are such that the metal in the ladle, ready to pour, is not materially different from well-melted crucible steel. The principal difference, as Prof. Richards has pointed out, is that one is made in small quantities—in smaller ingots—and that the second has not the advantage of the small ingots that the crucible-makers make. I do not consider that the metal itself, ready for pouring, is superior to the electric steel.

The triplex process is being tried out at South Chicago by the U. S. Steel Corporation. A 15-ton furnace has been in operation, and there are three additional furnaces—the 15-ton furnace to receive the open-hearth metal. It will take the product of the 20-ton furnace and is actually in construction at the present time.

MR. HOFFMAN: What is the percentage of loss in the alloy compared, say to the tungsten and chrome and to the crucible method?

PROF. RICHARDS: I have no direct experience, but it has been said to me that there is less loss in the rare alloy metal in the electric than in the crucible. In fact in some cases, if the rare metal becomes oxidized and gets into the slag, it can be reduced back again into the metal in the electric furnace, which is impossible in the crucible.

### ALLOY STEELS EMINENTLY SUITED TO THE ELECTRIC FURNACE

THE CHAIRMAN: The crucible furnaces are primarily not suitable for making alloy steels and as yet we can't get out the high carbon alloys; in the electric the cost is materially lower and you can add what is necessary in the furnace itself. You can heat it as long as you wish without any material loss. You couldn't do that in a furnace with exposure to the atmosphere.

MR. SMITH: Then it would be particularly suitable for hyper-chrome?

PROF. RICHARDS: Is it not true that all the alloy steels which have been made in the crucible are being made with equal facility in the electric furnace?

THE CHAIRMAN: I think it is.

PROF. HOWE: Mr. Chairman, would you consider high-speed steel made in an electric furnace equally as efficient as the same steel made in the crucible furnace.

THE CHAIRMAN: I have seen no test running side by side, but I know that half the high-speed steel is made one way and half the other, and I would hate to pick out which was made which way. The advantage the electric method has for making high speed is not as marked as in the cheaper alloys.

MR. JOHNSON: Concerning the triplex process at South Chicago, I might say that last month I went through the Illinois Steel plant there and the second furnace had been operating about a month. Both that furnace and the old 15-ton furnace are running on triplex when they can get enough open-hearth to run them, otherwise they give the product to the Bessemer. They are also using chrome brick with good success.

### MELTING COLD CHARGES IN THE ELECTRIC FURNACES

THE CHAIRMAN: We have had very little experience on that because our original furnace was not suitable for melting cold product; it was intended as a refining process and we have only recently started on cold product. But a large percentage are operating on cold charges. Greater power is put on the old style furnace, but no higher voltage.

MR. HUBBARD: Practically all the smaller furnaces use cold



melting—2, 3, 6, and 1 ton are on cold melting. The bigger furnaces, like the 15- and 20-ton, are working on the liquid.

Trouble in getting started on cold melting depends upon the charge. Many furnaces can regulate it at the very beginning, at the starting of the current, and the regulators have taken care of the current very well.

PROF. RICHARDS: In a Norwegian plant, steel ships are broken up and melted in an open-hearth furnace and then the charge is transferred to the electric furnace and although they found that they could get electric power at \$6.40 per H. P. per year they found it cheaper to operate with coal at \$6 a ton and to melt in the open-hearth furnace and refine in the electric.

MR. TUCKER: It has generally been conceded that the product that is made from cold charges is better than that made from hot charges. Why should this be so, provided you can heat to the same temperature and under the same conditions?

THE CHAIRMAN: I don't think there would be any difference between the finished product whether it is started from a cold charge or a liquid charge; if it is deoxidized it will get deoxidized just as well one way as the other. We have several furnaces working on coal scrap and on hot metal and so far as I have been able to find out there is no difference between the two finished products.

MR. JONES: In ordinary carbon steel, with the same analysis, the statement has been made that steel made in an electric furnace is of much superior quality as regards physical quality compared with steel made in an open-hearth furnace. Can anyone tell me what the scientific reason for that is, if that is true?

PROF. RICHARDS: I think the solution of that has been found, and it is because there is a chance to deaden up the steel in the open furnace; you can keep the steel melting in an electric furnace without oxidizing it, but it is kept melting under oxidizing conditions in the open-hearth. There is also opportunity during dead melting in an electric furnace for the settlement of the slag inclusions in the steel. That is the real difference between crucible metal and the open-hearth, the small amount of slag and foreign matter included or suspended or diffused or emulsified in the steel. Crucible steel and the electric furnace steel are alike in that they are freer from foreign materials than either open-hearth or Bessemer.

THE CHAIRMAN: Electric furnace steel, when properly melted, pours fully as quietly as the best crucible steel you ever saw poured, even down to eight or ten carbons. It is quiet in the ladle and it is quiet in the furnace. It can be agitated in the furnace by various means, but it doesn't have to be. It is quiet in the ladle and in the ingot. One gentleman, a large consumer as well as maker, wrote me at considerable length on this subject.

"Whether it is oxygen or something else provided—there are those who will not admit the injurious effects of this element—there certainly is a difference between open-hearth and electric furnace steels in three respects: *First:* Electric furnace steels are generally freer from non-metallic inclusions than open-hearth or Bessemer. It is not necessary to go into the reasons for this beyond the fact that it is held for a longer time in the final finishing stages at temperatures which maintain the bath in so thin a state as to allow the slag and non-metallic compounds to rise to the surface.

"*Second:* The electric furnace steels seem to have a considerably wider forging range, that is, they can be put through forging operations at a higher temperature than open-hearth steels without permanent injury.

"*Third:* Electric furnace steels seem to have a wider hardening range than open-hearth or Bessemer steels, that is, they may be reheated for their quenching to higher temperatures in the latter grades without becoming overly coarse-grained. Just why these two latter conditions hold true, I am at a loss to say. It has some times appeared to me that the oxygen or whatever is not removed in the open-hearth process acts as a catalyzer or as a stimulator to grain growth."

This gentleman (Mr. Zimmersheath of the General Motors

Company) is responsible for the specifications in use for a very large quantity of alloy steel.

MR. JONES: Mr. Chairman, may I inquire how large a charge is used in an electric furnace?

THE CHAIRMAN: From  $1\frac{1}{2}$  to 20 tons, which is the largest now being installed.

MR. JONES: Assuming an average ton why couldn't you get the same in the one as in the other?

THE CHAIRMAN: Tentatively you will—but 10 tons of crucible steel is very considerably more than 10 tons of electric.

MR. WATERHOUSE: I don't think I understood what Professor Richards said about electric pouring but I do understand his other proposition about the continuity or elongation of the production period. We have in our laboratory a decidedly large tonnage of electric steel and we have never found the difference he speaks of. What particular visible property or change takes place, provided the test is of the same steel? What is the visible property that changes when you make the same steel with an electric furnace?

THE CHAIRMAN: Principally in advancing the ductility; not in the maximum strength. Since that has been done in the electric steels it has been done in the open-hearth as well and the open-hearth is a great deal better than it used to be, since the electric steel came into the field.

MR. WATERHOUSE: What would you expect of 25 elongation carbon, open-hearth steel? In steel made as well as it can be made in the open-hearth and made as well as it can be made in the electric, would you expect the elongation to be different, or the chemistry? We have found practically no difference.

THE CHAIRMAN: I have no experience with it in plain carbon steel and I cannot tell you what elongation you will get. Mr. Zimmersheath has demonstrated that by a range of temperatures without destroying the ductility.

MR. WATERHOUSE: Professor Richards some years ago took out a patent on the use of an acid lining in electric furnaces. I remember some years ago a gentleman who claimed great things for acid linings and I would like very much to know if that has been followed up recently. Perhaps Professor Richards can tell us just how the acid lining is coming on. It seems to me there is a great chance for it in the triplex process if it is going to work. We can start with the basic as there is need for a basic lining to remove sulfur and phosphorus.

PROF. RICHARDS: Most electric furnaces have been run with basic lining because it is economy of refining improper material in the furnace and making high grade steel from low grade material. But, where good material which does not need refining is to be put in the furnace, a slag lining is quite practicable and is being used to a large extent. I must disclaim my patent for a lining—that must have been someone else—but the acid lining is in considerable use at the present time.

#### POWER COSTS

MR. MORGANSMITH: It is the ambition of the Detroit Edison Company to furnish electric power for steel plants at a price that will put the water power people out of business. I don't know how we are going to do it, but we are on the way. We have on paper boilers which exceed 45,000 kilowatt capacity. What horse power a year can the electric furnace industry stand?

PROF. RICHARDS: It is generally understood that the power cost in running a small furnace and making steel castings is a minor part of the cost of making the steel. There is an electric furnace where I live in Easton, Pa., that I think had been running for about four years making steel castings from cold charges. They buy the power for melting the charges and pay 1 cent per K. W. hour or \$88 per kilowatt year. That firm is making a profit and is satisfied with the business. There are firms refining metal or making steel on a large scale who need power much cheaper than that to operate. But I think the power

question is a secondary one with most electric furnaces. The horse power is practically negligible. But if you are making low carbons, plain steel to compete with open-hearth steel, then the cost has to be considered and I think that possibly somewhere around  $\frac{1}{2}$  to  $\frac{1}{4}$  cent per kilowatt hour or lower may be required.

MR. BERRY: I think the figures are about correct. I think one of the great mistakes of the power companies in this department is lack of appreciation of the value of this industry to them. I am only a consumer of electric furnace steel and I would like to speak in a neutral way. In the first place it is an ideal load for any power plant. All alternating current plants need contracts to tide them over certain periods in the day and by well-made contracts I think the power company, whatever they charge, would get most of the money if the plant was installed without any cost of installation to them. I know of three instances due to the lack of appreciation of this very fact where the steel manufacturer is building his own power plant, which is a great economic waste.

MR. CROSBY: The question of the electric furnace situation is one that has been thoroughly covered. I think the central stations throughout the country in the past three or four years have been bending every effort to get all the information possible upon this class of business with the idea of making a rate commensurate with the service. We have in Detroit two Héroult furnaces, one a 6-ton and the other a 3-ton, operating on our system, and another 15-ton and a 10-ton Kronholdt coming in. This has supplanted the converter process and the operators are perfectly satisfied with the result and I believe that we are convinced that they are producing a superior casting at a much lower cost than they did by the converter process—in fact, the company making the steel ingots at the Kronholdt furnace is erecting a plant which will have room for five ingots eventually. These consumers all have a rate between  $\frac{3}{4}$  and 1 cent per kilowatt hour. The larger the consumption and the greater the number of furnaces the lower the rate per kilowatt hour. But the idea of operating electric furnaces is an awfully big schedule. The theory that the furnaces should get the power cheaper because they use it at a time when others do not use it, is wrong. A manufacturer has no right to expect a cheaper price because the other fellow pays the overhead.

PROF. HOWE: Most of us know that there is a difference between light and power—why not charge two rates?

MR. CROSBY: The people who are using central station power to-day on the basis of what the traffic will bear will not be doing it 5 years from to-day. There is no distinction between light and power other than a distinction between classes of service. A man who is utilizing lighting under the Edison service 10 hours a day can get the power rate. As a matter of fact they have lighting circuits in their plants directly connected with the power meters. The distinction comes only in the load of the factory and the character of the service. Electric lighting service has to be regulated and the distribution cost is infinitely greater than the distribution cost of power. Consumers of large amounts of power up to 10,000 kilowatts involving less overhead expense and no transmission expense can get it at a lower rate, but there is no distinction between light and power and none between power and heat. The electric furnace load is not necessarily better than an industrial load and some industrial loads are better than the electric. There are large factories in Detroit which use from two to five thousand kilowatts perhaps throughout the twenty-four hours with no more than twenty to twenty-five per cent variation, while the electric furnace goes from no load to 1500 or 2000 kilowatts. There are several central stations throughout the country supplying the modern arc furnaces, and of course, if the modern arc furnace is properly installed, it should be better than the average motor proposition.

#### RELATIVE QUALITY OF ELECTRIC FURNACE STEEL WITH REFERENCE TO CRUCIBLE STEEL USING MUCK IRON

THE CHAIRMAN: When the electric furnace was first introduced the impression obtained that you could start with anything and make first-class steel. I don't think that is the case. In order to get good steel out of an electric furnace you have got to use good material and you are taking a chance when you start with inferior steels. I think the wrong impression was created at the start that you could make tool steel out of anything.

PROF. RICHARDS: I want to make one prediction, and that is that when the steel workers who are working on electric furnace steel have accumulated as large an experience as has been accumulated in the making of crucible steel, there will be no more crucible steel made. (Laughter.)

MR. BERRY: I would like to say something on the Army and Navy question. We have got from Washington all of the specifications for steels used by the army and navy and as a starting point are making a very careful study, with these specifications as the basis, to see what special preparation we can make to meet the demands of the government inspectors.

MR. WATERHOUSE: Can you control an electric furnace more uniformly than the open-hearth? It is well known to the men on the furnace—in the open-hearth—that you never have any one temperature.

MR. YOUNG: I think it is a little easier to control your source of heat with electric furnace than it is with either a gas furnace or an oil. It can be done quicker. It is largely a question of the skill of the operator in observing temperatures and watching the conditions.

MR. WATERHOUSE: Is not that the reason the one type of furnace sells better than another?

MR. YOUNG: That is a selling point for electric furnaces.

#### USE OF URANIUM

THE CHAIRMAN: We have all heard more or less about uranium steel, but I have done nothing personally.

MR. HOFFMAN: The American Steel Company at Pittsburgh has been experimenting with uranium steel. Possibly our experiments would coincide with those of others. The uranium flux calls for 5 per cent tungsten and 3 or 4 per cent chrome—in other words, the same high speed composition, with the exception of, say, 12 per cent less tungsten, to do the same work. Our experience was that it made a very good tool and did very good work, say for two grindings. The second or third time we used the tool we would have to get it hardened again—in other words, it didn't seem to hold its efficiency.

THE CHAIRMAN: Two-tenths uranium was supposed to take the place of 12 per cent tungsten?

MR. HOFFMAN: Yes, sir.

DR. C. M. JOHNSON: I have had some little experience in the manufacture of experimental uranium steel—a little only. Our own experience was that in preparing the uranium so that we have a strictly uranium steel as the starting point, after considerable experimentation we were able to produce from the ore a uranium cast of less than 1 per cent, the tungsten 5 per cent, chrome 3 or 4 per cent, the other constituents being iron. Then the next step was in alloying the uranium with the iron in the ordinary method of making crucible steel. This was found to be quite difficult. The extreme affinity of uranium for oxygen caused in the first experiments the entire loss of the uranium. There was none there at all, put in in the ordinary way. But we finally succeeded by protecting it in the crucible by diffusing the ferro-manganese and other particles; we actually succeeded in getting uranium steel—the carbon under 40, the manganese between 30 and 40 and the uranium about 0.3; the steel was very disappointing. It was short of the ordinary forging heat and altogether uninteresting from a practical



standpoint. It seems to me that the most interesting part of the whole thing is the extraordinary affinity of uranium for oxygen, so much so that I think it is pretty safe to class it as having the strongest affinity for oxygen of any element alloyed with steel that we know of in the groups of ordinary alloys of steel. In endeavoring to make metallic uranium by the thermic method we soon found that there was no reaction between the metallic aluminum and uranium—no thermic reaction. The gist of the whole thing is that a uranium steel containing only 0.3 per cent did not promise to be of any value.

In this connection I have seen quite a few advertisements in which uranium steel is spoken of as the last word. Of course that is an advertisement. It is like the claim for liquid heating in an electric furnace. The furnace sellers claim everything and the manufacturers of uranium seem to do the same thing. Our tests were very disappointing as far as they went, though we had to stop to take up other matters, but as far as we went first-class chrome-tungsten steel was better by 200 per cent than the tests we made. Of course that does not show that there may not be some combination of percentages of uranium at ordinary high-speed characteristics which may prove a benefit, but so far as we were concerned we did not feel encouraged. Such low carbons as between 30 and 40 apparently do not harm the steel and we succeeded in making a very good set, but it was a pretty expensive set, and in that respect was a "set back" also.

In this connection I have in mind this, that we have a conference here from which we hope to have some good results and undoubtedly already have had—we have gotten together, if nothing else—and what occurs to me is that we are here for each other's good rather than to carry away information without giving any. Can we not consult as to how we can make standard high-speed steel better than it is being made at the present time? Now, those of us who are interested in high-speed steel have combinations and analyses of uranium, tungsten and so forth, and we might see which is best. Now, what can we do to improve this best, what alloys can we add? At the present time I don't feel encouraged with the conditions of uranium for high-speed work. With the other alloys which are cheaper, is there not one that we have which will give us an immediate improvement in high-speed steel? One that is not so hard to get as uranium. Uranium, I believe by recent quotations in small lots, is something like \$7 per lb. and American tungsten has been rising in price but it won't stay there. I might say, too, in this connection that there is a party going about representing what is supposed to be a reputable firm in Chicago whose one ambition seems to be to find uses for tungsten, because they claim that they have such large deposits of it. Of course we all have heard these claims for tungsten; someone comes along and says he has found a big deposit, so big that it would become a drug on the market. Now, these parties are claiming something along that line and making statements that tungsten ore in large quantities is in sight and that they can get it if there is a sufficient market for it, and can make a large profit by selling it at \$5 a unit, which we all know is probably the lowest price ever made for tungsten concentrates. Their aim and worry and hustle at the present time is to find a wider market for tungsten and they say that they are not worried about where they are going to get the tungsten from. I told the party that I didn't believe he had it and his answer was "No, I don't suppose you do, for nobody ever produced such a quantity before." At any rate I don't believe it, but they are still traveling around. The theory I have is that the best way to improve high-speed steel is to work on some of those elements which we know improve high-speed steel. The element in my mind is tungsten, and that is the thought that I wanted to bring out in this connection, if we are going to get any good out of this congress, if we are all to take away an

idea, and none of us will carry something off without benefiting the other.

THE CHAIRMAN: The question is on high-speed steel, the kind of materials to be used.

MR. JONES: I should like to inquire if any of the gentlemen present have had any experience with an alloy steel recently put on the market which runs from 16 to 17 per cent chrome and has no tungsten whatever. I have recently had a run-in with it against high-speed steel.

THE CHAIRMAN: I have known of something of that kind. It was first introduced a number of years ago. We haven't heard very much of it since. If anyone has had any experience with it I would like to hear from him. The cobalt method has been abandoned by almost every maker. It caused quite a controversy in Sheffield running in competitive tests with the best Sheffield steels, but it was finally found that cobalt was not worth while and it was abandoned.

DR. JOHNSON: Mr. Chairman, in the matter of cobalt steel you will find some people who insist on it emphatically at this time, but others seem to have lost interest. It seems to me that the cobalt high-speed steel has a special field and will, perhaps, continue to have it for some time to come.

THE CHAIRMAN: I don't mean to say that it has altogether been discontinued, but it is not the great improvement it was expected to be.

MR. BERRY: To what extent has the electric furnace been used for the recovery of deleterious elements? And what furnace is considered best for that? And another point is the effect of these deleterious elements on the product.

DR. JOHNSON: I can say in regard to electric tin that the effects are to render the steel red-short, and the use of it seems to make the steel brittle if it is there in sufficient quantities. If I were making specifications I would insist that the tin content should not be more than 10 per cent at the outside, and you know that copper is something along the same line. My theory is that the higher the melting point of the added the better the results. If we went on the basis of using a whole lot of good material we would get better results still, as, for instance, molybdenum and a higher per cent of tungsten—would be a fine proposition, for instance, with 20 per cent of tungsten, and I think that really the only reason that we don't put in 18 or 20 per cent of tungsten is that it costs too much money. At the present time my pet theory is to put more tungsten in steel.

THE CHAIRMAN: You would have to start clear of some of the high ones, if you want uranium.

DR. JOHNSON: Yes, I suppose we must take good things in small doses. It will not do to go too far; if we carry it too high, we may get it to where we won't speak of the melting point but rather of volatilization.

MR. WATERHOUSE: Can you say anything about my question as to furnaces?

THE CHAIRMAN: I have had no experience myself in regard to the matter of recovery in smelting operations of any kind.

#### AMERICAN DYESTUFF MANUFACTURE

CHARLES H. HERTY, *Presiding*, Chemists' Club, September 27, 1916

THE CHAIRMAN: What are we going to do about the dyestuff legislation that was passed recently at Congress? We want in this case a common council. Let the chemists and commercial manufacturers of this country show that they have the same view and prove to the country that they are entitled to cooperation. There may be quite a wide difference of opinion on certain points, yet at the end let us feel that we have taken a definite decisive step that will mean something to us.

MR. WIGGLESWORTH: The first consideration in the dyestuff problem this country has had to face since the war was whether the economic conditions permitted the establishment of the industry. Abroad quite a large number of manufacturers had found it impossible of manufacturing and disposing of their goods profitably without some understanding, and various methods were employed to control prices enabling them to have a great power, not only in their own country, but in the entire world, and whatever methods were necessary in the various countries were taken by the citizens of those countries. In England and France it was done by making certain concessions to France and other countries, but in this country we have not established the industry and it was not necessary to make any concession. The tariff was the one serious factor that might be made to work in favor of the establishment of the industry and prevent a monopoly of the American market.

We have to recognize that a business of \$15,000,000, which is the amount of dyes imported in the U. S., is a very trifling sum of money, and when we read the amounts of the European purchases in America it seems almost infinitesimal, and it would not offer any great commercial inducement to the large manufacturer. We have been given the privilege since the Exposition opened of examining the Department of Commerce's analyses and statistics covering the importing of dyes previous to the war. Dr. Norton estimates in the neighborhood of 6000 of these dyes and as near as I could get at it, it comprises not less than 2000 difficult commercial processes that would involve 9, 10 or a dozen steps in each process and various complete apparatus, much of which is not manufactured in this country. After the dyestuffs bill was passed by the Senate an exception was introduced, we understand, and Dr. Herty has reason to know that this was at the instigation of one single consumer, the largest buyer of indigo in the world. For some reason he was not satisfied to limit the exception to indigo, but must include other articles.

DR. NORTON: Personally, I feel that the tariff has a slight role in this connection. It will be a help to us temporarily, but we must be absolutely certain of freedom from unfair competition in order to build up our dyestuff industry. I am sure that our President, and that Dr. Hesse and Mr. Wigglesworth will feel that I am violating no confidence when I state that in the U. S. there are not three other men who have had more influence in crystallizing public sentiment in the form of this revenue bill. A census of dyestuffs has been compiled for your use. It is the first instance in any country that there has been an attempt to put in complete form this question of quantity, and classification of our dyestuffs. In the course of a few weeks it will be entirely at the service of the gentlemen who were planning for the rational economic evolution of our American dyestuff industry.

MR. SCHOELLKOPF: When the European war broke out we were fortunate in having enough imported intermediate products on hand to keep our plant running for about three months. During this period we hastily improvised temporary plants for making important intermediates such as benzidine, H. Acid, and Dinitro Benzol. With the aid of these we were able to continue the manufacture of such important colors as Direct Black, Direct Blue, Acid Black and a number of others. Previous to the war we produced approximately 120 colors. As our stock of intermediates gradually became depleted we were soon only making about 15.

In the spring of 1915, after the English blockade became effective, there was a panic among the users of dyestuffs, and they all turned to the American manufacturers and expected them to fill their wants on very short notice. Our Company proposed to meet the demands made upon it by erecting the necessary plant and selling the output on contract. On this basis we went ahead and by January 1, 1916, were producing colors at the rate of about one million pounds per month. To

give you an idea of what this means I wish to say that before the war we were capable of producing only 3,000,000 pounds annually. So that in the short space of a year and one-half we had quadrupled our output.

Early this year, we proposed not only to increase our production but also to increase the variety of colors on the same basis as we did in 1915. The consumers again responded in a most encouraging way with the result that we now have in the course of erection in Buffalo a plant which will be capable of producing approximately 30,000,000 pounds annually or one-half of the tonnage which government statistics say is used in this country under normal conditions. To summarize them, we have increased our production from 3,000,000 to 30,000,000 since the war began, and will make after January 1st approximately fifty colors, whereas early in 1915 we were making only fifteen.

We, as well as the other manufacturers of dyes, have been criticized for not making a greater variety of dyes. Some people seem to have an idea that it is so very simple to produce almost any shade or quality desired. To those people I say they haven't the slightest idea of what they are talking about and usually I am right. To be perfectly frank I think the progress both as to quality and variety made in the last two years is truly remarkable if one stops to consider the difficulties which it has been necessary to surmount. In time and with the proper encouragement the American manufacturer will produce every color that is necessary and do it just as well as our foreign competitors ever did.

In quality our products are absolutely identical with those formerly imported from the other side and in some cases better. As to the poor quality of American dyes, the 50 or 75 dyes that are made in this country cannot possibly do the work of the 300 or more which were formerly imported. The manufacturers do not claim they will, but many dyers try to make them do that work. The results are bad and the dyer blames the quality of the dyes when as a matter of fact he knows better.

For purposes of National Defense it is absolutely vital that this industry should be developed. It is not just newspaper talk about dye factories being converted into ammunition plants on short notice. It is a fact, and a very reasonable one, too, because the same materials are used in producing dyes and ammunition. After the war I believe you will see the industry established in all of the warring countries, and the governments will, if necessary, even subsidize the manufacturers in order to keep the plants in operation. England and Japan have already done this and the others are sure to follow.

We have established a research laboratory under the able direction of Prof. C. G. Derick. Laboratories such as this have been a source of much of the success achieved by the large factories abroad. No research work such as this has ever been done in this country because the industry has been, as I have said, unable to support it. Conditions having now changed, let us hope that so vital a necessity to the success of the industry may be accomplished.

The Tariff Bill, passed a few weeks ago by Congress, is far from perfect for a number of reasons:

*First:* It does not provide for the duties as recommended by your Committee in that it provides for a surtax of only 5 c. instead of 7 1/2 c. on finished colors, and only 2 1/2 c. instead of 3 1/4 c. on intermediates.

*Second:* It exempts alizarin colors and indigo. These colors have never been made in this country before because they were always on the free list, but if we are to have a self-contained dye industry we must also make these. Under the new law I do not think this development will take place.

*Third:* Why should the duties be gradually reduced after five years? The bill provides for a Tariff Commission. Why not let the Commission decide when and how much the duties should be reduced or even raised? Isn't that what the Commission is for? Furthermore there is the clause which states that if 60 per cent in value is not produced in this country within five years that the surtax shall be removed. This is highly



objectionable particularly inasmuch as Alizarin and Indigo colors are exempted, because these colors make up 20 per cent in value of the imported colors and the remaining 10 per cent is taken care of by patented colors which cannot be made here under any circumstances. Unless these latter are made here it will be difficult if not impossible to fulfill this part of the law. The unfair competition clause is in my opinion very weak. It puts the burden of proof on the American manufacturer and not on the importer as it should be. Furthermore, if goods are dumped in this country it is necessary to prove that it is done with the intent of destroying or injuring an industry in the United States. Doesn't it seem impossible to prove such intention if it is denied?

Taken all together, I do not think that this bill will encourage very many people to invest their capital in the dyestuff industry, particularly if they have had any experience in it.

MR. DOW: The omission of the specific five-cent duty from indigo, whereby the only remaining protection is 30 per cent *ad valorem*, puts indigo-makers in a very unenviable position as compared with the other dye-makers, for the reason that a specific duty automatically loses its protective feature at the very time it is most wanted because a lowering of the price abroad during trade war also lowers the amount of duty and makes it relatively easy for the foreigner to compete, and put the unexperienced, new American industry out of business.

Mr. Dow also explained the present status of their indigo plant at Midland, Michigan, and stated that the plant would be turning out indigo commercially about the first of the year.

#### RESOLUTIONS ADOPTED

On motion by Dr. Alexander, a committee was appointed, consisting of Dr. Alexander, Mr. Wigglesworth, Dr. Mathews, Mr. Schoellkopf and Dr. Beckers, to express the sentiment of the meeting on the recent Dyestuffs Revenue Bill. The resolutions follow:

WHEREAS, the Revenue Bill (Title V, Dyestuffs), which recently passed the Senate after hearings of representatives of producers and consumers, accorded to all classes of dyestuffs without exception an *ad valorem* duty of 30 per cent and a specific duty of 5 cents per lb., and

WHEREAS, in the final conference between the House Ways and Means Committee and the Finance Committee of the Senate, and without further hearings, "Natural and Synthetic Alizarin and dyes obtained from Alizarin, Anthracene and Carbazol, Natural and Synthetic Indigo and all Indigoids whether or not obtained from Indigo, and medicinals and flavors" were made exceptions and to carry no specific duty and to have only the 30 per cent *ad valorem* duty;

The Dyestuff Conference of the American Chemical Society, in a meeting held in New York Sept. 27th, without a single dissenting vote, condemns the exception of these dyestuffs from this specific duty as this exception undermines the very foundation upon which it was hoped that the American Dyestuff Industry might be built. It makes it impossible for the American manufacturer to meet the requirements of this Bill "if, at the expiration of five years from the date of the passage of the Act, the President finds that there is not being manufactured or produced within the United States as much as 60 per cent in value of the domestic consumption of these articles, he shall by proclamation so declare, whereupon the special duty imposed by the Section on such articles shall no longer be assessed, levied, or collected;" and

WHEREAS the value of these excepted classes of dyes amounts to approximately 30 per cent of the dyes consumed in the U. S. A., without considering the dyes patented by foreign manufacturers;

Therefore, be it Resolved that we condemn the removal of these dyestuffs from the special tariff accorded then by the Senate as detrimental to the establishment and development of the American Dyestuff Industry and subversion of the best interests of the American people.

DR. DOW: Coöperation among the manufacturers of dyestuffs would be against the Sherman law. It could not be done

among Americans. Foreigners can do it to Americans, but Americans cannot do it to Americans themselves.

The following resolutions, read by Dr. Mathews, were adopted:

WHEREAS, Director Ralph, of the Government Bureau of Engraving and Printing, declares in a statement to the *Oil, Paint and Drug Reporter*, in the issue of October 2, 1916, that while he is in sympathy with the idea of purchasing dyes for the use of his Bureau from American manufacturers, he has found it "impossible to obtain supplies, although during the past two years he has made every effort to get them;" and

WHEREAS, Director Ralph declares himself ready to-day to purchase large quantities of reds if he could get them; and

WHEREAS, Director Ralph has placed an order with a German manufacturer for the delivery of "Printing Red" (Lake Red No. 1), 40,000 lbs.; "Permanent Red" (Lake Red No. 6), 20,000 lbs.; "Chinese Blue," 25,000 lbs.; and "Prussian Blue," 60,000 lbs., which can only be delivered by authority of the British Government in temporarily raising the embargo now existing to allow such shipments from Germany to the United States Government;

Be it Resolved: That we believe it the province of the American Chemical Society to investigate the status of the American dyestuffs manufacturers as possible source of such dyes for government use, and that the matter be referred to the previously appointed "Legislation Committee" for investigation and reported as a guide to the American chemical dyestuffs industry in thus meeting the demands of the United States Bureau of Engraving and Printing.

MR. WIGGLESWORTH: The Government has never inquired whether they can get those colors or not.

MR. MATHEWS: These colors are no doubt alizarin lakes. The Government wants 145,000 lbs., a considerable item, and quite a line for the American dyestuff industry to go into.

THE CHAIRMAN: Just at the time the Dyestuff Revenue Bill legislation at Congress was pending there suddenly appeared in the papers of my state in big headlines an article regarding a tremendous development that was going on in North Carolina, a \$5,000,000 dyes and munitions plant was to be erected within the next twelve months, and the remarkable thing about it was that, a week after that statement appeared in the papers, the same published statement was used on the floor of the Senate as an evidence that we needed no particular legislation for this industry in this country!! That we were coming along fine! The company has already failed and yet they had this influence in the U. S. Senate.

#### AMERICAN-MADE CHEMICAL GLASS AND PORCELAIN

ARTHUR H. THOMAS, *Presiding*

DR. FREAS: Porcelain and glassware for laboratory work has been in a rather bad way for two years now since the war; practically very little has come through since February after the war began, and the stock that has been on hand has been pretty well used up. There was considerable for the first half year scattered in the warehouses of the country, but in the last year and a half that stock has been used up. Institutions in most cases have had a good stock on hand so that the situation has not been as critical as it might have been otherwise. The quality of glassware used in the laboratories is quite different from the quality used elsewhere for other purposes. It must be resistant to alkali, to chemical use, to heat and to ordinary laboratory bumps. Chemical porcelain and glassware has been put out by some manufacturers similar to that found in cheap restaurants, in all respects—simply something to hold solids. At Columbia University we were fortunate enough to get in a \$20,000 shipment before the war began. We have not had in any of our laboratories any of the new porcelain and very little of the glassware. I would state that the glassware situation is one of the most encouraging things to me that we have had in the

past two years, in the way the manufacturers have improved the situation, but they have not gone far enough yet. Quantities are rather limited yet and deliveries are not prompt. Variety will, of course, as you know, be extended as time goes along. It is foolish to say that we can start out and make porcelain without any training scientifically. You have got to come back to the laboratory and laboratory men; they have got to have control of it. As you know, all educational instructions are entitled to duty-free importation of glass. With the institutions dollars are dollars. We will import the thing from abroad, regardless of what the effect may be on the neighboring factory that would like to get the business to build up that business. Are the men that have started in the manufacturing of these goods going to be protected after the war ends? There certainly should be some method by which we could encourage the industries and not handicap knowledge.

There is a great deal of knowledge required for the building of microscopes. During peace times instruments of that kind are not for military purposes but for educational and medical purposes. It is worth while to foster these industries, simply because when the time comes we cannot get these things from abroad. I am just as much in favor of building the industry for building microscopes and it is just as important as our Nitrate industry.

MR. E. C. SULLIVAN, Chief Chemist Corning Glass Works: I think it is within the possibilities that the American manufacturer can compete with the Germans in time. Although that you cannot do to-day. Manufacturers are making very vigorous efforts to meet the demand and within a reasonable time we shall catch up. In the case of the firm with which I am connected we have increased our facilities largely, and it is only a question of time. We cannot pay a high rate at 8 hours per day in competition with the foreign labor, and expect to give our ware to the universities on the same basis that foreigners can import it. Industries are in the business of making money.

MR. COOPER, Syracuse University: Universities are warranted in buying liberally. We are going to be educated up to buying a better quality of glassware, finding that breakage is less and that it really pays us. We ought to be in a position to compete with Jena glassware. Glassware imported from Germany is cheap and fragile.

DR. FREAS: You cannot pay 40 cents an hour for help to turn out the same product at the same price that you can when you pay 8 or 10 cents an hour. I do not agree with Dr. Cooper that the glassware we have been importing from Germany is cheap and fragile. We had been getting a very fair quality of glassware before the war. There is considerable doubt what will be the actual conditions after the war. We must control duties or bounties. What the conditions will be abroad depends on how long the war lasts.

MR. SMITH, Case School of Applied Science: Our Technical School has had to buy quite some apparatus, but are free to buy whatever they want to. It is a fact though that a great many state universities are compelled to get comparative bids and get the goods from the lowest bidder. We should have those laws changed so that they would read "the cheapest American-made goods." When the war is over I intend to keep on buying all apparatus that it is possible to get from American makers. But these state universities cannot do this, and I think they are legally prevented.

DR. FREAS: I would like to know if Prof. Smith four years ago had wanted \$1000 worth of glassware, what he would have done, if American glassware had cost him \$1300 and imported would have cost \$1000?

PROF. SMITH: Four years ago I was not aware of the lack of patriotism I was exhibiting, but I am to-day, and expect to be in the future.

MR. DAVIS, Eli Lilly & Co.: Most of us have tried at various

times to blow glass in the laboratory, and I have seen several skillful chemists try so simple a thing as welding of two pieces of tubing together and say "I cannot do that. That is something for a professional," also, "Something I was never expected to do in my work." These things I regard as fallacies, and it is time that we rid our minds of them. Some think that glass blowing has to be taught over a period of years; that it requires a large outfit; that we must have special glass. I know that glass blowing can be taught. In teaching glass blowing I should start the student with some very simple problems. For instance, the bending of glass tubing. After he had learned the bending of a tube, might try bending of larger tubing; then I should give him the blowing of a bulb. Then he can learn to close the end of the tube. With a week's practice he can become perfect in any one of these operations. Then he can put the lip on the tube; blow a bulb in the center of a tube; try an internal joint. A week's practice will make the student practically perfect in that. He may then learn to make a base so as to put a base on a test tube. The student will shortly find out he is then able to make any piece of glassware that is demanded. I see no reason whatever why the student in the average college could not take up glass blowing and learn it. There is no necessity for a large outlay of glass tubes for glass blowing. My equipment consists of a blast lamp, old pair of scissors and an old file. There are no blue bottles made in America from which you can blow tubing and blow glass.

MR. WEISS, Chief Chemist, Barrett Co.: We have had pretty good luck in getting most everything we need as far as our requirements are concerned. The American grade of glassware is equal to others, equal to if not better than Bohemian. One gentleman said that they have been having a lot of trouble in getting a creosote oil retort. We have not found anybody in the United States who can make them; they do not seem to know how or do not want to make them. There will not be a stock of retorts to last another two months. We are anxious to get some one who would make them or could make them.

DR. THOMAS: I am interested in the advisability or practicability of having our American training schools take up the question of glass blowing as a trade. No matter how much money there is at the present minute, there is nobody to do the work. Someone in the German laboratories has done something on the order of what Mr. Davis has shown us.

DR. ELDRIDGE: I think that Dr. Thomas' suggestion in regard to training schools a very good one. Before Mr. Davis came into our laboratory it was quite an undertaking for anybody to make anything. Probably half a dozen or more of our chemists now think nothing at all about blowing glass since Mr. Davis has come. He blows all his own glass that he cannot buy. After the war consumers will continue to buy American-made apparatus, even though foreign ware will be made more cheaply.

DR. FREAS: I believe there is foreign-made apparatus in considerable amount being sold in America to-day, and in competition with the men who are trying to get out American apparatus at this very time. I do not believe that any amount of reasonable appeals to the purchaser is going to avail very much.

Dr. Davis when asked how long a time was required for a man to become a glass blower, said: "twelve weeks' time, devoting one-half hour to an hour each day, would make a man proficient in the twelve first stages, and with these stages you can work up the other pieces of apparatus."

DR. SCHOLES, Fry Glass Co., Pittsburgh: There are a number of points in connection with duty-free importation. One thought is that a large part of the income of the colleges and universities is on manufacturers' profits, and it seems only fair that the universities should help to foster the industries all possible. It seems to me entirely inconsistent that universities and col-



leges should get their scientific apparatus every small part of their expenditures duty-free, whereas they do pay the regular price for everything else they use. If the university is building new chemical laboratories they make a great outlay for steel, but it has never been suggested that steel should be furnished to them duty free, or that paper should be furnished duty-free to schools and colleges. It is rather inconsistent that the schools should expect to get their glassware at a reduced price and at the same time pay regular prices for the large number of other supplies they are made to pay duty on, that are higher in this country than they are abroad. Regarding the manufacturing of glassware, a great deal depends upon experience before starting out. Germany has had various experiences. Our experience dates from the beginning of the war. Users should be lenient with us a year or two until we are able to train our men. We value criticism. We are glad to know wherein we fail so that we can make improvement. There is no reason why American glassware cannot be made as good as it can any place in the world. But we are back on experience.

DR. DAVIS: Of all the tubing I have ever worked I prefer the blue lined Jena. It works best in the fire. It is a special glass and it is very difficult to obtain it in all sizes. It is almost impossible to obtain it now. Before the war our glass was almost exclusively Goulak. Since the war I have been getting Goulak. American concerns are putting out a glass that is equal to Goulak. Specializing in particular lines of glass blowing is being carried out in this country, one man doing a certain thing, and another a different sort. I visited a factory here in New York, and as I was being shown around I was interested to note that here was a man winding coils, and was told that "This man winds all our coils. Here is another that makes all our stopcocks."

W. A. LONG, Corning Glass Works: One of the most particular things in this country in the matter of glassware is the optical glass. How much would the 14 in. gun amount to if we had no field telescopes or range finders? At the present time in the U. S. we have practically no manufacturer who is able to turn out sufficient glass to cover this field or to make it of sufficient quality, because they have no protection.

MR. THOMAS: The porcelain problem has so far proved difficult. It seemed to a number of manufacturers that a good chemical porcelain can be produced very quickly. It took the Germans (?) 150 years. Japanese have been making porcelain for 4000 years, one kind or another. It is a very complicated adventure and we must not claim too much before we get there. There is no question but that the work is going to be done and it deserves support. We have not made porcelain equal to that in Berlin.

### INDUSTRIAL ALCOHOL, ACETONE, ACETIC ACID

ARTHUR D. LITTLE, *Presiding*, Chemists' Club, September 28, 1916

THE CHAIRMAN: I suppose it is not too much to say that those of us who expected an immediate enormous development of alcohol consumption in the arts have been disappointed by the comparatively slow way in which its introduction has grown. One obvious reason, perhaps the only vital one, is that the price of industrial alcohol has never reached a point which has made it broadly available, especially as a fuel. I believe that the great development of industrial alcohol which we still feel sure of for the future is bound necessarily to come. The production of denatured industrial alcohol for the year ending June 30, 1912 was 8,094,000 wine gal.; in 1913 this had risen to 9,831,000 gal; in 1914, a total of 10,404,000; and in 1915, 13,987,000 gal.

Another reason for lagging development is undoubtedly still the government restrictions. You can't do in this country as they do in Germany, arrange things so that any small farmer

may set up a still and run his product over into a sealed tank in which it remains until the government finds it convenient to come around and denature it. Any modification of those restrictions which would tend to greater simplicity would be of vast help in this particular industry and it would seem that there ought to be some possible way, although I have never heard one suggested, of denaturing the mash so that there need be no subsequent supervision.

I believe that the great development in industrial alcohol will not come until it reaches a price of 35 c. per gal., which I believe is well within the range of our vision.

The raw materials for alcohol production in a large way are corn, potatoes, molasses, wood waste, and waste sulfite liquor. The last two, although in some respects the most suggestive and interesting of all, are at present of almost wholly negligible importance. It is worth mentioning however that with the exception of the wood waste and the waste sulfite liquor, all the other materials mentioned are substances that are highly valuable as human food and it is, I believe, and I think it won't be long before it is realized, that to use material which is valuable as food for the production of alcohol is an economic, if not a commercial waste.

The potato distilleries are located principally in Europe, very largely, as you know, in Germany. The distilleries using corn are found principally in our middle western states. The molasses distilleries are along our southern seaboard and the eastern coast of the United States. The production of alcohol from wood waste is carried along commercially, so far as I know, only at Georgetown, South Carolina, and at Fullerton, Louisiana, and the production from the waste liquors of the sulfite process for pulping wood, which was originally initiated commercially in Scandinavia, is now carried on at only one plant in this country, which is at Mechanicsville, New York—the plant of the West Virginia Pulp & Paper Company.

I might say in passing and as showing how slowly these things develop, even when they are obvious, that I remember very well that at the Chicago Exposition in 1893 the Waldorf-Zelsdorf Fabrique in its very fine exhibit there had a five gallon bottle, or more, filled with a high grade of alcohol derived from its waste liquor. Then, because of its rather unique character I want to call attention to the great plant of the Curtis Bay Chemical Company at Baltimore, which I understand to be connected with the United States Industrial Alcohol Company where they are producing on a large scale alcohol made from molasses merely as an intermediary product for the production of acetone by way of acetic acid.

The war has, of course, proved an enormous stimulus to the production of acetone and to a very considerable extent to the production of alcohol as a solvent for the manufacture of smokeless powder.

Some years ago the electrical testing laboratories in this city carried on an interesting series of tests in which they showed that gallon for gallon, burning the alcohol in a mantle lamp and the kerosene in an Argand burner about a little more than twice as many candle power hours were derived from the alcohol as from the gallon of kerosene. That was not a directly comparable test, but yet in each case the fuels were burned under the conditions which give the best results.

Then there is a growing use of alcohol as a heating agent in special cases. You are all familiar with the very wide introduction of solid alcohol, so called, "Steero" and the other products of that kind, which find their market because of their convenience. I was told not long ago that every buffet car coming into the Pennsylvania Terminal was required to use no other fuel than alcohol. Also in the case of many of the heaters used for heating freight cars, it has been found in many classes of freight that alcohol is the best fuel for those heaters, because the

products of combustion do not tend to contaminate the materials in transit.

**ALCOHOL AS FUEL, PRIMARILY IN INTERNAL COMBUSTION ENGINES**—The number of automobiles in the country is I suppose not far below 3,000,000. At 24 H. P. per car, which is certainly low enough, you have about 60 million horsepower in gasoline internal combustion engines. That is more than the total potential horsepower in water power in the United States, and it is very much more than the total steam horsepower. Obviously there is not going to be enough gasoline to go around. Some people speak of the possibility of replacing gasoline with benzol. Benzol would not keep the cars going more than a few days. Kerosene is never going to come into use in pleasure cars, because of its tendency to crawl and leave an oily surface over its container and everything around.

So we must come, I believe, to the conclusion that the only fuel in sight which promises to replace gasoline and to hold down the price of gasoline, which has already risen in some parts of Canada to 39 c. per gal., is alcohol, and fortunately it has already been demonstrated that in those processes having the production of alcohol from waste cellulosic raw materials, we have a method which promises by its development to furnish alcohol ultimately at a price which will enable it to compete with gasoline.

In this connection it may be interesting to hear a telegram which has just reached me from Mr. Groves who has been in charge of the plant of the du Pont Powder Company, making grain alcohol from yellow pine wood waste.

"Your letter forwarded to me from Wilmington did not reach me until yesterday. Sorry I did not receive it in time as it would have been a pleasure to have been present. Trust that those interested in ethyl alcohol from wood wastes realize that the process is a great commercial success and that the interest in this subject will grow accordingly."

(Signed) J. STUART GROVES

That is intensely agreeable to me and I hope will be of interest to many of you.

I have already at different times pointed out the enormous amount of wood waste which is available for the production of ethyl alcohol in the yellow pine districts alone and referring only to yellow pine waste and eliminating all the larger waste which might be available for paper making or other purposes, there is still enough left there and wasted every day to make 600,000 gal. of. 95 per cent ethyl alcohol from that one raw material, and of course the process is one which lends itself to many forms of cellulosic waste.

It is claimed, but with what right I have not determined, that yields approximating those of wood may also be obtained from peat and that straw is also available as cellulosic raw material. At any rate, I think it is safe to say that nature produces something like ten billion tons of such material every year and that our future supply of alcohol would seem to be reasonably secure.

The particular process to which I am referring has since 1819 developed from the use of 141 parts sulfuric acid to 1 part cellulose down to somewhere about  $2\frac{1}{2}$  per cent acid; the time of treatment has also been greatly reduced. In its elements the process now consists in taking saw-dust or wood waste and spreading it over with diluted sulfuric acid, preferably putting it into a digester or converter which has a protective lining, a heat insulating lining, and then bringing it quickly up to the critical temperature, corresponding to about 85 lbs. pressure. Approximately 25 per cent of the wood is converted into saleable products, a considerable proportion of which are sugars and of those sugars a large part are fermentable. The cooked chips are extracted with water and lime added to neutralize the acid; the sulfate of lime settles and the liquor is drawn off and then treated almost precisely as with molasses. The process is really one for producing fermentable sugars from wood, and the rest of the operation is that of the molasses distillery with special ferments.

I have not been able to obtain the exact figures of the acetone production. It has been enormously stimulated by the war and it must be in the neighborhood of 10,000 tons or more per annum. The raw materials for its manufacture are the hard woods, acetone of lime and calcium carbide through the intervention of sulfuric acid and mercury salt, and a special bacillus (*bacillus micerans*) which has been analyzed in a work in Germany. There are a number of methods of wood distillation and the separation of the acetone from the alcohol distilled.

Dry distillation with lime is the regular and most practiced method. Steam injection is sometimes used at the end of the process.

It has been found that acetic acid even when diluted in the form of pyroligneous acid, can be easily converted into acetone by passing through a tube or a chamber heated to about 500° C. over a catalyzer. Dr. Squibb, as you may remember, did this fifteen years or more ago. Another process for making acetone passes the pyroligneous acid over a tube heated to 575°. Benson and Darrin, of Seattle, have studied this process and in a recent article in THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY claim the following advantages for this method: Higher yields, lower operating expenses, the elimination of the large consumption of lime, under-drying of the acetate, continuous operation, low cost of apparatus, easier control.

Finally we have the process for the manufacture of acetone from carbide, the carbide being first converted into acetate, the acetate then being oxidized to acetic acid, and the acetic acid then converted into acetone either by the catalytic process or by the distillation of the acetate of lime.

The Freer Company have patented a process for acting on sugars in the presence of inert and neutral material by the *bacillus macerans* and thereby producing ethyl alcohol and acetone. This process was mentioned at the time of the Eighth International Congress of Chemists here.

Acetone is used principally in the manufacture of smokeless powder as a solvent, particularly, in the cordite manufactures and it has various other solvent uses, which you may call "peace" uses in connection with cellulose nitrates. It is used as a basic raw material in the manufacture of chloroform, for low grade as an absorbent for acetylene, and for other minor uses. The use first mentioned is the most important one and has been tremendously increased by the war. The others have not been appreciably affected, if we except the manufacture of chloroform, and so far as the use of acetone as a solvent for acetylene goes, there has been a great diminution owing to the substitution of electric lighting on automobiles, in place of the acetylene being carried in the Prestolite tanks, where, as you know, it is dissolved in acetone. Also a certain cheaper class of acetones have been substituted.

There have been as a result of the war large additions to the manufacturing capacity for acetone; particularly the great plant of the Curtis Bay Chemical Company at Baltimore, and there has been an especially interesting development through Dr. Matthewson of the Shananigan Falls Power Co. in the synthetic production of acetone from calcium carbide by way of acetylene.

I have here a resolution passed by the Canadian Manufacturers Association at its last meeting at Hamilton, which is of interest in connection with the subject of industrial alcohol.

"WHEREAS alcohol in pure or denatured form is a necessary raw material for a large variety of industrial processes, and

"WHEREAS some of the processes for which it is a necessity are already being carried on in Canada, but with only moderate success, due to the lower cost and easier conditions under which manufacturers in other countries can obtain this material, and

"WHEREAS the equalizing of conditions would not only stimulate the growth of existing industries, but would lead to the establishment of new ones to the obvious advantage of the country as a whole; and

"WHEREAS, many other countries have found it to be to their



advantage to reduce greatly and sometimes to remove altogether the excise on alcohol when employed for industrial, scientific and humanitarian purposes, and

"WHEREAS, we believe that the legislation and regulations governing this matter should be so formed as to encourage the distillation of alcohol in Canada by making it profitable for the community to use the domestic rather than the imported article; Therefore be it

"Resolved: That the Canadian Manufacturers' Association place itself on record with the federal government as requesting the removal of the excise duty or the inland duty, provided the alcohol always is under suitable regulations and restrictions:

"(a) When employed for manufacturing purposes under which the alcohol would be lost or unrecoverable;

"(b) When used by hospitals and asylums and infirmaries for bathing purposes;

"(c) When used by laboratories or educational institutions for purposes of scientific research;

"(d) When used by hospitals and museums for the preservation of specimens."

DR. MATTHEWSON: We have been working on the process for 8 months now in an experimental way and it has been successful so far. We are making now in the neighborhood of 100 lbs. of formalin per day and an equivalent amount of acetic acid and acetone. A large plant is fairly well finished and we hope to start operating in about three weeks' time.

We have met principally mechanical difficulties in the process, and have finally gotten a material to stand the action of sulfuric acid.

In the oxidation of the formaldehyde with acetic acid we found very many difficulties. We experimented there with oxygen, and we found that both are fairly successful. One of the greatest difficulties there is the danger of explosion of the formaldehyde, but with proper regulations and proper material for the containing vessel, the danger of explosion is almost entirely eliminated. Both in the first and the second stages we are able to get over 90 per cent yields in the third stage; we are making catalytically acetate of lime by passing it through hot tubes. We expect to turn out by Christmas time 10 or 15 tons of acetone per day.

It is doubtful if the process is likely to be persistent under peace conditions. Of course, as far as acetone is concerned we know it won't be. The over-production of acetone has been too much. The acetone will have to go, but I believe we can compete successfully, as raw materials are quite cheap and our method of production is comparatively developed.

DR. BATES: There is one process which Dr. Little omitted and which is now being placed on a commercial basis in Canada at Toronto. As you know Ontario has recently gone dry and that has left the whiskey distilleries without much to do. One of these distilleries has been transformed and is now manufacturing acetone, using corn as a raw material.

You referred to the bacterial action on sugar, producing ethyl alcohol and acetone. This process is also a bacterial action on corn or starch, as raw material, giving alcohol even in larger amount than acetone along with  $\text{CO}_2$  and hydrogen. This is a most interesting process and one that could not be predicted theoretically. It originated in England with the Syndicate Products Company and has now been practically established in Canada on a commercial basis. The process of using acetylene as the raw material generated from calcium carbide—if it turns out to be a commercial success as expected—will be a real technical triumph for Dr. Matthewson in particular and for Canada in general. In the past Canada has not had the privilege of developing many new processes and industries along the chemical line. The war is not what you might consider a benefit to Canada or anybody else taking part in it, but it has been a stimulus to several branches of chemical manufacture.

As to the acetone business after the war, I am not big enough to predict anything about it. We want acetone and more acetone. Naturally the tendency is to produce as much as

possible in Canada and to make Canada and the rest of the Empire as independent of outside sources as possible; but if we have to buy any elsewhere it will be from the United States.

One other process which I spent some time on developed in the fertile brain of a certain French Canadian who claimed that by mixing starch and lime in certain proportions and heating this under pressure in a retort he could obtain a very high yield of acetone, in fact the yield of acetone claimed was 70 per cent—more than the theoretical possibility with the use of starch as a raw material. Nothing has yet been done with the 10-ton order which was given him. I might say, however, that I tried the distilling of a mixture of starch and lime, and there was actual acetone produced in small amounts.

DR. COMBY: Alcohol and acetone is practically altogether used as a solvent for gun cotton in the explosives industry.

THE CHAIRMAN: There is a use for acetic acid anhydride which promises to become important enough to be of interest and that is in connection with the production of cellulose acetate. Cellulose acetate has many of the physical properties of nitrate of cellulose and would undoubtedly replace nitrate of cellulose for many purposes were it not for the fact that it is somewhat more expensive. Nevertheless, some war uses for cellulose acetate have been found, for example it is being used in the manufacture of a varnish for aeroplanes. It has the advantage of giving a surface which is non-inflammable and waterproof and I presume preservative. We have seen in the newspaper accounts of aeroplanes with transparent wings and those wings, if such aeroplanes ever flew, were undoubtedly of some special form of cellulose acetate, probably the form known as cellophane, but cellulose acetate is finding a current demand in special lacquers and the cellulose acetate sheets are coming into use in situations where the explosive quality or a higher degree of inflammability of the nitrate would make it dangerous. For example, automobile goggles are now being made with cellulose acetate, the upper portion of the goggle being stained a fairly deep brown so that the wearer of the goggle, if he suddenly comes upon an automobile with blinding light, merely inclines his head a little so as to look through the upper portion of the shield and have the light cut down to something that does not disturb his vision.

Still more recently the production of a waterproof artificial silk from cellulose acetate has been accomplished on a commercial scale and a plant of considerable size, which will make initially 100 lbs. per day of such artificial silk, is now under construction in South Boston, Massachusetts. A possible development of its use may call for rather large quantities of acetate anhydride. Cellulose acetate ought to be and would be the basis of every moving picture shown in the world if the public were sufficiently enlightened to demand it, because the film has been proved wholly suitable for this purpose. It has been made in very large amounts, and several hundred million feet have been put out, but it is slightly a little more expensive—and it is that slight increased cost per foot which still exposes our theatre audiences to the danger of theatre fires from the explosion of moving picture films.

It is made by treating purified cellulose with acetic anhydride and a little sulfuric acid. If nothing else is present except acetic acid as a diluent, the acetate is formed and goes into solution and then when the mixture is poured into water the acetate separates out in a sort of curd which is broken up and washed and dried. The great disadvantage is that the dry curd is heavy and holds on to particles of acetate and it is almost impossible to get it out. In the process invented by Merrick, the one this silk company uses, the product is formed in the presence of benzol and, being insoluble, preserves all the characteristics of the original cotton just as it does in the usual process of nitration.

Can we hear from somebody who represents the Curtis Bay Chemical Company?

PROF. WHITAKER: I was somewhat surprised to hear our concern referred to as a producer of acetone because for several months I have been listening to the consumers and the inference is that we are not producing any.

I don't know that there is anything new of interest, technically, about the plant. The manufacture of vinegar is carried out in the usual way. The building used for this purpose covers something over ten and a half acres of ground and the vinegar is neutralized in the form of calcium acetate which is retorted in the usual rotary retorts.

THE CHAIRMAN: I have no definite knowledge regarding the process used by the West Virginia Pulp & Paper Company but I understand that the usual sulfite liquors contain a very small proportion, less than 1 per cent, of fermentable sugar, and that after the liquors are neutralized with lime the yeast is added and fermentation carried forward and the distillation then of the beer and the high wines is carried out in the usual way. I do not know the technical details of the process, however, with any degree of accuracy.

DR. WILLCOX (of Pennsylvania): I might add that the sulfite liquors under proper conditions of production run something over 2 per cent sugar and it is possible with proper conditions and proper technical handling of the liquor to get a beer containing about 1 per cent of alcohol, which, of course, brings it within the range of probable commercial use.

THE CHAIRMAN: I have been very much struck with the quality of the alcohol produced by that process. In Norway the reports were that it was always seriously contaminated with sulfur—that does not seem to be the case here.

DR. WILLCOX: It varies from one cook to another. At times a liquor will give all sorts of sulfur compounds and even free sulfur, but it is possible in the still to get rid of it.

THE CHAIRMAN: If a purely personal reference is to be forgiven, it may interest you to know that I began my career as a chemist, and a little later was superintendent of the first sulfite pulp mill in America. We struggled along to make 4 tons a day with a 10-ton plant and finally failed for \$2,000,000. Mr. John Luke was superintendent of the paper mill at that time, and with his brothers organized a company with about sixty thousand dollars of real money and took a plant that cost \$137,000, and made \$90,000 in the first 6 mo., and for a long time I think that out of every two dollars they received one dollar was profit, and the prediction to-day is that they are producing 6,000 tons a day. I would like to give you a résumé of the trials and tribulations that attended the development of the sulfite process—it would sound like an Odyssey.

DR. PHILLIPS: Reference was made a little while ago to acetic anhydride. I remember a good many years ago that acetic anhydride was being used for the extraction of essential oils, and it was found to be very effective. I wonder if that method is being used, or if it has been developed further? I have heard nothing of it in recent years.

THE CHAIRMAN: I don't know anything of that. Of course it is often used in the manufacture of vanilla.

DR. GIBNEY: As a representative of the Ordnance Department of the United States Army, I am interested in the subject of alcohol, and I was interested in your account of the synthetic manufacture of alcohol from cellulose waste. I would like to ask with regard to the purity of the alcohol which is produced. For our purpose the alcohol should be of the highest degree of purity and the highest degree of strength. I would like to ask as to the purity of that alcohol and also as to the possibility of producing an alcohol commercially higher than 95 per cent.

THE CHAIRMAN: It is perfectly feasible to produce from wood waste a 95 per cent alcohol which is of the grade of cologne spirits. You can readily see that you are much less likely to

get fermentations than when dealing with a thing like corn. There is no more difficulty in producing alcohol of any strength by that process than in the case of any other raw material.

DR. KYRIDES: I have been interested for several years in alcohol and acetone, not as an adjunct of war but rather as the means of carrying out pacific trades. I believe that if you can produce alcohol as cheaply as gasoline you would be able to prepare rubber synthetically. I have worked on it about three years. I know if you had acetone cheap enough you would be able to. I was talking to a gentleman yesterday who said he was working on magnesium and he said that it would be possible to obtain magnesium for 14 c. per lb. and on that basis the price of magnesium could be brought down to about 4 or 5 c.—if you can get alcohol you can get acetone—if you can obtain alcohol at a reduced cost. As to when we can obtain alcohol cheaper, it is up to the chemists. Twenty-five cents would be fairly cheap.

THE CHAIRMAN: Do you see any prospect for the production of synthetic rubber at a price below that which it is now being grown at on the plantations, which I understand is not over a shilling a pound?

DR. KYRIDES: I have not thought of that proposition very deeply. At the time I was working the price of acetone was rather high, but I think it can be produced for less than 25 c. a pound.

MR. BRECKLER (of Louisville, Kentucky): I have been associated with the alcohol business now for about twelve years and have been very much interested in some of these facts that have been brought out to-day. It is not generally known that one of the greatest troubles in the alcohol industry is the fact that there are so many internal-so-called-political troubles that actuate the different distillers in their dealings. For instance, one of the large alcohol concerns which was mentioned to-day is now obtaining molasses from Cuba for the manufacture of alcohol. Molasses to-day on the open market is selling for about fourteen cents, when you can get it, but the trouble seems to be that it is not to be had. This concern, very frequently at the time when the Cuban planters were in a great deal of difficulty, obtained molasses at quite a low figure. Now the total molasses produced in the United States and Cuba would supply about 50 per cent of the present demands for all purposes. This molasses, of course, gives the concern that can use it a big weapon in the hands of a few distillers against the distilling industry. The possibility of producing alcohol at a lower price primarily must come from the distilling industry, I believe, because with all due respect to the Ewing and Tomlinson process it has been operated for about seven years and there is only one plant that produces it and it has not played a very great figure yet in the alcohol market, though of course the future possibility is still a matter of some doubt. But the concern that can produce this alcohol has a club over the heads of the rest of the industry, and they might think it desirable at times to furnish alcohol momentarily at quite low prices. Of course I don't say it will be done or has been done, but the situation has simply become this, that the rest of the industry waits on what the molasses alcohol people are going to do. Now, then, there is only one hope for alcohol that I can see, and I have figured the question over very frequently, and that is, as was mentioned, the sulfite liquors. Here we have a liquor that contains 2 per cent of fermentable matter and very possibly could be made by evaporation to contain 6 or 8 per cent, a medium which would produce alcohol very economically. On the other hand, the unfortunate part of that industry has been that the process requires special skill and training to operate. The Swedish process requires the acclimation of the yeast to the liquor and that is a matter of some little difficulty. The Norwegian process carries difficulties, as it primarily depends upon the casein from skimmed milk for nitrogenous matter,



and the percentage is too small to have the fermentation take place in regular fashion. With the high price of nitrogen, or nitrogenous matter in this country, that in itself is somewhat of a problem. However, I must say, that after seeing a process of this kind in operation I feel a great deal more confident in the process itself than I ever did before and it is absolutely the only hope because it is the only process with interested parties, and what I mean by that is that parties interested in foreign processes cannot hope to control. That is something where as many mills as want to put in the alcohol process are at liberty to put them in. Any other process is bound to be shut up sooner or later by interested concerns. As regards denatured alcohol, outside of the fuel industry there were about 25,000,000 proof gals. of denatured alcohol, of which an estimated quantity of 5,000,000 gals. went into the explosive industry for export. Now, had that paid taxes the administration in Washington might have found a little redress from their present deficit. The Commissioner of Internal Revenue has suggested that some effort should be made to tax it because the industries in which it has been used have not cheapened their price to the ultimate consumer, and the Government is suffering a loss in gauging this alcohol. I might mention, of course, the industry we see the most—the ether industry. It has resulted in great reductions, but that forms a comparatively small part of the consumption of alcohol.

THE CHAIRMAN: I would like to bring out one or two points in reply. I am rather sure that if the representative of the West Virginia Pulp and Paper Company had been present he might not have agreed with the last speaker in the wide-open situation as to patents. I have made some rough figures here which may be of value—they may be a little off—they are made on the basis of 6,000 tons a day, 25 gals. of waste liquor per ton and 2 per cent of sugar. There would seem to be, roughly, enough waste liquor in the country to produce about 200,000 gals. of alcohol a day. Some of the mills, of course, are comparatively small.

I do not think there is any probability that molasses will ever again be as cheap as it used to be before the war, because of the possibility of its consumption in making alcohol, and before the war there was a rapidly increasing diversion of molasses into that field.

I would like very much to inquire how cheaply molasses alcohol can be produced, say with molasses at 4½ c.

MR. BRECKLER: You can add 3 c. for overhead, per proof gallon. This does not allow for containers and freights carried through containers, or for overhead and interest and depreciation—including that, I should say about 10 c. per proof gallon or twenty cents roughly for wine gallons.

A VOICE: The people who say that alcohol can be produced at 25 c. absolutely are dreaming.

MR. BRECKLER: That is my opinion. I would like to say something else in regard to that. My figures are based on the production of 4 billion pounds of sugar per year. That represents 1 billion tons of hydrocarbon that was not used for sugar and could be utilized. That only produces 650,000,000 proof gallons per year or about 5 per cent of what the production must be to supplant gasoline.

THE CHAIRMAN: Here is an interesting fact in connection with the sugar industry. One-eighth of the entire sugar crop of Louisiana is sent to the burners with the back ash; so that one-seventh of the world's production of sugar is burned up. Now that sugar is there in the cane perfectly available for fermentation to alcohol. Furthermore the cane itself is there suitable for conversion to alcohol by a process like the Ewing & Tomlinson process; if it is permissible I would like to correct the last speaker to this extent that there are now two plants running under the Ewing & Tomlinson process and the plant at Fullerton is producing about 2,000 gals. a day, and sometimes 2,500 or more.

MR. BRECKLER: How long can it run with the modern prices of alcohol?

THE CHAIRMAN: That is what we are trying to find out. We have faith enough in its possibilities to keep calling upon our friends for more money. It is one of those things which is certain, however, for it has gone so far that the other alcohol producers may just as well make up their minds that the people who are back of it are going to keep at it until there is no question about its commercial success. I don't know how many of you may have read that inspiring book of Robert Kennedy Duncan's on the Chemistry of Commerce as to the benefits that cheap alcohol would afford the community. The day is coming when alcohol can be had by the small user at 25 c. per gal., and when that day comes the consumption is going to be multiplied by a very great factor. I have referred to the use of alcohol in internal combustion engines. Now, of course, nobody claims that alcohol has the same potential energy that gasoline has, but on the other hand it may be used under far more favorable conditions and up to a pressure of 180 lbs. without back-firing. There is no danger of explosion. The fire risk is reduced almost to nil, because a bucket of water will put it out at once. So that on the basis of equal prices, I believe that alcohol will begin to displace gasoline.

DR. JOHNSON: I would like to ask a question. I have been surprised to hear nothing said about wood alcohol for any purpose for which wood alcohol is used. Are there any uses of ethyl alcohol that cannot be replaced by methyl alcohol? The gentleman representing the United States Army spoke of making alcohol of 100 per cent purity. It is very well known that ordinary industrial ethyl alcohol cannot be produced at more than 95 per cent, and you can produce methyl alcohol at 100 per cent, or practically chemically pure. I have great curiosity to know what is the field of uses of those two materials in which one is limited from the other.

THE CHAIRMAN: Is it not a fact that the normal price of wood alcohol is so much greater than that of denatured ethyl alcohol that the wood alcohol would not be likely to replace the ethyl?

DR. JOHNSON: That I do not know—whether it is for some chemical reason or simply a matter of price.

THE CHAIRMAN: I think it is simply a matter of price. I wonder if Dr. Reese would say anything.

DR. REESE: I think it is largely a matter of price, not of purity.

## MANUFACTURE OF PAPER PULP AND BY-PRODUCTS

ROBERT B. WOLF, *Presiding*

Grand Central Palace, September 29, 1916

THE CHAIRMAN: Chairman Fletcher in asking me to open this meeting suggested that a discussion on the scientific control of industries would, perhaps, be the best thing to start with. I would like to make a plea for a more definite control of organizations from the scientific point of view, and a scientific effort to organize and study the problems of management scientifically.

The mill as a whole should be one vast laboratory for doing qualitative and quantitative work. Processes should be so recorded throughout the entire organization that all the variables that enter into manufacture have to do with the quality and quantity of the output should be recorded, and so recorded that comparisons can be made easily.

In the manufacture of wood pulp in our own organization we have been able to effect a saving of 17 per cent in the yield from a cord of wood by simply studying and applying the laws that had to do with the structure of the cellulose; the reason we could do that in a comparatively short time was that the organization as a unit was doing this work, and not a group of individuals. The organization as a whole had a definite memory

and the data of things that had to do with organization were recorded in such a way that those laws could be studied.

You must have an organization memory apart from the individual memory. Everything affecting the organization must be recorded at a definite central point in such graphic form that results can be studied and used by everyone.

Retention is a thing that can be plotted daily in the mill. You know the amount of filler that is being furnished, and if there is an accurate record kept of the retention and then plotted alongside of that figure, say, plotting it mathematically, the percentage of retention, 30 or 40 or 50 per cent, plotting in all these things, the percentage of calcium carbonate in the filler, the kind of filler used, the amount of lime, the amount of sizing used and the character of the sizing, all that could be plotted in a definite way with relationship to the retention and in a short time the organization would find itself in possession of an enormous amount of information, and then, when we come to the February meeting we will have something worth talking about.

MR. CARRUTH: There are so many variables in any consideration of the retention of clay, some of which Mr. Wolf has touched upon and some of which he has not, that under the present organization of our mills (as most of them are organized) cannot be recorded. But my belief is that that is the only way to do it; but it takes time to convince those who have been brought up in another school that that is the way to accomplish results and in the end to make the biggest profits.

One phase of the filler retention problem that was not yesterday touched upon at all, and in one way it has nothing to do with filler retention, yet in another way it is a very important phase, and that is the other ash-forming ingredients that go into the paper. We have, for instance, so much china clay added to 100 per cent of stock. In a simple case of that kind it is easy to determine the retention; but, if in addition to that hundred per cent of fiber we had as a part of that fiber, we will say, 10, 20 or 30 per cent of old paper, which in itself contains varying quantities of filler, we have introduced a variable which is very hard to control. This results in very curious retention figures. We are getting now in our mill a retention figure on every lot of paper made that contains any filler at all, and it is not at all unusual to find 160 or 180 per cent of filler in it. And of course we know where it comes from and without a great deal of very careful work, but with these old papers coming into the stock, the retention figures which we obtain are almost utterly valueless.

MR. GRIFFIN: If you are going to make a large and uniform product, you can control it very easily. A large corporation making a comparatively simple number of products cannot very well undertake to make small quantities of specialties. The small mills will have to add to the selling price of their goods in order to make a profit. A large mill should not undertake the making of small orders and specialties.

Inequalities will exist in the paper business as long as we make paper, because the paper maker will necessarily always be obliged to use paper from back orders and slutches, as we may call them, the clay slutches or the filler slutches, and unless we use filler papers you would hardly be able to make the same kind of finish. It is no discredit to have an order sent back because of the amount of clay in it—if there is a paper that contains a large amount of filler for a super-calendared paper, the manufacturer is bound at times to get a larger amount than he planned.

But the real thing to do is for the mill to study its own problems and develop its own individuality and to keep the records and keep the memory of these records and it will soon work out the best scientific control for the retention of filler that I know anything about.

THE CHAIRMAN: Mr. Griffin made a statement awhile ago about the finding of fault with a man for what he was supposed to have for finish. I have found that the very best thing to do is not to find fault with the man but to give him the record of what he is doing and let him find fault with himself. If we can do that, the desire on the part of men to do good work is what prevents your organization from having down hill slips, as I heard a man express it.

MR. POPE: I hope that the manufacturers of paper in trying to perfect their industrial problems in the plant will not lose sight of the finished product. It seems to me that a uniform industrial organization which will have control of the finished product and make the finished product always of uniform quality would be a problem solved that would be gratifying to the printer.

MR. NIXON: Mr. Pope says that the object of all this work that we are putting our time in is that they may benefit by the things that we intend to benefit by in the mill. If it were otherwise we would not be having this conference. We are endeavoring to make the mill 100 per cent perfect so that there will be a return to the man who is using the product, and we hope to do it.

THE CHAIRMAN: It may interest Mr. Pope to know that the more we organized, the less the paper-users kicked about the product. Our pulp has always presented a color problem involving much discussion and dispute between buyer and seller. Particularly is this true of sulfite pulp. The usual custom is to refer to the standard or contract sample; but this is unsatisfactory, because such samples change and fade. Another difficulty has been the texture of our pulp which made it difficult, if not impossible, to produce a permanent standard which could be used by comparison. The disc idea has been modified and developed by the Burgess Sulfite Fiber Company by replacing paper discs which I have in mind by brass discs surfaced with mixtures of plaster of Paris and various shades of material made of bichloride of potash. These discs have been worked up into a standard system for checking the color of their birch bark pulp and now constitutes an original controlled method in their mill. Our own laboratory has adopted their system and we are now checking the color value of all birch pulp received. The system seems to have worked perfectly satisfactorily and it may be of interest to you that since we have started this scheme we have been able to recover quite a sum of money from the dealers who have supplied us with a low grade pulp which we would not have been able to do under the old system. They said they were giving us the same thing that they were before, but the last sample didn't show it. We are trying to work back to pulp paper discs in place of the Burgess brass and plaster discs for our soda pulp tests and unbleached sulfite. The reason we are doing it is because the Burgess method requires a very large number of discs and a considerable outlay of money, space and power, which our laboratory space does not allow us to make.

There seems to be a possibility of getting away from this difficulty and confusion. Professor Ira H. Monsel, of Boston, has given his life to the perfection of a system of color, or a nomenclature for color.

Professor Monsel's system states color in three dimensions: hue, value and chroma. Hue (*e. g.*, the difference between red and green) depends upon the wave length of light; value depends upon the quantity of the light irrespective of its color; chroma is the intensity of the light and the intensity of the color and depends upon the height of the wave crest. These three dimensions should be susceptible of experimental demonstration. Professor Monsel has placed on the market a tintometer: ours expresses values to within 2 per cent. The other dimensions are not so easily made. The hue can be obtained accurately with the spectroscope, and the chroma value



by some arbitrary scale, I am a little hazy about that. It would seem that something is needed to make this system of universal value and if the demand arises undoubtedly this instrument would be forthcoming. Prof. Monsel's charts are being used as the basis of color study in a number of our public school systems, of which I believe New York City is one.

There are other instruments on the market for the determination of color. The Ives tintometer is one. This system should have a very large field of usefulness. Our experience with it is too slight to warrant any attempt at discussion.

DR. KRESS: At the Forest Products Laboratory we are of course interested in determining as closely as we can all of the physical qualities of the papers that run over our machines. We have done a little work with Ives' tintometer. We started out by making dyes in which we use a varying amount of colors per thousand pounds of stock, and by making our readings through the red, green and blue, and plotting the results, we found that we could give a numerical expression to color, accurate within 4 per cent. Two matches made from dissimilar colors compared under the Ives tintometer gave the same result. We then made a few dyes on different combinations of color under natural light, and they changed under artificial light. It is interesting that under the Ives tintometer both of these papers which matched under ordinary daylight matched while under the Ives tintometer.

The difficulty with any color instrument so far is not to get the readings but to interpret the results.

MR. CARRUTH: The Monsel charts which have been produced, of course, are not complete. It is almost inconceivable for anyone to make out a set of complete charts; there would be an infinitude of shades. By taking these charts even as they are to-day you can very nearly state the color of any sample which you have. The difficulty for the paper men is that these charts are not complete in the higher values wherein paper values lie. The paper man who is going to use the chart will have to do some work on his own account to give numerical expression to color—but the hue will hold absolutely no matter what the color may be.

MR. KING: I would like to say a few words about coöperation between the manufacturers of color as it is manufactured more or less to-day and the users. We are coming to a point now where we are having to use anything that we can get. I would like to see if some form of committee could not be appointed by this association with, say, a couple of members from our American dyestuff manufacturers, and members of the German firms who have made color in the past, and also men from the mills where a great deal of color is used, that would help us to know more about the new colors. We knew about the German dyes before, we know the proportion of the strong basic dyes, and we know about the sulfite—but you might bring out my point that you should not hide the effect of hydrolysis on American dyes if they are to be used in the future—we should come together and try to find out as many points as possible about these dyes and thus promulgate the use of them in our mills in the next two or three years while these chaotic conditions exist.

JUDGE MOORE: I found when the question came up of protecting the dye industry in America that there were scarcely a dozen voices raised among the paper manufacturers as to the wisdom and advisability of doing so. I hope you will not think of me as suggesting politics. So far as the paper industry is concerned, both parties are alike, so that there is nothing political about it. In the first place our product is put on the free list; we have got to meet the competition of the world in selling our paper. On the other hand, the things we buy they are proposing to protect. Now, has it not occurred to you that

the foreign maker of paper can take these foreign dyes and put them in his paper and send them in free of duty and beat us in our home product; that at the same time we must compete with him in his colored papers, but are not permitted to buy the cheap dyes? I do not say that dyes should not have protection, but I do say that we are obliged to compete with the world in selling our product and we ought to have the privilege of the world's market in buying our materials.

DR. SCHUTZ: I know that some mills have a set of enamelled plates for any kind of material, white in different tints or shades, some of them more or less blue or pink; and they use the plates as factory standards. They use them as well in the bleaching plants as in the paper plants. They are absolutely reliable because they do not change. Bleached sulfite will change very quickly, say within a few months, if the particular pulp should contain even a small percentage of lignum.

MR. HATCH: Some four years ago the mill that I am connected with was using in the vicinity of 60 colors to produce about 16 shades. So I started a little investigation; we reduced our number of colors from the vicinity of 60 to probably 15.

#### EFFECT OF THE TEMPERATURE OF THE WATER USED IN THE BEATING OF PAPER STOCK

Cellulose is a colloid and as such is affected by the general reactions or processes which affect colloid substances. In general, we know that pure cotton cellulose when treated with alkalis tends to hydrate and swell up. This is the action which is desired in the process of treating cellulose in the manufacture of paper. The mechanical rubbing of the cellulose in the presence of water produces a certain amount of hydration which aids in the remaining together of the fiber and in the production of a stronger sheet of paper.

We are situated on the Connecticut river and have the difficulty of loss in strength in our paper in the summer.

We plotted curves showing the strength of our paper over the entire year, and the temperature of the water we use; we found that as the temperature of the water in the river rose above 75° F., the strength of our paper began to take a decided drop. By arranging a source with uniform water temperature under 75° we succeeded in straightening out that curve greatly.

THE CHAIRMAN: I would like to ask Mr. Hatch whether he attributes this loss or gain in strength to the temperature of the water or whether it is directly or indirectly caused by the weather, or whether he made any tests on the sizing qualities of the paper when made with colder or warmer waters.

MR. HATCH: We found that as the temperature rises the sizing is not so good. We attributed that in part to the fact that cellulose hydrate is not so rapidly formed at the higher temperatures and we get less of the cementing quality of the cellulose hydrate which is in itself to a certain extent the sizing agent.

THE CHAIRMAN: We took some pulp that was made in the winter time and used that pulp in the summer and got the same falling off in strength as when using the summer pulp.

MR. CARRUTH: I might possibly add that in making a paper where the hydration effect is carried to the limit, we have noticed that a pulp made in the winter will produce apparently a parchimentized effect more rapidly than a pulp made in the summer and that effect we found and proved to be due to the pulp, not all of it, but in part, to the pulp, because some pulp of the same manufacturer who had not been running in the summer but which had been stored and was actually made the previous winter, gave us more nearly the desired results. Of course there might have been other elements in that—there might have been a difference in the manufacturing process although it was pulp of the same manufacture. But there is no question that the results as given by Mr. Hatch are absolutely correct.

## WASTE SULFITE UTILIZATION

MR. WALTER H. DICKSON: The utilization of refuse from industrial processes has of course attracted a great deal of attention within the last two years since the war started in Europe, and the scientific world in this country and the scientific societies and mining technologists have been looking into it and I do not think it was appreciated what was going to waste in this country, not alone by the layman. Last year something like 9,000,000 lbs. of sulfite pulp were produced per day. Two causes bring about the utilization of waste material or refuse. The pollution of water courses and streams may force mills to do something with their liquors, or some phases of the war have necessitated the utilization of what was formerly waste, such as the recovery of the products of the distillation of coal in this country. This condition of absolute necessity of utilizing refuse in this country is really not pressing the paper mills all over the country but in some places it is, and I believe that was the condition in one or two mills, which was the beginning of the use of sulfite liquor in this country. The Robinson Process Company people were the first to use the liquor waste in this country. Another was the Rogers plant and a third the Covington plant of the West Virginia Pulp and Paper Company. Their first work was the utilization of these liquors in binding compounds or adhesives, and from that followed the development of tanning extracts. Next, my own company developed tanning extracts and also binding compounds. Some five different companies in this country at the present time are interested in this, more or less. The Muskegon Extract Company and the International Paper Company have done some work. The West Virginia Pulp and Paper Company have developed some work for the recovery of alcohol and the Cumberley-Clark people have also taken up the alcohol recovery problem. The utilization of the waste liquors in Europe did not find very rapid progress until very recent years. They were forced to become more active in this because of stream pollution and there are quite large developments abroad now. They are producing very large quantities of the material known as cell-pitch which is concentrated sulfite liquor brought down to the solid mass. This product is shipped in very large quantities, and is being used for various binding purposes. The tanning industry abroad is using very large quantities of this material. That has been brought about because of the necessity of utilizing low grade fuels. There is very little in this country of that production, but there are certain developments now which may open up some use for it in this country, as you all know who have kept in touch with it. In Sweden there is quite a large development in the way of producing alcohol. But the production of alcohol from sulfite liquor does not take care of the pollution of the stream conditions which some of the mills are confronted with. It is only a partial result, and it is my information that the best results can be obtained where alcohol is produced in connection with the production of other products.

In Europe recently there has been considerable work on producing cattle food from this material, with more or less success. It contains, as you know, the basis of food, the question being the getting rid of the sulfur compounds. It has also been proposed in the manufacture of explosives—I cannot say with what success—and I understand that abroad they are using large quantities as a substitute for resin in the charging of shrapnel shells.

The principal products being produced in this country to-day are tanning extracts and binding compounds. It was a long, hard fight to establish these products on the market but they are now thoroughly established. I think the failures in the beginning for road work and adhesive purposes have been due more or less to not having analyzed the conditions under which they had to be used.

The possible products which can be produced of waste sulfite liquor are quite numerous. We have in sulfite liquor all the chemical elements to produce a numerous range of products. It is a question of work and a lot of it. I might mention with good authority that the Robinson Process Company before they got to their turning point spent something over \$500,000, and I know that my own company spent \$200,000 before we got to the turning point. There are to-day being produced quite a large amount of color compounds and dye compounds from waste sulfite liquors, and it has great possibilities. There has recently been a number of patents taken out disclosing a method of precipitating out certain of the elements in the sulfite liquor as solids, and they have been used in combination with oxychloride cement, as loading. I have seen such floors which looked very good indeed. I, myself, have recently succeeded in separating the sugars completely from the sulfite liquor, from the rest of the organic compound. Also I have been able to obtain, by combining certain other matters, a resinous compound absolutely resistant to all acids and alkalis. It is in a very crude condition and it will require a great deal of work to get it in commercial shape.

PROF. MCCUE: There is another possibility in connection with the use of waste liquor. I have been educated as a lumberman and having had considerable experience in that before I went into chemistry I feel that some use must be created for this material which will not require such an enormous effort and expenditure of money in the way of introduction and that this consumption must be exceedingly large. If we take the figures of the total production of sulfite and see what is running down the streams in the form of organic matter, whatever use can be developed that can generally be adopted must require an enormous consumption. It is not the fault of the paper manufacturer that he is not recovering it. I do not doubt that to-day there are other sulfite manufacturers in the country who would be gathering this material if you could show them a market. There must be an enormous development possible in its use by roads, or some other use may be developed.

Now, if the stumpage value of our timber goes on and increases at its present ratio from year to year and approaches anything like the stumpage values in other countries, then there may be the possibility of our using less valuable trees, such as the hemlock and the quick-growing pines of the South, by transferring the organic matter and putting it into these inferior woods. It may not alter the structure, the wood structure, but the mere fact of filling the pores and solidifying it entirely alters the working properties of the material. Yet that is not a chemical problem or an engineering problem; it is really a lumbering problem.

I do not know whether you are aware of it or not, but the manufacturers of Kraft papers in Europe, as far as I know, always select metallic sulfite for hydration and give it very much less time for hydration than the ordinary sulfite; but not only that; even if it is hydrated to the same extent, it makes a more transparent paper. We all know that sulfite makers make a pulp more hydrated at one time than another. One maker can make the cellulose if it is fresh, but if it is kept for six months and dries out until it becomes dehydrated it becomes more difficult. Manufacturers of dressed pulp always got the best results with fresh material which had not been dried. The difficulty of hydrating and drying pulp imported into this country is exceedingly great compared with the demand for that price of material, and the problem of hydration and dehydration is such a variable one. The manufacturers use such various methods—I have seen manufacturers making Kraft paper put steam into the beater and expect to benefit in that way—they wanted to make it free and wanted it dehydrated. The problem is one which has to be considered under a number of conditions.



MR. DICKSON: The normal sulfite production in this country is from 4500 to 5000 tons a day with a total solid material in the waste sulfite liquor between 75,000,000 and 100,000,000 tons a day. That has to be taken care of. Whatever use or uses are going to solve this problem, it is not going to be the dyeing industry or the high-class adhesives, but some use or uses which will consume a large tonnage at a very small margin of profit.

A VOICE: What is the ratio in the finished sulfite liquor between the sulfite itself and the organic solids in the waste liquor?

MR. DICKSON: In the amount of production of sulfite, I believe the figures are surprising, something like 15 per cent cellulose, 47 per cent is thrown away.

THE CHAIRMAN: What can be recovered is 47 per cent.

MR. DICKSON: To a ton of sulfite you ought to recover 1200 to 1500 lbs. of solids from the waste liquors.

MR. MCNAUGHTON: In the waste sulfite liquor, which is the combination of the sulfite materials in the wood together with the inorganic chemicals used in the digesting process, I think it could be taken as a safe figure that approximately 180 to 200 lbs. of sulfur per ton of pulp produced could be found present in the waste liquor, and from 150 lbs. and upward of lime combined in various ways, depending on the quantity of lime used in the manufacture or cooking of the liquid for the reason that in the cooking process the sulfur retained is that combined with the lime and organic material, whereas the lime is not volatile and is retained in the waste liquor regardless of how great a quantity is used in making the cooking liquor. From what I have been able to read and gather from conversation the preparation of the waste sulfite liquor for use as road binder is a case of straight evaporation, where the inorganic matter is evaporated with the liginous; in case of the tanning process the inorganic particles such as lime and magnesia must be separated out. The difficulty in preparing a good tanning is in getting the lime and magnesia precipitated out, leaving the resultant material of a nature which does not injure the texture of the leather.

MR. BENJAMIN HORNER: I have some samples of wire—perhaps you would like to look at them—sixty-five mesh. You will notice that in the cracks formed there is a spot of some material which is probably caused by the crack. The practical paper-makers in our mill attribute it to pitch. It does not seem to be that because other spots that are smaller than that would be more likely to be pitch and still they have not caused the cracks as indicated by larger spots. Perhaps some of the men here have had some experience on that line and can explain that. It is a problem that has caused a great deal of difficulty with us.

THE CHAIRMAN: I am glad to hear him say that he does not think these spots are caused by pitch, because we always get blamed for them.

MR. GRIFFIN: I would ask this gentleman if he has made any attempt to analyze the substance in those spots?

MR. HORNER: No attempt has been made to analyze them at all. You will notice that the spots have been steamed off so that there is practically none of the material which caused the spots originally.

MR. GRIFFIN: I think it would be very instructive if you would make an investigation of what you find in the spots. Sometimes something has happened as the process went along.

MR. LIPSCHUTZ (Sugar Chemist): I would like to know what loss is sustained in the separation of the mineral element of the sulfite waste from the organic matter. The organic matter in the solution, is valuable and the inorganic matter is not. Has anything been done for the separation of the elements? I am engaged in the sugar industry. I think the subject should be investigated separately from the mineral side, especially in sugar refining.

In the sugar industry the molasses is circulated in stills formed by parchment paper outside of which there is

a circulation of warm water. Supposing the mineral elements are carried off by the water and that there is a concentration of the organic matter in the stills formed of parchment paper. The other industries are amplifying the system for treatment of this kind. I never saw a sample of sulfite water but I think it would be very interesting. If the members of the Chemical Society have access to the solution they might work on the subject and interest the paper-makers in their line. Of course you must have the chemical section interest the paper section, it seems to me, but I do not want to take your time. It is a subject that came to my mind, that it might be interesting in that line. I myself have tried to think of a method sometimes, although I am not a paper-maker, but a chemist—tried to find a method of separating ink from paper. I have succeeded in getting a process for the mechanical separation of carbon—of the ink from the bulk—a mechanical process, and working on that line, I came into the meeting of the paper industry to see if I could find some information about that point.

MR. MILLSPAU: I think you paper people have a problem a great deal more important to you than some of your chemical problems. Mr. Wolf has spoken about the human element in your mills. It is very easy to get a cost system and a rating system that tells you your cost, but it is not worth the time taken unless it is taken intelligently. You have in your own ranks, every one of you, one or two young fellows, who have some education, high-school or otherwise, whom you could send somewhere for special training, to some college where they have a system of scientific management and training, where they could get all the details of how to put the system into the plant, and who would know how to operate it after it got there. We have a splendid system of cost-keeping, but to get the men for it that know something about the business in itself is another matter. I am going to make a suggestion that you start a scholarship—each mill—and provide every year for one or two of your young fellows, who will come back to you under contract. I have been following the paper mills for a great many years and I am frank to say that I never saw such a sloppy method of conducting costs as the average paper mill has—they simply *hope* they are getting ahead.

MR. GRIFFIN: I think the paper-makers should pay their chemists more before they establish scholarships. I have no complaint to make, but I am speaking for a lot of others.

MR. MILLSPAU: It is not the technical man, the chemist, he is more able to take care of his end of the game, it is the fellow who graduates out of the ranks into a clerical position who is able to analyze and keep track of your costs and show the other fellow how he is coming out—not merely a recorder of what is on the time card.

THE CHAIRMAN: Following Mr. Mills' suggestion I found it profitable to look upon our organizations as a whole as an educational institution. If you can't take the men at the plant and teach each man to do his job more intelligently you have failed in one of the main requisites.

MR. STEVENSON: I want to endorse heartily the last point that Mr. Wolf has made that it is up to the mill to educate its men and from my own experience I want to state this simple instance. I came pretty nearly getting fired from one position because I was found in another department seeing how the material was handled before it came to mine. I think attention paid to giving the men in one department an idea of the processes, no matter how simple they may be, will help them to carry out their own end of the shop more intelligently—

THE CHAIRMAN: If we are going to make progress in the plant each man must know the whole scheme of the thing. If he knows only one department he can't help the organization ahead. We encourage this in our organization and a great many other organizations are doing the same thing. Every man knows his place in the organization.

## MEDICINAL CHEMICALS IN AMERICA

HAROLD HUBBERT, *Presiding*  
Chemists' Club, September 29, 1916

THE CHAIRMAN: The list of articles placed on the prohibited list early in the war by the British Government embraces the majority of the products which we, in this country, would be compelled to replace by home manufacture in the event of war.

If we examine the situation that confronted us in the chemical field in 1914, the outstanding feature is that the quantity and quality of highly trained chemists, and especially of chemical engineers, was quite inadequate. For the rapid development of a new chemical industry, even one in regard to which considerable data is available in the literature, there is required highly developed research ability, enabling the works manager to be placed in early possession of the scientific information necessary for the erection of a semi-industrial installation. This, in turn, demands the services of an efficient chemical engineer, thoroughly conversant with sound engineering practice and possessed especially of plenty of common sense. There has never been a time when the American capitalist was more willing to invest his money, or, so to speak, "take a chance" on the development of some one or other chemical industry. It is to be regretted that, in a number of cases in this particular field, such failures as have occurred are, it is to be feared, directly attributable to the poor training received, either by the chemist in the scientific research work or by the chemical engineer on the industrial side.

A true coöperation between the university and industry can find no better exemplification than that shown in the development of the manufacture of salvarsan by the Synthetic Drug Company of Toronto. Immediately on the outbreak of the war, the Toronto General Hospital found itself practically without any of this material, and at once applied to Prof. McCallum, professor of biology in the University of Toronto, for his assistance in this predicament. The matter was taken up by Mr. McCallum, Jr., with the assistance of the university and of financial backing obtained in Toronto, and thanks to the fine spirit of coöperation shown by the university medical staff, the hospital force and the chemical workers, after some twelve months they were in a position to place on the market a product called by them diarsenol, which is claimed to be the equal of the German product. It is in this sense that we may look forward confidently to an increased coöperation between the medical departments of the universities and the workers in the industrial field. Furthermore, it is surely not an unreasonable request to make that those firms whose profits have been so abnormally swelled by the prevailing conditions of the last two years, should now come forward and subsidize such universities as are willing to devote some portion of their time and equipment to the development of the purely scientific, as contrasted with the commercial side.

At the outset, there were many difficulties to be overcome before progress could be made in the manufacture of new products in this field, but thanks to the efforts of several firms a supply of equipment (glass-lined autoclaves, containers, etc.) suitable for this purpose was soon available. It may, however, be noted incidentally that the price of such apparatus will have to be reduced very materially, if these firms expect to be able to compete with foreign manufacturers after the war.

What then is to be the future of the industry? It must at once be admitted that here also we shall have a case of the survival of the fittest, and it would seem that such survival will be conditioned by several factors: (1) The ability to manufacture all the raw products required. (2) A highly efficient technical staff. (3) A capable sales organization. (4) The existence of adequate home or foreign markets, or both. (5) Suitable tariff protection.

With regard to the first item, there ought to be no question, in view of the enormous increase in the output of coke oven by-

products, of obtaining an adequate supply of raw materials at a nominal price, and the industry might well begin to consider if it is assured of satisfactory safeguards along these lines.

MR. T. NARODNY: No country, with the exception of the United States, has so favorable conditions for chemical industry as Russia, as there is hardly a raw product that is not to be found in abundance in its territory. There are vast amounts of Glauber's salt, saltpeter and aluminates unexploited in the Caucasus, Ural and Altai Mountains. There is no mineral or metal that cannot be found there. Russia has imported, imports now, and will import chemicals of distinctly foreign origin, medicinal novelties mostly all the patent medicines, medical instruments, hospital supplies and products of this nature. Russia will continue to import dyes and dye substances, drugs of tropical nature and novelties. Russia has a high protective tariff on certain chemicals, expensive drugs, medicinal instruments, patent medicines, etc., while the tariff is low in fertilizers, chemicals needed for industrial purposes, etc., varying from 15 cents to \$5.00 per lb. The export of general chemicals to Russia is pretty simple, but that of medicines requires a special permit if the same is not handled by a Russian wholesale drug store or agent of chemicals.

As to the possibility of American chemical trade with Russia, I should think that the export of medicines, high-priced chemicals, patent medicines, novelties, dyes, surgical instruments and hospital supplies would pay. I do not believe that an American manufacturer of low-priced chemical products can stand the high ocean freight, the slow delivery, and the tariff, as compared with Russian-owned or European manufacturer. It requires at least three weeks for a shipment to reach Russia from here. Even should the freight become \$10.00 a ton from New York to a Russian port and \$3.00 from a port to Moscow, it certainly cannot compete with the freight of \$3.00 from Germany or \$6.00 from England, to Moscow, that can be delivered in a week.

If the American manufacturers of certain medicines are able to keep down the price, supply first-class goods, and comply with the Russian trade traditions, they, to my mind, have the biggest chance for a future trade with Russia. If started right away and carried on systematically, the American manufacturers of medicines, surgical instruments, hospital supplies and patented novelties could establish a permanent and large trade with Russia. For the coming ten or twenty years, Russia will be internally more interested in developing the steel and machinery industry, or the industry of such commercial chemicals as soda, ammonia, sulfur, etc., but will hardly have an opportunity to pay due attention to the production of medicines and goods connected with it.

As Russia has vast resources of all kinds of raw materials that are needed for chemical industry, cheap fuel and labor, it would be perhaps most profitable that the American firms establish branch factories over there. There are certain lines of chemical products which it would pay to undertake, particularly those of the coal-tar, crude oil, wood, etc.

A Russian drug store is quite a different establishment from an American. It looks more a semi-official than a private business concern. Instead of glaring signs, the Russian drug stores—*aptekas*—have the gilded eagle of the official establishments, and the name of the firm in small letters on the door or the window. Every drug-store manager must be a graduate of the pharmaceutical faculty of a university, and is considered a highly respectable public functionary, like a doctor or a judge. He sells nothing but actual drugs either to the prescription of a physician or independently. He cannot deal in stationery, soda water, cigars, dyes or products used for industry.

The Russian wholesale drug trade is carried on through large jobbers, commission houses or agents in the first place, and then through the provincial and district wholesale houses, in the second and third places. A country with 180,000,000 in-



habitants offers a large field of trade for the drug industry. Medicines are perhaps the most lucrative items of the chemical industry to export to Russia. The Russian drug and chemical market is now all exhausted and, as soon as the war is over, and the freight and exchange conditions get normal, there will be a rush for those drugs which the country needs most. If the United States and Canada are ready to grasp the opportunity of the Russian chemical trade right now, they can absolutely control it. The Russian Medical Department is ready to furnish the list of what is most urgently needed, and coöperates with the foreign importer of drugs and chemicals. It is said that Russia needs now most of all medicines connected with war hospitals.

Russia offers a special opportunity for the sale of surgical and clinical instruments, thermometers, rubber goods and hospital supplies. These were mostly imported from Germany and France, though there are a few establishments in Russia who produce some surgical instruments.

There is a big market for the rarer alkaloids such as atropine, scopalamine, aconitine, etc., in Russia.

Russia has very much crude oil but the oil industry is very primitive. The machines in the factories are driven by crude oil. They also need paraffin and gasolene.

EDITOR OF THE OIL, PAINT AND DRUG REPORTER (*Paper read by the Chairman*): The drug producing trade of the United States is in the midst of a transition period, the full extent of which cannot be realized until there shall have been made some comprehensive and definitive census of the number of establishments engaged, the number of workmen employed, the amounts of materials used and the valuation of the output, particularly for the past two years, or since the beginning of the European war in August, 1914.

It is perhaps unfortunate that the latest obtainable summarized statistics of the industry are those of the census of manufacturers of the United States for 1914—the first war year—but up to that time the growth registered in the output of druggists' preparations, patent and proprietary medicines, and compounds, and similar articles coming within the scope of the term "drug trade" was persistent. From a truly "infant industry" in 1850—sixty-six years ago—with 143 establishments, 827 workmen, \$1,427,375 invested, and an output of \$3,508,465 in products, the industry has grown to the more than respectable total of 4,082 establishments with a valued product of \$172,008,946 in 1914.

The fact that our manufacturers can not only supply their domestic demands—which have increased at least proportionally with the decrease of foreign importations since consumption has continued on an increasing scale here—but have been enabled to ship during the fiscal year ending June 30, 1916, \$129,666,580 worth of chemicals and drugs to foreign buyers is very indicative of the new importance of the industry to this country.

Conditions have been abnormal, it is true, but such was the normal growth of the drug trade prior to the war, and so great have been the changes and development of productive ability during the two war years, that it can be deduced with perfect safety that when the war shall be brought to its conclusion, products of American manufacturers for the drug trade will be marketed in every country in this hemisphere, Latin and Pan-American, Asia, Africa and even Continental Europe.

DR. COBLENTZ: The Food and Drugs Act has not succeeded in curbing the patent medicine trust. Tremendous lots of concoctions are consumed but they have received a very serious setback since the Food and Drugs Act. The values sold total a greater amount than foodstuffs consumed.

MR. C. E. VANDERKLEED: The sale of biological products such as serum, antitoxins, etc., would greatly exceed \$6,000,000 in 1913.

MR. HUBBERT: An examination of the papers contributed to scientific literature discloses the astounding fact that 46 per cent of the total contributions were on biological subjects. Thus the need of cooperation of the medical schools with the industry. There is considerable difficulty in getting suitable containers and glassware for storing drugs.

DR. COBLENTZ: There was no line of industry that was so hard hit by the war as the manufacture of medicinal chemicals. As soon as the supply ran out there was a general division of what was left in order to supply the demands. The market was soon supplied with a lot of low-grade and highly adulterated raw materials. The Central Powers took up all the barium and strontium in sight. Recently there was a lot of strontium offered on the market, which was found on examination to contain 50 per cent clay. Barium peroxide was on the market but could not be used, except in making a low-grade technical peroxide. In attempting to supply the wants, some of our American manufacturers are inclined to underrate the value of high-grade chemicals and without the aid of chemists will slam together anything and think that will answer. We have to be just as careful as the foreigners. The Germans are able to supply high-grade material, and we cannot afford to supply low-grade quality.

Belladonna and digitalis should be cultivated in this country at a profit. Another difficulty we encounter in endeavoring to supply organic medicinals is to get the manufacturer to manufacture raw materials, such as phenol and salicylic acid. What will become of us after the war comes to an end? Will we have tariff protection? We need phosphorus compounds. Where are we going to get these? We cannot get bromine. There are quantities of bromine in this country. If our own manufacturers could manufacture and import less we might be able to establish this line of chemicals and relieve some of the prices. This war has brought out chemical glassware superior to Jena ware, not only in resistive powers but in regard to weight. We are receiving to-day American ware that can be made of any degree of thinness and will stand any amount of rough usage. We are to-day doing better than Germany was ever able to do before. But we deal with many alkali substances and all have an erosive action on glass. Here are some results of some tests I have made:

Area in sq. mm. converted into sq. decimeters. Alkali content given as Na <sub>2</sub> O in milligrams per sq. decimeter surface. Time 50 hrs. Temp. 90° F.			
Ampoules, Resistive Glass.....	0.23 to 32 mg.		
Ampoules, Unknown.....	1.7		
Amber, Unknown.....	1.1		
Resistive Tubing.....	0.43 to 0.47		
Resistive Glass Tube, Ampoule.....	0.36		
Amber Packers.....	1.2 to 1.6 mg.		
Amber Packers, after washing with dilute acid.....	0.6 to 0.72 mg.		
Amber Packers, another lot.....	6.0 mg.		
Amber Bottles.....	1.2 to 1.5		
Amber Bottles.....	3.6		
Amber Bottles, washed with acid.....	0.13 to 0.8		
Green Packers.....	1 to 2 to 9.2		
Flint Packers.....	2.0		

MR. PIERCE: If bromine is so much desired, why is the price so low at the present time?

MR. COBLENTZ: Try to buy it.

MR. PIERCE: I had the experience of having been called in in the preparation of bromine. We got the bromine all right only to find that the price had dropped to \$1.15, which is the last quotation I know of.

MR. RAUBENHEIMER: Amber ware is really more soluble than the flint ware. Among chemists it is so understood. The manufacturers in this country do not pay as much attention to the alkalinity of glassware as they do in other countries. Every ampoule before using should be washed with diluted hydrochloric acid. Regarding supply of chemicals, I have frequently had the same experience. You cannot get bromine, even in small quantities. The same thing holds true with a great many chemicals. A short time ago I wanted 100 lbs. of precipitated sulfur and could not find a firm in greater New York who could supply it.

MR. MINER: When an effort was made to meet the demands of the canning industries in this country by furnishing glass enamelled ware, it was usually the case that the first demands were rather arbitrary. Slight changes in design would result in less cost. If an effort is made in this country to protect this industry in which we are all interested a standardization of process is necessary to permit the establishment of the apparatus industry. When you come to a tonnage basis you get down to figures that are satisfactory. For apparatus made on a jobbing basis, you must pay the price.

MR. McKEE: Investment has been so heavy in many cases that the manufacturers have stopped. It is not worth while to go into the manufacture in a case where your units have to be large and where you have to move away from a community in order to avoid nuisances, such as in the case of sulfur dioxide. It requires a large investment if we are going to use our by-products, and it is questionable whether it be worth the fight in some of these cases.

DR. COBLENTZ: It is the duty of Congress to take some action in regard to protecting these embryonic industries in this country, but no one is willing to invest time or money or trouble because of the everlasting question of tariff and protection. If the trade had been assured that there would be sufficient tariff to allow for a marginal compensation, the various factories now would increase their output and add to the number of articles produced. Most factories are putting up very cheap places and with an idea of using them to some other purpose after the war.

MR. YOCUM: It is difficult to establish what the commercial value of some of the supplies are. There is no reason that we should be dependent upon anybody outside of such a country as this. We have been in a hurry. The price of creosote oils has advanced greatly with no apparent reason. At the present time we are not importing in all probability as much as we did in 1914.

DR. COBLENTZ: It has interested me for some years why we imported so much and did not make more. There is no longer any beechwood creosote brought in from abroad. It is impossible to get a creosote that will come up to the U. S. Pharmacopoeia. We would like to see a real beechwood creosote once more.

MR. YORK: The specific gravity as given is very difficult to ascertain in the U. S. P. Nothing specifies what apparatus should be used or where the thermometer should be placed or anything about it. The next writing be more explicit in regard to this particular line.

MR. HIBBERT: Is it not possible for a manufacturer to compete after five years with other countries if they have succeeded in getting out a good material?

DR. COBLENTZ: We have cheap raw materials. It is a question of labor.

#### MISCELLANEOUS CHEMICAL INDUSTRIES: CONVERTIBILITY OF PLANT

WILLIAM H. GROSVENOR, *Presiding*  
Grand Central Palace, September 30, 1916

THE CHAIRMAN: The men criticising the works, those planning the works, and those utilizing the material from the works have a broader perspective frequently than the chemist who is engaged in some particular phase of the plant work, or than the corporate officer who is engaged in the overhead. Each of us can glean something from the other.

Convertibility of plant means convertibility not only to a pacific occupation, but such convertibility to a pacific occupation as will permit, if possible, the re-convertibility into the munitions of war. Our Government is taking very much more active steps, largely through non-Governmental agency at first, but taken up now by a definitely appointed Government Bureau—to preserve so far as possible and to develop as far as possible

the plants which are necessary for this country to have to preserve itself in case of trouble, so that convertibility from the war basis to the peace basis may expect to have such coöperation from the Government as can reasonably be expected in a democracy.

What we are all interested in, perhaps, is the specific instance, and as this is an experience meeting, it rests with the Chairman to confess first. In one company in which we are interested the convertibility problem came up almost simultaneously with the creation of the work. In planning the work it was remembered that this war might last but a few months. Our friends in Wall Street had told us that it would last but 8 months; the bankers said that it could not possibly last longer because there was not enough money to keep it going. Nevertheless, we felt it would be desirable so to plan the work that it could be run for some time, on the one hand, and that it could be as rapidly and easily shifted to a non-war basis as possible. Convertibility, therefore, presented less difficulty for us, and perhaps less difficulty than for many, because our work was not carried far beyond the raw material stage.

The industries other than those making new raw materials are faced with much more serious difficulty, but there are a great many of those industries, most of them small, that are very essential to our own national life if we are to be independent. We of a democracy are so apt to say that we are free people. As a matter of fact we are more absolutely enslaved, or were becoming more hopelessly enslaved to Germany, France and England than we would have been had any one of them possessed and administered our government. That may seem surprising, but men who have been professionally into the detail of the metal business far more than I have been able in the last two and a half years to tell me that in less than ten years Germany would have controlled absolutely the metal industry of the United States; that they were deliberately reaching out to obtain the control directly or indirectly of the metal industries, and we have since that time seen many evidences of it—not in any hostile spirit was this control sought, but purely as a matter of commercial existence—just as a country selects one or two products to be developed as a part of its policy.

The United States is planning to go so far as to give to certain firms different orders for different quantities of material, any material that enters directly or indirectly into the necessary war munitions and it is covering almost everything that is used in life, and giving these orders without bidding and without what would ordinarily be recognized as competition in order to preserve the ability and possibly the very identity of forms of business or methods of process that would be wiped out, perhaps, under normal competitive methods from abroad whether or not the tariff is in existence. There is, therefore, at Washington a rather clear recognition of the fact that we must hold together the nucleus of some of these industries that have been developed here or we will have to pay a very terrible price for our oversight when the time comes.

The country could not possibly consume in time of peace the explosives nor the automobiles we are making here to-day, although we are getting to be pretty strong on the consumption of automobiles. I was noticing some statistics in the automobile business the other day, because it touched our business a little and there is a surprisingly small amount going abroad to-day in spite of the railroad tracks that are lined with them on the western side of the city. The metallurgical industry has taught us chemists a little. They got together and not only told their problems but told their solutions and the metallurgical industry has advanced rapidly. We are altogether too secretive for the best interests of the business.

MR. H. A. LEVY: Can you propose a more reasonable way of coöperation to move away from the secret methods which have been prevalent among chemical workers?



THE CHAIRMAN: That has been proposed, but it will be necessarily a matter of growth. This organization, the Chemical Society, is a step in that direction, necessarily a hesitating step. It is something you cannot force. The American Institute of Chemical Engineers is perhaps more aggressive because the men who are members of the Institute have a certain greater degree of freedom as a consequence of the means of selection. They are men who are either running the industries in one capacity or another, owning them or managing them.

Also the Army and Navy Bureau has collected all this line of information. We have about 16,000 plants that are manufacturing material actually required or supposed to be required for military purposes. The Government is now able, without any red tape whatever, for the United States Government to step into any plant of the United States and take it over without any legal proceedings or anything else and make any of the necessary administrators of that plant officers of the United States Army and put the firm to work. What they are trying to do is to find out what can be done in the plant.

MR. LEVY: The point that I had in mind broadly, is that there are a number of concerns working along the same lines in different research work, laboratory work, and some of them are perhaps duplicating their work in their laboratories. I mean concerns having different research laboratories. The General Electric Company has avoided that by putting up a plant in Cleveland and purchasing a lot of plants in connection with it, and they are doing research work at one point. They are taking up research work where the other men left off.

THE CHAIRMAN: And yet it remains for an entirely independent organization having nothing whatever to do with either the Lamb Laboratory or the General Electric Laboratory or the Westinghouse, or any one of those companies, to turn out the work which has to do with replacing platinum wire in every lamp they make and I don't know how many thousand dollars they paid the people for the patents, but it was quite well up.

One of the large companies is getting into condition for nitrating a great deal of cotton, particularly linters for making nitrate cellulose. There is some talk of an effort to make a high-grade paper mill out of that plant later on.

MR. CLAUSEN: The question of cleanliness is of paramount importance and you couldn't use linters for that reason.

I have never seen linters cleansed from any possible speck at all.

THE CHAIRMAN: My understanding of their plan is that it is not so much to continue the use of linters as to continue the use of the plant on other grades of cotton or other grades of pulp for the manufacture of paper, leaving the plant as a whole earning some sort of interest on the investment, or running it for the purpose of paying taxes and employing the people they have been using and keeping them together as a unit. How far back into the lower grades of cotton they will go, or whether they will use linters at all, I do not think has been so much the discussion as it has been as to whether they can use the plant in some way and keep it alive and prevent it from going to rack and ruin.

MR. MOLOWITZ: Is the government also looking after the supply of the manual labor that will be necessary to manufacture the various products? Have you any idea of the percentage of men employed at present in the manufacture of munitions that might have to go back to peaceable employment again?

THE CHAIRMAN: It would be rash, perhaps, for any one man to make an estimate even though he had studied the question very carefully, but it hardly seems possible that the ratio should be less than 60 or 70 per cent, if by munitions you include all the parts which are now going into shells; but don't forget that the same machine that to-day is turning a screw for the nose of a trap, is perfectly capable of turning a screw for a typewriter or

a sewing machine, and many were making screws for typewriters who are now making screws for shrapnel, and will turn back to making screws for typewriters or sewing machines after the war. Of course there are the lathes, the particular processes and the turners, all that type of machinery, what we call machining tools; many of the special machines that are not so special that they cannot be used except for munitions, can also be continued in use after the war.

MR. MASSIE: May I ask along that line, is there any bureau, either private or governmental, which makes any effort to classify the men so that skilled people can know where they are needed?

THE CHAIRMAN: Not yet, but I hope to see the time in the near future when either under the Bureau of Commerce and Labor something of that kind will be done, or else under this Committee.

MR. JORDAN: As President of the Board of Education in my town I conceived the idea a great many years ago that we should supplement our manual training and domestic science and that class of things taught in the school, first with a primary industrial school, which would take the children and educate them naturally into differentiating colors and sizes and shapes of things, taking textiles generally. I devoted more time to the things connected with textiles, dyes, spinning, and things like that, and then I established and got the City Council to agree to support, if we furnished the building and the material, an Industrial High School. This Industrial High School commenced a three years' course, devoting four hours each day to academic work, and four hours each day to manual work and it was for both men and women, coeducational. And at the end of that time if they had worked for some institution for a month, and we have had daily reports of their work, that entitled them to a graduate's certificate. So far our waiting list has been very crowded—through these efforts we have taken boys, some of them who have failed to move up in grades in the academic high school, who upon their graduation have received as much as three dollars a day the first day.

I think something should be done all over the United States to ascertain from everywhere what the people are doing, so that we can say to these graduates that they will have an opportunity. For instance, I get my gardener through the government, through the Labor Distribution Bureau. He is a foreigner, I am sorry to say—either an Englishman or a Frenchman or a German or a Swede—but he comes from the Government—I wrote to the Labor Bureau Department for him. It helps the man, and it helps me. Now, that ought to be carried by the Government to a higher plane than it is on now. I think that supplemental to that there should be an investigation by this Association, or by someone, to find and ascertain all over the country if there are capable natives—capable citizens, whether foreign born or native—and that they should receive the first consideration for employment by all manufacturers in the positions of profit and advancement.

MR. MOLOWITZ: Will the pay of the munition workers be governed by the Government in case of war?

THE CHAIRMAN: That has not in any way been touched upon, except that the statute says that these orders may be placed without bidding and at a fair price, and that it shall be obligatory on the people to make the stuff and it will be fine and imprisonment if they do not.

I don't feel that any question of that kind would ever come up. There are no more patriotic men than our laboring men in this country. The difficulty as I see it is not with the laboring man, but it is his walking delegate who is peculiarly lacking in any idea of patriotism in so many cases. I do not think it is the fault of the laboring man, and I think it is no criticism adverse to the

members of the unions that we find the unions in the aggregate so diabolically arrayed against law, order, patriotism, the militia and everything else.

MR. ADAMS: Is not the American League doing something in that line?

THE CHAIRMAN: It was the American League I had in mind, and they are doing a great deal in that line, although lacking Government coöperation and driving support, as yet, but I think it definitely planned to co-ordinate that with the Federal movement.

MR. ADAMS: They have no connection with the Government as yet.

#### RESOLUTIONS ADOPTED (OFFERED BY MR. JORDAN)

Recognizing the laudable and growing movement throughout the Union to educate the youths of the country industrially and scientifically, and believing that Americans should be encouraged in securing and filling the more important responsible positions in the establishments desiring such employees, and knowing this would in turn be serviceable to the industrial establishments themselves;

*Be it Resolved*, That this Society urge upon the Government and will co-operate with it in making a thorough investigation along this line to the end—

- (1) Ascertaining the extent of the movement named; and
- (2) To assist both the employer and the employed in bringing them together on the lines indicated above.
- (3) That this Society urge upon the Government to co-operate with it in making investigations to accomplish the purposes of this resolution."

(OFFERED BY MR. MASSIE)

WHEREAS, The permanent and efficient growth of American industries requires a constant and growing supply of specially trained employees, and

WHEREAS, The proper assimilation of the country's personal talent, both native and foreign, equally require the proper placing of individuals in localities and in work where their training and ability will be most productive to themselves and to the general welfare of the country.

*Resolved, Therefore*, That we earnestly urge the United States Government to provide an adequate special Bureau, the duty of which shall be to investigate the demands and needs for employees of all kinds, to inventory and classify so far as possible all persons, both native and foreign, needing or seeking employment, and to assist in bringing the employers and possible employees in contact with each other.

MR. POTTER: While the resolution offered covers what we wish to convey to the Government, if the Society expects to go forward with it, it seems to me that besides passing this resolution it is very essential that a Committee be appointed who are competent to handle the matter, confer with the proper officials and follow it up—otherwise it is apt to be "gratefully received" and filed among the archives and nothing heard of it again. But if there is a Committee to present the matter and ready to co-operate and advance definite suggestions as to what is to be done, perhaps there is a chance of getting somewhere with it, and I suggest that such a Committee be appointed after deliberation, and that men be chosen who are best in a position to give their time and some weight of authority to the proposition.

THE CHAIRMAN: You have heard the suggestion. It may be considered as placed in the form of a resolution for action, that such a committee be appointed. I think a simple motion that such a Committee be appointed would cover it. Do you so move?

MR. POTTER: I so move.

This motion being duly seconded, was unanimously carried.

THE CHAIRMAN: I take it that you would prefer in this case, from the form of your statement, that the usual practice be not adhered to of appointing the maker of the motion the Chairman of that Committee, or of appointing the Committee at this time.

MR. POTTER: That is correct. I personally would not be in a position to undertake it, and I think the Committee should

be appointed after careful consideration and should be a Committee appointed to really do something in behalf of the Society.

THE CHAIRMAN: And preferably, that the Committee be appointed by the Council of the Society so that it would have official recognition.

## OILS AND MOTOR FUELS

R. F. BACON, *Presiding*. Chemists' Club, September 30, 1916

R. F. BACON, *Chairman*: Some of the problems that we want to talk about are: relation to motor fuels; lubricating oils; petrol industry. The great problem is flexibility in refining. The ideal situation would be one where the refiner could take any crude and make from that crude just exactly the products demanded. Our biggest need is for gasoline. There has been a tendency lately to increase the production of casing head gasoline, but there is a feeling that such blended gasolines are not as good as straight cut.

DR. MABERY: Crude oils must be thoroughly understood. Laboratory methods have proceeded about as far as they can go. Refining is necessary. We need funds to carry out the affair. We shall find things in petroleum that we do not know about. We need to know what the refiner is doing, his methods, etc. The general public does not care how the crude oil is refined so far as it answers the purpose. The consumer does not know how to select the product that is used in the machine. What is necessary to bring out that work? There should be a line of individual investigation of motor oils and fuels carried out on a broad scale. All products should be taken up and examined thoroughly, including frictional tests. Machines should be constructed that will show these tests. In that way every product that is placed on the market can be standardized, and there should be a regulation by law just as with fertilizers. After the man is instructed as to the different grades of lubricating oils he should know by the oil he selects that he is getting the most suitable oil, so that he will get the best value out of his product. Institutions ought to take up this investigation. A laboratory is needed that can follow out these investigations on a large scale, to become public property. So far as refining is concerned, it depends to a large extent on the way the refining is carried out. Not altogether on the composition of the oil but what has been learned by actual experience. (Display of three or four lubricants. One sample sold for \$100 per gal.) The important point in lubricants is the wearing quality and I am convinced that the theoretical end of it is first. There should be broad investigations concerning the quality of every lubricant that is on the market. And the results should be stated in such a way that the laymen can understand them. The time has come now when research has got to take hold of the petroleum industry from start to finish. Nothing leads to that better than competition. Where there is competition we may be able to introduce products that will determine their value. We need a larger supply of gasoline that will hold the price where it is now for there are indications of the price going higher unless we have something on hand to cut it down.

THE CHAIRMAN: I would suggest that students in the universities be put on some one phase of the petroleum field. In crude oils we have thousands of compounds that have never been found out about. Refining companies would be willing to make the preliminary fractionation and the products could be turned over to laboratories.

DR. MABERY: Regarding lubricating oils—we cannot depend on the specific gravity or viscosity. The best test that can be made of any oil is to distill it in vacuum to avoid decomposition and then determine the specific gravity of the distillates. There has got to be some standard. In the first place, the general public is entitled to know the source of the oil. General tests



of the oil should be made; then worked out in a practical way on a starting motor car with a testing machine running along with it, to show its actual value. That should be adopted as a standard from which to value any particular oil referred to. It thus comes down to determining the durability practically and scientifically.

DR. DAY: Shall we get out a government report, describing in detail standard products for comparison? In the past more has been accomplished through means of specific brands guaranteed by private manufacturers.

DR. SALISBURY: Standardization should begin with the raw material and not with the finished product.

THE CHAIRMAN: Only from good crudes can be made good lubricating oils.

DR. SALISBURY: There are better lubricating oils to be made from certain crudes. What are those crudes? What is their character? Can other crudes be brought to the point where these crudes are brought? You will get a different product from every crude. Can anybody tell me how to get a better emulsion? I am using simply finished products. The standardization we get is a commercial one and not a standardization of service.

DR. KELLEY: Dr. Mabery did not say anything about the temperature at which the viscosities are to be taken or change of the viscosity with the temperature in the examination of the different cuts. Oil loses viscosity rapidly with the rise in temperature.

DR. MABERY: The value of an oil depends on its elastic quality. Viscosity determinations of the oil are the only way it can be done, to get the consistency of the lubricant and see what the oil should be considered to do. The matter of color has to do much with the same principle.

DR. DAY: What lubricants hold up best?

DR. MABERY: I do not know positively.

DR. BAKER: Tests on lubricants do not tell you anything, Dr. Bacon has said. I cannot agree with that. Tests do infer something in so far as their application to lubricating goes. Many people make tests and are unable to interpret the tests. Dr. Mabery has suggested standardization. This would be alright if our crude oils were uniform and if the refiner could always get the crude he wants. Frictional tests are good, but if we consider frictional tests they would have to be based on one specific purpose. Cylinder oil and gasoline would not be tested on the same machine. Dr. Day says brands are not uniform. Brands do run practically uniform in our experience.

DR. DAY: How would you identify the oil?

DR. BAKER: There are certain characteristics in the oils, and if this oil is run under one condition it may be possible to get one result, where if it is run under another condition you may get another result. I was called in to see what was causing an emulsion in a certain system. The oil was used for engines and emulsified. I examined the original oil, and they had used about 1000 barrels in the system. But the system had not been cleaned for 6 or 7 months. The emulsion was due to organic substances getting into the oil.

MR. W. F. PARISH: (Brought up points that would tend to show that specifications covering the product for use of lubrication oil are of disadvantage, entirely on account of the fact that mechanical conditions of the machine are constantly varying factor.) Difficulty is always experienced in getting machine users to use exactly the proper oil or to maintain the use of the proper oil after it has once been demonstrated that a fixed lubricant will give the highest results. The machine or motor user is not primarily interested in the question of lubrication even if he is told that a certain standard would be necessary for his motor. The difficulty would be that the motor would very likely change very rapidly, which would require a different standard.

DR. CONRAD: Dr. Mabery's suggestions are all right. When you come to the refiner's point of view, what are you going to do? Refiners at Franklin try to get the fuels as uniform as possible. Once in a while you get an oil that is supposed to be the same, but sometimes they miss it. Durability and lasting quality is necessary. In turbine service they need an oil that lasts longest, sometimes weeks, months and years. The oil that lasts longest is the cheapest. There is a great field for the universities and schools, also the Bureau of Standards, in this line. Oils from different fields show different characteristics. How will you ascertain which is the best? There has been great improvement in the refining processes since ten years ago. In fact, ten years ago we did not know much about lubricating oils.

THE CHAIRMAN: Are there any processes that make gasoline other than the pressure process in which one obtains a product that is not too unsaturated to refine?

DR. GRAY: Gravity has nothing whatever to do with the properties of a crude oil. Gravity of the gasoline varies with the crude. The distillation test is the same for every one of the gasolines so that distillation tests should be used instead of gravity tests.

MR. ROBBINS: Gasoline of high specific gravity has more power than gasoline of light Baumé gravity. Power back of a light gravity gasoline is greater per pound than the heavy.

MR. RITTMAN: Dr. Bacon asked about gasoline savers. The gas savers used are kerosene vapor or a heavy gas vapor, with added materials such as camphor, naphthalene, nitrobenzene, and some even use the explosives nitroglycerine and trinitrotoluol. The eastern part of the United States are using a very inferior quality compared with other parts of the country. The end-point may be as high as 450 to 500° F. The mid-continent insist on an end-point under 425° F., whereas the Pacific Coast insist on an end-point under 375° F. The tendency throughout the country as a whole is to use heavier gasoline. In other words, the gasoline can is chiefly filled with kerosene.

The design of the engine is extremely important in the use of gasoline. The old type of manifolds had a lot of exposed surface before the fuel reached the engine. This was very inefficient because the heavy parts of the gasoline would condense and not be available for consumption. New types of automobiles all have compact manifolds in which the vapors are not condensed once they have vaporized.

The oils from different countries vary widely. A gasoline made by cracking Kern River crude contained as high as 25 per cent aromatic hydrocarbons and under careful auto test gave a mileage of 30 per cent greater than a straight run gasoline with paraffins. Argentine Republic oil, on the other hand, produced a gas very low in aromatic and high in paraffins. Japanese oils were different from either of these.

Motor fuels are of commercial value. Many experts throughout the country are working on this problem, using every conceivable kind of apparatus and processes. Their efforts are earnest and the result can only be success. I absolutely believe that the motor fuel problem is a thing of the past for several years to come at least, despite the fact of the great increase in the number of automobiles.

DR. R. E. HUMPHREYS: We are using 300 stills at Whiting, Ind., with a charge of 250 lbs. each. Much time has been spent on the by-product asphalt which is produced in connection with the use of the Burton process. This asphalt approaches very closely the asphalt produced in South American countries. It is not greasy, and, all told, has been found superior to the asphalt formerly produced by blowing air through the residuum from mid-continent oils. This material is largely used in the vicinity of Chicago from oils produced in the mid-continent field. I do not believe that we need fear a shortage in motor fuels.

## SECOND EXPOSITION OF CHEMICAL INDUSTRIES

The Second Exposition of National Chemical Industries took place September 25th to 30th, occupying two floors in the Grand Central Palace, New York City.

At the opening meeting Mr. Charles F. Roth, one of the very efficient managers responsible for the organization of the exposition, introduced the speakers.

Dr. Charles H. Herty, President of the American Chemical Society, explained that it had been the fixed determination of the managers and advisors of the exposition to make the chemical show a place for earnest men of the country to bring together their products, not for the purpose of boasting, but to demonstrate their ability to meet the situation and thus to afford inspiration for the future. In other words, the exposition was planned to be not only a showing of what had been accomplished, but also the assembling of resources of the nation concerning which expert representative men of the various industries could consult and give and obtain expert advice. Such displays will undoubtedly bring about coöperation of state govern-



ments, railroads and national government by setting forth how the resources of the nation may be best put under chemical direction, for the primary responsibility for the development of these resources rests chiefly upon the chemists of the country; that the necessity of such coöperation is required by other nations is indicated by the recent unification of the dyestuff industries of Germany and the chemical conference of the allies, during which they agreed to interchange technical knowledge in place of continuing individualistic efforts as heretofore.

Dr. Lawrence Addicks, President of the American Electrochemical Society, called attention to the development of the electrochemical industries from the modest beginning of electric batteries to manufacturing processes that require the highest type of chemical engineering. Electrochemistry has the peculiar character of forming the meeting place for electrochemists, physicists, metallurgists and physicians, thus helping to break down the barriers between so-called pure science and engineering. The high prices of the present time are constantly bringing about fields of new uses for materials and especially the lower grade materials which must necessarily replace the shortage of the higher priced ones. In the great awakening that has brought about coördination of industrial resources for national defense, Dr. Addicks considers the accomplishments up to the present as merely an earnest of what is to come.

Mr. Thomas J. Keenan, Secretary of the Technical Association of the Pulp and Paper Industry and Editor of *Paper*, spoke in place of President Daniels of the American Paper and Pulp Association.

"The papermaker stands next to the highest place in the

industrial world, for the latest census of manufactures shows that in America the manufacture of paper is second in importance only to the steel industry. The total invested capital is estimated at \$500,000,000, in round numbers, while the annual value of the manufactured product—pulp and paper—amounts to \$350,000,000."

Dr. Ira Remsen, formerly president of Johns Hopkins University, was enthusiastically received by the audience, and expressed his desire to have it thoroughly understood that he had always been interested in chemical industry in spite of the numerous statements that had been made to the contrary. The truth of the matter was that his contributions to chemistry had been at the other end of the line, since it had always been his belief that industry grows only when science grows.

Mr. Adrian Nagelvoort, co-manager of the exposition with Mr. Roth, called attention to the fact that the industrial developments of the last year were possible only in such a country as America, a notable instance being the fact that the dyestuff firms of the country are now making 75 per cent of the quantity needed in 1913. The audience was then invited to visit the various exhibits of the "Second Chemical Show."

Unusually attractive features of the exposition were the moving pictures, shown every afternoon and evening, illustrating the processes of manufacturing a wide range of products. Acknowledgment was made to the Bureau of Commercial Economics for their collaboration in this program. These pictures included the following:

Manufacture of Iron and Steel Tubing, Black Powder, Fertilizers, Iron, Silk, Blotting Paper, Varnish, Silver Mining, Asphalt (Barber Asphalt Co.).	Do it Electrically.
American Chemical Society, April, 1916, Meeting. Leaving Danville, Ill., Chamber of Commerce Building.	Telling the Forest.
Industrial Plants on the Clinchfield Route (Carolina, Clinchfield & Ohio Railway).	Safety First.
Bureau of Mines.—Iron Mining Operations, Manufacture of Coke. Mine to Molder. Safe Method of Bituminous Coal Mining. Mining Magnetic Iron Ore. The Shooting of the "Lake View Crusher." The Manufacture of Portland Cement. Zinc Mining, Milling and Smelting. Dredge Gold Mining. Copper Mining, Milling and Smelting. Mining and Extraction of Radium from Carnotite Ore.	Light from the Rocks.
Westinghouse Electric & Manufacturing Co.	Striking a Light—Matches.
Mining and Smelting of Copper (United States Smelting Co., Inc.).	Irrigation in Southern Alberta.
Motor Manufacture (General Electric Co.).	Queen of Yuma—Water Power.
Distillation Apparatus (E. B. Badger & Sons Co.).	
Filtration of the City Water Supply and Disposal of the City Sewage, City of Baltimore.	
Water Powers on the Pacific (Great Western Power Co.).	
Petroleum from a Mexican Oil Well, accompanied by discussion by I. C. White, State Geologist, West Virginia.	
Manufacture of Paper.	
Making of Fine Tools.	
Dynamiting the Farm with Profit.	
First Aid in the Home.	
Sands That Serve.	
Time from the Stars.	
Manifold Uses of Concrete.	

### EXHIBITS

**Paul O. Abbé**—Grinding machines (ball or pebble mills), heavy, light and sifting mixers, improved rotary cutter.

**Abbé Engineering Co.**—Working models of the Abbé tube mill showing "Ideal" spiral feeder, double porcelain jar mill, special combination porcelain jar mill; section of pebble mill showing removable manhole frame with detachable flanges.

**Alberene Stone Co.**—A laboratory installation of bench, gas hood, and sink made of Alberene stone, various samples of cut stone, soapstone linings for pulp furnaces.

**American Apparatus Corporation**—An exhibit of laboratory furniture, laboratory apparatus and glassware in general, and American-made porcelain ware. Also Riche calorimeters, Lenzman-Kober colorimeter, Stokes water still, cement and oil testing apparatus, electric heating appliances, autoclaves, thermometers, hydrometers, etc. By way of novelty, a 50-gal., oval-shaped glass flask with 1/16-inch wall.

**American Chemical Society**—Journals published by the Society, charts indicating growth, and a dummy of the 3-vol. decennial index to *Chemical Abstracts* now in course of preparation.

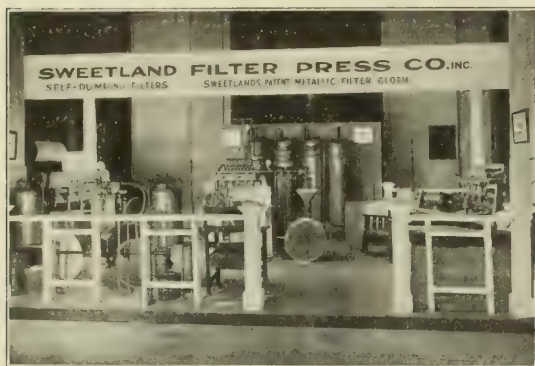


**American Coal and By-Product Coke Co.**—Model of flueless oven, a wall brick, illustrations of certain by-product apparatus, and colored, diagrammatic sketch of the Roberts method of destructive distillation of coal and method of by-product recovery.

**American Electrochemical Society**—An automobile, stripped, with descriptive placards attached to various parts, purporting to show the economic effect of electrochemical products on modern industry.

**American Institute of Mining Engineers**—A booth for visitors.

**Arnold, Hoffman & Co.**—Products of the Mathieson Alkali



Works, Castner Electrolytic Alkali Works and the Nitrogen Products Co., for whom they are sales representatives.

**Atlantic Gulf & Pacific Co.**—An information booth.

**E. B. Badger & Sons Co.**—Exhibited photographs and drawings of different installations and chemical plants designed and manufactured by them; also a sample copper apparatus.

**J. T. Baker Chemical Co.**—"Analyzed Chemicals," C. P.

**City of Baltimore**—A miniature reproduction of the city showing its harbor and dock facilities.

**Barber Asphalt Paving Co.**—Showed a complete line of the Barrett refined coal-tar distillation products, synthetic products made therefrom, useful to the dye, pharmaceutical and photographic trades; also numerous specimens of customers' manufactured articles. Different grains, growth of which had been promoted by using their sulfate of ammonia with potash and phosphate.

**Bausch & Lomb Optical Co.**—Apparatus for micro-photography, lanterns for lectures, and samples of their made-in-America optical glass.

**Beach-Russ Co.**—Exhibited jointly with the Abbé Engineering Co. De Rycke centrifugal steam separator and grease extractor, acid pump, and a showing of interior of their rotary vacuum pump. A No. 4 rotary pressure blower in operation, pumping up a pressure of 10 lbs.; model of a filter press. A demonstration of their high vacuum pump, exhausting a red liquid and pulling it up a 34½ ft. graduated glass tube to within 0.1 in. of the barometer reading.

**W. Becker's Aniline & Chemical Works**—An exhibit of all the most important aniline dyes and intermediates as well as textiles, carpets, leather, headwear, paper and other goods dyed exclusively with American dyes made by them from American raw materials.

**Bethlehem Foundry & Machine Co.**—Nitric acid condensing apparatus, fume pipes, anodes and cathodes all made of tant-iron; also gray iron apparatus such as nitric acid retorts, nitration, reducers, sulfonators and acid eggs.

**The Bristol Company**—Complete line of indicating and recording instruments and pyrometers, thermometers, etc., featuring their new continuous flow wet and dry bulb recording

thermometer or psychrometer and demonstrating their automatic temperature compensator for Bristol's electric pyrometers.

**Brown Instrument Co.**—Stationary and portable electric pyrometers, recording thermometers and automatic heat-control instruments for furnaces, retorts, etc.

**Buffalo Foundry & Machine Co.**—A vacuum drum dryer in operation reducing a sulfite waste liquor of 50 per cent moisture to a dry powder, and bottles of various materials made with the dryer. Factory size of nitrator, caustic pot, sulfonator evaporator, vacuum shelf dryer, fusion kettle, crystallizing pan also built for vacuum, nitric acid retort and condenser; autoclave, 1000 lbs. working pressure; laboratory size autoclave.

**Butterworth-Judson Corporation**—A line of heavy chemicals, oxide of alumina, iron nitrate, tin crystals, sodium phenylate, benzol sulfonate, etc.

**The Carborundum Co.**—A line of manufactured products showing the uses of carborundum, including grinding wheels for all purposes, sharpening stones, abrasive paper and cloth, cast silicon chemical ware, carborundum pyrometer protection tubes, dental wheels and goods for dental purposes.

**Carolina, Clinchfield & Ohio Railway**—Products made and natural resources located along the "Clinchfield Route." In the same booth was the exhibit of the Federal Dyestuff & Chemical Corporation.

**Carrier Engineering Corp.**—A "Carrier" air conditioning and drying equipment in operation.

**Celluloid Zapon Co.**—Different applications of "Zapon." Lacquers and enamels applied. Leather cloth was displayed in the same booth by the Zapon Leather Cloth Co.

**Central Foundry Co.**—"Universal" cast-iron pipe, bolts, etc.

**Chemical Catalog Co.**—Showed the 1916 edition of the "Chemical Engineering Catalog."

**Chemists' Club**—A booth for visitors.

**Coatesville Boiler Works**—Exhibit of materials used in their tanks, boilers and stacks. Photographs of their steel plate work for chemical manufacturers.

**E. J. Codd Co.**—Chain screen doors demonstrated.

**Condensite Company of America**—A display of printing plates, auto ignition apparatus, the Edison disc phonograph



record, miscellaneous electrical ignition apparatus, moulded Condensite parts as applied to various apparatus.

**Contact Process Co.**—Exhibited a line of their products including mixed acid  $\text{HNO}_3$  (42°), *Aqua fortis* (41½°), oleum (50 per cent), salt and nitre cake, etc.

**Corning Glass Works**—A complete line of glassware including "Pyrex" chemical ware and transparent oven ware, lenses, optical glasses, lamp chimneys, lantern glasses, tubes, etc.

**Corn Products Refining Co.**—A line of various corn products such as dextrines, starches, corn syrup, Karo, etc.

**J. H. Day Co.**—Hunter's New Sifter and Mixer; Pony mixer (8 gal.); models of sifters, mixers and pulverizers.

**DeLaval Separator Co.**—The DeLaval Clarifier and Filter; specimens of unclarified and clarified oils, medicines, grease, etc.

**Denver Fire Clay Co.**—A complete line of assayers' and chemists' supplies including crucibles, muffles, scorifiers, a



pulverizer, crusher, cupel and laboratory flotation machines, assay and melting furnaces, etc.

**Detroit Range Boiler Co.**—A line of metal bilge barrels.

**J. P. Devine Co.**—Exhibited the first vacuum double drum dryer made in America, in operation; working models of a dry vacuum pump and a surface condenser; also a high pressure (1000 lbs.) autoclave and a nitrating kettle.

**The Dorr Company**—Working model of three-deck washing classifier operating on a combination of silica sand and indigo dye; also models of a thickener or continuous settler and an agitator or leaching tank.

**The Dow Chemical Co.**—Chemicals, including synthetic indigo, dye intermediates, chlorides, bromides, etc.

**Downington Manufacturing Co.**—A model of the Miller duplex beater for pulp or nitrocellulose, in operation, and a small beater, laboratory size; also some yellow-pine products of the Empire Chemical Co. recovered by the Clope process.

**Driver-Harris Wire Co.**—"Nichrome" products: castings, carbonizing and heat-treating boxes, pyrometer protection tubes, and baskets of various sizes for metal cleaning, dipping and heat-treating processes.

**E. I. du Pont de Nemours & Co.**—Chemicals and mixtures for industrial, medicinal and laboratory uses. In the same booth Fabrikoid, a leather substitute, and also the topping fabrics of the Fairfield Rubber Co.

**Duriron Castings Co.**—Acid, alkali and rust proof castings and apparatus; agitator kettle, nitric acid condenser. Demonstration of a 1½-in. centrifugal pump.

**Thomas A. Edison**—Organic and inorganic chemicals; coal-tar products; motor-truck size of alkaline battery.

**Eimer & Amend**—A complete exhibit of laboratory supplies including the Barnstead automatic water still electrically heated, Freas electric oven and vacuum oven, Emerson adiabatic calorimeter, Zeiss photomicrographic outfit and a line of multiple replaceable unit electric furnaces of the muffle, crucible, tube and organic combustion types; also Fry and Pyrex laboratory glass-ware and Coors Colorado porcelain ware.

**Electro Bleaching Gas Co.**—Chlorinating apparatus, samples of caustic potash, muriate of potash, para-dichlorobenzol, monochlorobenzol, etc., and fabrics bleached with liquid chlorine.

**Electro Chemical Co.**—An exhibit which dealt with electrolytic bleaching showing finished and unfinished bleached products such as paper, hole-proof hosiery, etc. Models of a laundry unit and a paper mill unit.

**Electrolytic Zinc Co.**—Samples of electrolytic zinc, magnesium powder (99.5 per cent pure) and aluminum dust.

**Electron Chemical Co.**—Photographs of installations of the Allen-Moore electrolytic cells.

**Elyria Enameled Products Co.**—Enamel lined mixing kettle with special oil jacket for high temperature work, enamel lined apparatus for experimental and industrial use. Models of high-speed agitators. Demonstration of resistance of enamel to sudden temperature changes.

**The Fabra Co.**—Information booth.

**Foote Mineral Co.**—An exhibit of the "unusual" ores, *i. e.*, ores of the rarer elements such as molybdenum, zirconium, tungsten, tantalum, uranium, thorium, etc. Laboratory ware manufactured from zirconium oxide. Stereomograph views of various mines including new American monazite deposits.

**The Foxboro Co.**—Recording and indicating instruments.

**Franco-Swiss Colours Co.**—Dyestuffs, and a demonstration of actual dyeing to prove their qualities.

**Freeport Sulfur Co.**—Samples of crude sulfur mined by the Freeport Sulfur Co. Sectional views of samples of sulfur-bearing rock showing the sulfur in its native form.

**Chas. F. Garrigues Co.**—Samples of chemicals used in connection with manufacture of explosives. Steel barrels of Draper Manufacturing Co.

**Geissinger Regulator Co.**—Demonstration of industrial temperature-control system for heat-control work; conveyor type ovens and large flue dampers in super-heaters.

**General Bakelite Co.**—Initial ingredients and various raw Bakelite compounds prepared from same. Electrical and mechanical applications of Bakelite.

**General Chemical Co.**—Complete line of atmospheric nitrogen products, Baker & Adamson C. P. chemicals, and dye intermediates of the Benzol Products Co. The Ryzon Baking Powder Co. exhibited their baking powder and its three ingredients.

**General Electric Co.**—A booth for inquiries.

**German-American Stoneware Works**—A full line of chemical stoneware including stirring and mixing apparatus, Meyer condensing tourill, 520 gal. storage vessel, and cellarius tourill. Also exhibited automatic acid elevator, suction filter for vacuum, chlorine generator, centrifugal pump, condensing coil, armored



exhauster (stoneware lined), revolving damper, gas cocks, pipe, and some magnesia ware.

**Glens Falls Machine Works**—A Tromblee & Paull rotary sulfur burner.

**Golden Chest Mine**—Tungsten ore from Murray, Idaho.

**Great Western Power Co.**—Photographs and information relating to the hydroelectric developments and possibilities of the electrochemical industries on the Pacific coast.

**The Emil Greiner Co.**—Scientific instruments, chemical glass-ware, thermometers, hydrometers, volumetric apparatus.



**Hardinge Conical Mill Co.**—A working model of their continuous ball and pebble mill; a stereomotorgraph showed pictures of various installations.

**Harrison Bros. & Co.**—A display of chemicals used in the manufacture of pigments, dyes and paints for fire works, linoleums and textiles.

**S. F. Hayward & Co.**—Exhibited a line of fire extinguishers, chemical engines, "Hayward" respirator, Maxwell Peerless



emergency fire hood, gas helmet, safety goggles, pure air supply apparatus to work in poisonous gases any length of time, and an oxygen reviving outfit.

**Frank Hemingway, Inc.**—Industrial chemicals, coal-tar products.

**Herold China & Pottery Co.**—Coors U. S. A. chemical porcelain for laboratory testing.

**Herman A. Holz**—Beighlee pyrometer equipment (180° deflection angle—12 in. scale) and portable Brinell meter. Samples of rhotanium as a substitute for platinum.

**Hooker Electrochemical Co.**—Samples of caustic soda, bleaching powder, monochlorobenzol and muriatic acid.

**Huff Electrostatic Separator Co.**—Electrostatic ore separator for minerals of all kinds; plumb pneumatic jig for same purpose.

**F. C. Huyck & Sons**—Advertised Kenwood Felts by pictures and pamphlets. Showed samples of woven woolen filter cloths.

**Industrial Filtration Corporation**—Rotary continuous vacuum filter in operation; model of the movable cell type applied to open tank filtration; working model of rotary thickener and clarifier.

**International Equipment Co.**—Laboratory centrifuges.

**International Glass Co.**—A full line of their American-made "Insol" beakers and flasks; also glass tubing, burettes, pipettes, weighing bottles, condensers, condenser tubes, stopcocks, separatory funnels, and special blown ware.

**Kieselguhr Company of America**—"Sil-O-Cel" in brick and powdered form with a practical demonstration by means of the torch test. There were stereomotorgraph views of the mining and preparation of "Celite."

**F. Kleinschmidt & Co.**—A model rotary evaporator.

**A. Klipstein & Co.**—Coal-tar dyes (indigo, sulfur shades, rhodamine, etc.), potash, varnish gums, oils, tanning materials including their "Oxi-tan," samples of leather, etc.

**H. Koppers Co.**—A model coke oven, and the primary by-products of coke made from various coals.

**L. O. Koven & Bro.**—A 450 sq. ft. Kelley filter press.

**The Laboratory Supply Co.**—A complete line of laboratory porcelain and glassware; Ohio Pottery Co.'s "Circle S" porcelain and also "Solno" chemical glassware.

**Lead Lined Iron Pipe Co.**—An exhibition of lead-lined iron pipe, valves and fittings for use with acids. A 16-in. lead-lined iron pipe used for hot sulfuric acid was of particular interest.

**Leeds & Northrup Co.**—A display of the following: Vreeland Sine wave oscillator; electrolytic conductivity apparatus; electrometric titration apparatus for determination of chromium and vanadium in steel and other alloys, in operation; indicating and recording pyrometers; complete bridge equipment for measuring electrolytic conductivities; apparatus for determination of hydrogen-ion concentration; portable wheatstone bridge, galvanometer; sensitive galvanometer with lamp and scale; constant speed high frequency generator.

**Lehigh Car, Wheel and Axle Works**—Samples of car wheel steel after different treatments. A model of the Fuller-Lehigh pulverizer. Fuller Engineering Co., and Lehigh Stoker Co., design and construction of grinding plants; Lehigh Foundry Co., acid-resisting casting.

**Life-Saving Devices Co.**—Demonstration of "Lungmotor."

**Arthur D. Little, Inc.**—Picture and blue-print floor plans of the new Arthur D. Little Laboratory at Cambridge, Mass.

**Luzerne Rubber Co.**—Various articles in hard rubber to resist chemicals, piping, acid buckets, acid tanks, fittings, tonic combs, dictaphone boxes, insulators and specialties.

**Madero Bros., Inc.**—Exporters of chemicals.

**Manufacturers' Record**—Citations from the magazine. Chart showing the U. S. in 1880 and the South of to-day.

**Marden, Orth & Hastings Co., Inc.**—A line of chemicals and dyes; a 380-lb. sample of Mexican logwood; a large sample of Hematoxylon Campechianum; wall cabinets containing a large collection of dyed wool, silk and cotton yarns.

**Merck & Co.**—"Blue Label" reagents and jars of hydroquinone, synthetic carbolic phenol acid, aniline oil, etc.

**Metallurgical and Chemical Engineering**—A booth for visitors and exhibitors. Programs of the Exposition.

**Metals Disintegrating Co.**—Samples of powdered metals.

**B. Miffin Hood Brick Co.**—Samples of Hood's pottery tile, and acid tower packing. Blue-prints and photos.

**Mine & Smelter Supply Co.**—Heusser analytical and assay balances, Lindsay oil furnace, Samson laboratory crusher, McCool pulverizer and Colorado clay products.

**Mississippi River Power Co.**—Photos of power stations, coal gas plants and maps.

**Monsanto Chemical Works**—Saccharin (U. S. P. and soluble), chloral hydrate, caffeine, coumarin, calcium, manganese, phthalic anhydride, and vanillin, etc.



**Multi-Metal Separating Screen Co.**—Models of screens used in industries; screens for sifting, straining and filtering; safety device and testing sieves.

**Nash Engineering Co.**—Hydro-turbine wet vacuum pump in operation. Xyloform chemical products: paint, varnish and grease-proofing compound.

**National Aniline and Chemical Co.**—A splendid line of goods colored or dyed exclusively with American aniline colors manufactured by Schoellkopf Aniline & Chemical Works, Inc.: hosiery, yarn, cloths, inks, rugs, leather, plush, linings, threads, shoes, shoe laces and shoe polishes, dressings and creams, artificial silks, embroidery, pencils, etc. Some aniline colors.

**National Gum and Mica Co.**—Mikal tallow, cold water paste, glues and gums, paper boxes made with Mikal cold glues, string finished with Mikal sizing. In the same booth was a display of logwood, chips and extracts by the Obex Laboratories Co. The Taylor Chemical Co. also exhibited their carbon-bisulfide and "Fuma" carbonbisulfide. An ultramicroscope was displayed for the benefit of the American Red Cross.

**City of Newark, N. J.**—Maps and photos of Terminal.

**Newport Chemical Works, Inc.**—"Newport" rosin with transparency was demonstrated. Benzol (first runnings and finished), toluol, solvent naphtha, ammonia liquor, etc.

**Niagara Alkali Co.**—Model of automatically and manually controlled apparatus. Liquid chlorine. Elaborate display of cotton, raw to bleached.

**The J. L. North Iron Works**—A practical demonstration of the North kettle; cast iron, steam jacketed and porcelain lined mixers and kettles.

**Norton Co.**—An exhibit of the Norton Alundum and Crystolon refractories and laboratory ware showing the applications of the

piece glass-enameled steel evaporator or crystallizing tank (open); one sectional lead lined steel tank; and a one-piece steel tank lined with vulcanized rubber, with lead lining secured by Pfaudler process.

**Pittsburgh Testing Laboratory**—A few chemical products, and data showing nature of the work being carried on.

**Precision Instrument Co.**—Gas analysis apparatus. Boiler control gauges for forced draft and natural draft; differential gauge; various types of recorders and recording gauges.

**Prest-o-Lite Co., Inc.**—Bunsen burners, various size storage batteries, lead-burning equipment and soldering, brazing, welding and cutting torches.

**Process Engineers, Ltd.**—Rosin sizing process for paper mills.

**Product Sales Co.**—Exhibited samples of crushed quartz, dry ground silica and crude kaolin.

**Pyroelectric Instrument Co.**—A "Pyrovolter" pyrometer for actual measurement of temperature.

**Raritan Copper Works**—Their new "Anaconda" electrolytic zinc, the first on the market; N. E. C. electrolytic copper. The refining of copper was shown in all its stages—from the blister, anode, cathode to the commercial shapes—and by-products of the same, including white arsenic, blue vitriol, nickel sulfate; selenium in three allotropic modifications, tellurium and gold and silver bars. Uses of selenium were shown in ruby glass and selenium electric cells.

**The Raymond Bros. Impact Pulverizer Co.**—Samples of product, ground and air separated, from stone to radium. Views of different types of pulverizers and air-separating machines.

**Research Corporation**—A working outfit of the Cottrell electrical precipitation processes for removing dust from gases.

**Richmond Waterproof Products Co.**—"Monarch cement" for cementing linoleums to concrete.

**Roessler & Hasslacher Chemical Co.**—All grades of cyanide, "Trisalyt" for electroplating, and chemicals.

**Ruggles-Coles Engineering Co.**—Exhibited a working model of their Class A, double shell, direct heat dryer.

**Schaeffer & Budenberg Manufacturing Co.**—Instruments for indicating and recording temperature, pressure, speed and power, consisting of gauges, indicating and recording thermometers, tachometers and tachoscopes; dial thermometer demonstration.

**Schaum & Uhlinger, Inc.**—Photographs of their centrifugals.

**Schutte & Koerting Co.**—Apparatus for lifting acids, water spray used in acid condensing plant, spray nozzles, strainers, K-line of valves, exhausters, steam jet chimney ventilator, noiseless heater, oil and tar burners, lead fittings, etc.

**Scientific Materials Co.**—A line of Fry resistance glass and Nonsol and Pyrex glassware. A Scimatco-Brinell hardness testing machine; Scimatco recorders; a Scimatco fine grinder in operation; and other apparatus of the "Scimatco" brand. Also a Fieldner molybdenum wound furnace (max.-temp. 1700°).

**Ernest Scott & Co.**—Samples of C. P. glycerine, oil extracted from cotton waste, and other recovered trade wastes. Blueprint of the Scott evaporator and photos.

**Seydel Manufacturing Co.**—Synthetics, textile chemicals and coal-tar derivatives; sizings; aeroplane cloth sized with "Sizol."

**Sharples Specialty Co.**—A small laboratory super-centrifuge operating at a maximum speed of 40,000 r. p. m. and a commercial size of super-centrifuge. Samples of fish oil, crude sugar medicine, extract, phenol, varnish, etc., showing both original and clarified material.

**T. Shriver & Co.**—Practical demonstration of the "Atkins-Shriver" filter press; electrolyzer and regular filter press.

**Sidio Company of America**—A complete line of "Sidio" pure fused silica products, "made in America."

**Solvay Process Co.**—Exhibited all grades of soda ash and caustic soda, also bicarbonate of soda and modified sodas used for all washing purposes. A display of products made from or by the help of alkalies. In a joint exhibit the Semet-Solvay



more ordinarily used apparatus in laboratory construction, the display of refractory products including alundum cement, pyrometer tubes, extraction thimbles, filtering crucibles, combustion boats and R R Alundum.

**The Palo Co.**—Line of chemical and metallurgical apparatus: fluorescope, microscope, microscopical lamps, Brinell meter, Lovibond tintometer, Sochocky-Willis radioscope, radium watches, etc. Assortment of Palo glass and porcelain ware.

**Paper**—The Technical Organ of the Paper and Pulp Co. Headquarters for meeting of the Technical Association of the Pulp and Paper Industry.

**The Paper Trade Journal**—Copies of their three regular publications, annual trade directory, and books published.

**Patterson-Allen Engineering Co.**—Various sizes of the "Everlasting" valve and photographs of it on various machines.

**Pennsylvania Salt Mfg. Co.**—An exhibit of their products including Greenland kryolith, various alums, caustic soda, bleach, cylinders of liquid chlorine, and samples of heavy acids. Also a display of customers' goods demonstrating the uses of the products; a working model of a salt well.

**The Pfaudler Co.**—Exhibited a 350-gal. jacketed mixing tank with enameled steel propeller type agitator; a one-piece inner tank with bottom of jacket bolted on to admit steam coils; a one-piece glass-enameled steel closed tank (850 gals.); a one-



showed some by-product coke oven ammonia products and derivatives, also designs of by-product coke ovens.

**Sowers Manufacturing Co.**—A "Dopp" seamless, steam jacketed kettle; section of a kettle showing construction; a vacuum pan; photos.

**E. R. Squibb & Sons**—Analyzed reagents brought out since the war. Also a line of medicinal chemicals.

**Stamford Manufacturing Co.**—Specimens of dry woods and the extracts therefrom. A collection of dyed textiles, furs, etc.

**Standard Aniline Products, Inc.**—Exhibited their dyes, resins and other chemicals.

**Stevens-Aylsworth Co.**—Models showing proper and improper tank agitator; sections of their tin, copper, lead, etc., coated tanks; pipe coils.

**Stone & Webster Engineering Corporation**—A photographic exhibit of their plant construction work.

**The Stuart & Peterson Co.**—Models of steam jacketed kettles, evaporating dish, still, autoclave, retorts, storage cans.

**Sturtevant Mill Co.**—Exhibited their ring roll mill, Newaygo separator, automatic coal crusher and sampler, sample grinder, laboratory roll-jaw crusher, and laboratory roll.

**Sweetland Filter Press Co.**—Small Sweetland clam shelf filter equipped with their metallic filter cloth, in operation on a sludge; a standard clam press with cotton leaves; a new rotatable leaf type filter press; samples of the metallic filter cloth.

**Swenson Evaporator Co.**—A demonstration of the standard double-effect Swenson evaporator and a display of materials handled in Swenson evaporators.

**Swiss Colours Co.**—Exhibited textiles, leathers, felts, etc., dyed with products of the American Aniline Products Co.

**Takamine Laboratory, Inc.**—Exhibited a diastatic extract, "Polyzine," and Newmalt, a substitute for malt extract; samples of imported Japanese chemicals.

**Taylor Instrument Co.**—Complete line of "Tycos" recording thermometers, recording and controlling instruments, thermoelectric and meteorological instruments.

**Technical Association of Paper and Pulp Industries**—A place for registration of members.

**Tennessee Coal, Iron & R. R. Co.**—Display of iron ore and by-products; coal and source of its by-products: washed coal, domestic coke, crude tar, benzole and toluol, crude light and heavy naphtha, etc.

**Tennessee Power Co.**—Views of their hydroelectric power house and equipment. Now supplying 56,000 H. P. to chemical and metallurgical industries.

**Textile Colorist**—A set of bound volumes of the publication.

**Thermal Syndicate Co., Ltd.**—Exhibited pure fused silica apparatus for laboratory and large scale industrial work. Also parts of "Vitreosil"  $H_2SO_4$  concentrators, nitric acid condensers, spent acid denitrators and HCl cooling equipment, together with drawings showing construction of the complete installations. To demonstrate its resistance to extraordinary temperature changes a "Vitreosil" crucible was taken from an electric furnace at 1000° C. and plunged into cold water, without breaking.

**Thwing Instrument Co.**—Electrical pyrometers, high resistance and multiple recording machines; radiation thermometers.

**Toch Brothers**—A line of barium products mined and made in America. Dryers, enamels, water- and acid-proofing paints, cement colors, waterproofing cement compound, and leather and moleskin finished with their Japanner's Prussian blue. Pictures of many prominent buildings painted with their products.

**Tolhurst Machine Works**—Centrifugals of the following

types were shown: suspended, self-balancing (in operation), acid wringer, laboratory, and solid curb, open-top type.

**Uehling Instrument Co.**—Fuel saving equipment: power plant economy apparatus, draft, vacuum and  $CO_2$  recorders, and recording barometers.

**The Union Sulfur Co.**—Arsenic-free sulfur, guaranteed 99%.

**United Cast Iron Pipe & Foundry Co.**—A splendid showing of all shapes and sizes of gray iron castings.

**United Dyestuff and Photochemical Co., Inc.**—Exhibit of sulfur black paste and powder, benzoic acid, monochlorobenzol, dinitrochlorobenzol, dinitrophenol and photographic developer "Hydrono."

**United Gas Improvement Co.**—Residual products, such as refined water-gas tar, waterproofing pitch and brick filler. Distillates: carboic acid, crude dead oil (light) and C. P. benzol.

**United Lead Co.**—Pieces of iron, steel, brass or copper pipe either lead, tin, brass or copper lined or covered; lined and covered fittings; lead and tin covered sheets and acid valves. Kemetalline. A small piece of lead pipe about 2,000 years old, from Rome.

**U. S. Bureau of Census**—Bulletins, maps, and charts giving data on chemical plants and related subjects.

**U. S. Bureau of Foreign and Domestic Commerce**—Publications, maps and charts.

**U. S. Bureau of Mines**—Five dummies equipped with different kinds of the latest devices for rescue work. A display dealing with the government work on radium. Scientific instruments, automatic mine door, etc.

**U. S. Bureau of Standards**—A table of Bureau Bulletins, a large display of scientific apparatus employed by the Bureau in its investigations; charts.

**U. S. Smelting Co., Inc.**—Electrolytic copper-refining tank in operation. Refined copper slabs. Products from its subsidiary companies: copper, spelter, zinc ores and concentrates, blast furnace slag, copper matte, cadmium (99.70), ores, silver and gold, etc.

**The Universal Fibre Co.**—Exhibit of seamless pulp packages and containers.

**Valley Iron Works Co.**—Exhibited two 250-lb. Vesuvius oxidizing sulfur burners, one of which was dismantled.

**Virginia Smelting Co.**—Specialists in glycerin, acids, quick-silver, wood pulp, nitrating cotton, etc.

**Weiller Mfg. Co.**—A working model of a diazotizing and precipitating machine. Also displayed samples of a finished product called "Sudan."

**Werner & Pfeleiderer Co.**—Vacuum and laboratory types of the Universal kneading and mixing machine; outfit used for making fulminates for cartridges; laboratory size rubber masticator used for making rubber compounds; copper bowl, rapid dissolver was in operation.

**Westinghouse Electric & Mfg. Co.**—Models of automatic control panel, and type "C S" motor for chemical plants. Voltmeter; D. C. ammeters; fans; Thury automatic regulating system for electric furnace control; models of especially insulated coils for chemical plant installation.

**Whitall-Tatum Co.**—"Nonsol" glass beakers and flasks; also filter papers.

**Williamsburg Chemical Co., Inc.**, Brooklyn, N. Y., showed samples of its monochlorobenzol, dinitrochlorobenzol, dinitrophenol and sulfur black paste and powder. Also exhibited Hydronol of the United Dyestuff & Photochemical Co., Inc., of Brooklyn, which is similar to the German Amidol.

**Zaremba Co.**—Showed a portion of a 40-in. single-effect evaporator with horizontal tubes. Parts and accessories for evaporator. Photographs of large installation, and detailed design of a crystallizing evaporator.

## NOTES AND CORRESPONDENCE

### PAPER AND PULP TECHNOLOGY COURSES AT THE UNIVERSITY OF MAINE

*Editor of the Journal of Industrial and Engineering Chemistry:*

I enclose a clipping from *The Chemical Engineer* for August, purporting to be an extract of a letter by A. D. Little in the *Philadelphia Ledger*. The date of its appearance in the *Ledger* is not given.

"There is no school of papermaking in the country, and one of our most urgent industrial needs is the establishment of special schools in this and other industries for the adequate training of foremen who shall possess a sufficient knowledge of fundamental scientific principles and methods to appreciate the helpfulness of technical research. The Pratt Institute at Brooklyn is fully alive to this demand and has shaped its courses admirably to meet it."

Mr. Little is the author of this statement, as it appeared in his annual report in February, 1913, as official chemist of the American Pulp and Paper Association. This statement is no longer true. It has not represented the facts since it was made, for in that same month of February, 1913, the University of Maine offered its first course in Pulp Mill Chemistry. Since that time this university has introduced ten courses, both classroom and laboratory, in Paper and Pulp Technology. Last year more than forty students in Chemical Engineering elected these courses.

The effort of the University of Maine to provide instruction in the principles and practice of paper and pulp manufacture has met with such success that this field has since been entered by several other institutions. Some graduate work has already been done at the University of Michigan and work in this field is contemplated by Syracuse University, Massachusetts Institute of Technology and McGill University.

It should be understood that the work at the University of Maine is not merely the following out in the laboratory of a few set formulas and their explanation in the classroom, as a trade school might do. The curriculum at Maine embraces instruction in the fundamentals of chemistry, physics, engineering, mathematics and languages.

Among the students in the Pulp and Paper curriculum have been men from New York, West Virginia, Michigan, Wisconsin, Minnesota, and even from China and India. Graduates are already widely scattered in the United States and Canada.

It is, therefore, quite incorrect to say that there is no school of paper making in this country, even though we lack some expensive equipment and have not the extensive support and encouragement (compared with the schools of Germany and France) that ought to come from the Paper and Pulp Industry.

UNIVERSITY OF MAINE  
ORONO, September 1, 1916

J. NEWELL STEPHENSON

### A. C. S. PROFESSIONAL INDEX

*Editor of the Journal of Industrial and Engineering Chemistry:*

In your editorial "Something to Think About" in *THIS JOURNAL*, 9 (1916), 768, you suggest that the A. C. S. maintain a card catalog showing the professional status of its members. The application of some such idea as this to the entire membership list of the society would undoubtedly be of much value to a large number of the members. As you point out, it is very easy to become a member of the society. Also there are institutions in the country which consider membership in the A. C. S. sufficient ground on which to extend their courtesies, and accept this qualification as an indication of personal responsibility.

As you probably know, the U. S. Department of Agriculture does maintain such a card catalog of all those employed in agricultural work under its jurisdiction.

This suggestion of yours is one worthy of serious considera-

tion, not only by the industrial chemists but by every member of the American Chemical Society, whether he be industrial, educational, or research chemist. Personally, I trust the idea will be followed out, and that we shall have such a directory available to all members just as our present directory is.

GRIFFIN, GEORGIA  
September 11, 1916

FRED H. SMITH

### CHEMISTS' PROTECTIVE ASSOCIATION

*Editor of the Journal of Industrial and Engineering Chemistry:*

While I feel that nothing is to be gained by a prolonged polemic discussion of the merits of Mr. Rollin G. Myers' proposal to form a "Chemists' Protective Association,"<sup>1</sup> I would like to close my discussion by pointing out that the keynote of my criticism of his proposal is that the efficiency of the individual worker and his attitude toward his work should be the basis of advancement. As a corollary to this proposition, I would add that I conceive it to be the duty of every chemist in charge of a laboratory to act as an inspiration to his men; to point out to those of promise who lack college training, by what means this lack can be made up (such means being for instance, work in Company schools where these are provided; the taking up of correspondence courses; evening study such as is afforded in many cities by the various evening schools, the extension work of Columbia University in New York City being a notable example; or where possible, actual attendance at some university or college, if for no longer a period than a summer session per year for several years) and, finally to encourage all their men, college-trained or otherwise continually to study and thus keep abreast of progress in chemical science. Here is where the effect of the American Chemical Society on the efficiency of the worker is felt. By becoming a member he gets the opportunity to meet men who are doing things well in chemical lines and through reading the journals he receives, he has an opportunity of keeping in touch with chemical progress all over the world. The use he makes of these opportunities depends solely on the man and if he makes the right use of them, I cannot see how he can fail to advance—measure his worth in any way you will.

On the other hand, Mr. Myers in his first article distinctly states in the second paragraph of the first column, p. 798, that the ends for which he advocates a "Chemists' Protective Association" are: "The first, to increase the financial return of chemists; the second, to raise chemistry to its rightful and just place among the professions." He then goes on to say: "The first end is the more important and cogent. For this reason the writer will make it play a predominant part in the discussion to follow." In view of the emphasis he thus places on the financial return to chemists, and the relation between personnel and wages, I hardly see how he can attribute to me the sentiment that "worth is expressed in earning capacity." Moreover, nothing of the sort was expressed in my former note, the nearest approach to such an idea being the statement that men capable of doing nothing but low-grade routine work should justly receive low salaries. This, of course, does not imply that all routine work is low-grade, for such is manifestly not the case. All routine work should be under the supervision of a competent and, preferably, a well trained man.

I have no objection to a broad definition of "Chemist" but I do object to one such as Mr. Myers proposes: one which by its very nature disheartens the ambitious young fellow, who, while lacking college training, is at work in a laboratory and meanwhile is making use of every chance to improve himself.

April 10, 1916

WILLIAM C. MOORE

<sup>1</sup> *THIS JOURNAL*, 7 (1915), 798; 7 (1915) 100, and 8 (1916), 383.



## PERSONAL NOTES

The Fairmont Chemical Company, Fairmont, W. Va., will erect on Tygart Valley River a sulfuric acid plant, costing approximately \$80,000, with a capacity of 10,000 tons per annum, to be operated by The Multiple-Tangent-System. An auxiliary plant for the manufacture of nitric acid will also be erected. The plans were by Ludwig A. Thiele, Columbus, Ohio, who will be the engineer in charge of construction.

Dr. H. S. Adams, of the department of physiological chemistry in the University of Chicago, has accepted a position as research chemist and pharmacologist at the biological laboratories of E. R. Squibb & Sons, New Brunswick, N. J. Dr. Anderson, recently chief pharmacologist of the government, is director of the laboratory.

Prof. Clarence W. Balke has resigned his professorship of inorganic chemistry at the University of Illinois and is now in full charge of the research work of the Pfanstiehl Company at North Chicago.

Arthur Marion Brumback, professor of chemistry in Denison University since 1905, and a member of the American Chemical Society, died on August 12th, aged forty-seven years.

The Sixty-eighth Assemblage of the Eastern New York Section of the A. C. S. took place on September 23rd, and was in the nature of a fall outing. Various points of geochemical and geological interest were visited and expositions and explanations given by Prof. J. H. Stoller.

Dr. L. H. Baekeland will represent the American Chemical Society on the Natural Research Council being organized by a committee of the National Academy of Sciences.

The 129th Regular Meeting of the Pittsburgh Section of the A. C. S. was held at the Mellon Institute on September 21st, with the following program: "Revision of Our Chemical Import Statistics" and "Ten-Year Index to Chemical Abstracts," by Secretary W. C. Cope; "The Properties of Some European Bonding Clays," by A. V. Bleining, U. S. Bureau of Standards.

W. C. Phalen has resigned his position as geologist in the U. S. Geological Survey and entered on his new duties as a mineral technologist in the Bureau of Mines, with headquarters in Washington.

Sir Charles Bedford has been appointed secretary of the Association of British Chemical Manufacturers. Address: Broadway Chambers, Westminster, S. W.

Dr. Arthur Lederer has resigned his position as chief chemist of the Sanitary District of Chicago, and will take up the course for health officers at Harvard Technology, Boston.

The following appointments, of interest to chemists, have been made at the Massachusetts Institute of Technology: Frederick G. Keyes, associate professor of physico-chemical research; C. K. Reiman, instructor in inorganic chemistry; E. W. Westcott, research associate in applied chemistry; R. E. Wilson, research associate in applied chemistry; C. L. Burdick, research associate in physical chemistry.

At the Throop College of Technology the following appointments have been made in the chemistry department for the next year: W. N. Lacey, University of California, instructor in inorganic and industrial chemistry; J. H. Ellis, University of Chicago and Massachusetts Institute of Technology, research associate in physical chemistry; and Ludwig Rosenstein, University of California, professor in inorganic chemistry.

The regular September meeting of the Chicago Section of the A. C. S. took place on September 15th, with the following program: "The Manufacture of Synthetic Phenol," by Prof. Harry McCormack, Armour Institute, Chicago; "Synthetic Phenol Resins for Printing Plates—A Special Application of Anhydrous Resins," by L. V. Redman, A. J. Weith and F. P. Brock.

Mr. A. B. Carter, formerly curator at the University of Chicago, is now associated with the Central Scientific Company.

The honorary degree of Doctor of Science was conferred upon Dr. Otto K. Folin, the Hamilton Kuhn professor of biological chemistry at Harvard, by the University of Chicago at the Summer Convocation.

Dr. Jean Felix Piccard, of the University of Lausanne, Switzerland, has accepted the assistant professorship of organic chemistry at the University of Chicago for the coming year.

Dr. Charles L. Parsons sails soon for Europe, where he will spend two months visiting plants in connection with the U. S. work preparatory to constructing a nitrate plant.

Fire has wrecked the plant of the Hydrocarbon Products Company at Lorillard, two miles from Keansburg, N. J. There were between 15,000 and 20,000 gallons of gasoline in the plant in tanks, and two of these blew up. The loss is in excess of \$50,000.

The body of Prof. Charles S. Prosser, head of the geology department of Ohio State University, and a well-known scientific writer, was found floating in the Olentangy River, near the University campus, on September 12th. Prof. Prosser, born in Columbus, N. Y., March 24, 1860, was a graduate of Cornell University and before coming to Ohio State had been instructor at Cornell, Washburn College and Union College. He was an assistant geologist of the U. S. Geological Survey and of the State Geological Surveys of Kansas, New York, Ohio and Maryland, also a fellow in the Geological Society of America and a member of many other scientific societies.

Dr. Leroy Clark Cooley, professor of physics in Vassar College from 1874 to 1907, died at his home in Poughkeepsie, N. Y., on September 20th, aged 82 years. He was born in Point Peninsula, N. Y., and was graduated in 1855 from the New York State Normal College, and in 1858 from Union College. He was the author of a textbook on physics, which was long used in colleges, and of many other scientific and literary works. Dr. Cooley leaves a widow, five daughters and a son.

Dr. Frank Maltauer, formerly of the Cincinnati Board of Health, has accepted an appointment as associate professor of bacteriology and public health at the College of Medicine, University of Tennessee.

The Council of the American Leather Chemists' Association has outlined the following work which will be subjects for Committee investigation during the winter 1916-17: Analysis of Tannery Effluent; Dye Testing of Leather with Artificial and Natural Dyestuffs; Solubility of Hide Substance in Salt (NaCl) Solutions and Effect of Alkali on the Soaking of Dry Hides; Determination of the Ash of Tanning Materials and Leather; Disinfection of Hides; Analysis of Sulfonated Oils; Comparative Analysis of Tanning Materials by the A. L. C. A.; Official Methods; Effect of Hard Waters on Tannia; Determination of Free Sulfuric Acid in Leather.

# GOVERNMENT PUBLICATIONS

By R. S. MCBRIDE, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

## GEOLOGICAL SURVEY

**Structure of the Vicksburg-Jackson Area, Mississippi** (With Special Reference to Oil and Gas). OLIVER B. HOPKINS. Bulletin 641-D, from Contributions to Economic Geology, 1916, Part II, pp. 93-120. Published July 18, 1916. "The object of this report is to show which of the areas in west-central Mississippi that were examined by the Survey are considered favorable and which unfavorable for the accumulation of oil, to discourage drilling in the unfavorable localities and thus to aid those interested in making conclusive tests to determine the presence or absence of oil and gas in the region."

**An Anticlinal Fold near Billings, Noble County, Oklahoma.** A. E. FATH. Bulletin 641-E, from Contributions to Economic Geology, 1916, Part II, pp. 121-138. A description of the anticlinal fold and a discussion of the possibilities of developing an oil and gas field here are given in this report.

**Pottery in 1915.** JEFFERSON MIDDLETON. Separate from Mineral Resources of the United States, 1915, Part II. Published July 26, 1916. A study of the tables shows that the pottery industry has made much progress, that the value of the domestic output has nearly doubled in the last 15 years, that from an industry of minor importance, both as to quality and value, the pottery industry has risen to great importance, both as to quality and value, supplying large quantities of wares of ever-increasing excellence, and that this country has reached a state where it is practically independent of the old world in manufacture of pottery, more than four-fifths of the wares now sold being domestic. The imports of pottery, which have always been a large factor in consumption, reached their maximum value in 1907 and have declined since that date, the acceleration of the decline in the last two years being doubtless due to the European war. In 1915 they were valued at less than half as much as in 1907.

The exports of pottery have never been very great, especially of wares of the highest grade, but the latter have been increasing and in 1915 showed their maximum value.

"The value of all domestic pottery marketed in 1915 was \$37,325,388, an increase of \$1,927,227, or more than 5 per cent, over 1914. This value was the largest on record except that for 1913, which exceeded it by about 2 per cent. The pottery imports decreased \$1,770,507, or 21 per cent, and the ratio of production to consumption was the highest recorded. Every product, as classified in this report, except one—China—increased in value in 1915, compared with 1914. White ware, the product of largest value and the one of most general interest, reached its maximum value in 1915, as did also the commonest of pottery products, red earthenware.

"The value of white ware, including china, but excluding sanitary ware and porcelain electrical supplies, was \$17,654,398 in 1915, an increase of \$301,633 over 1914. If the value of sanitary ware and porcelain electrical supplies be added, the total for 1915 would be \$30,318,816, or more than 81 per

cent of the value of all pottery products and an increase of \$961,512."

**Feldspar in 1915.** FRANK J. KATZ. Mineral Resources of the United States, 1915, Part II, pp. 43 to 53. Published June 26, 1916. "The marketed production of feldspar in 1915 was nearly 16 per cent less in quantity than in 1914. On the other hand, the decrease in value was very slight because of the small increase in the price per ton of crude spar and a material increase in the price per ton of ground spar; also, because of a larger proportion of spar first marketed in ground form. The quantity and value for 1915 were also less than for 1913, but much greater than for former years.

"The average price for spar sold crude in 1915 was \$3.46 per long ton as compared with \$3.43 in 1914 and \$3.41 in 1913. The average price in 1915 of ground spar was \$8.33 per short ton as compared with \$7.40 in 1914 and \$8.31 in 1913. The average price per short ton for the entire production in 1915, that is, combined sales of both crude and ground spar was \$5.54."

This report also includes a discussion of the composition and properties of feldspar, geology and mineralogy, commercial availability, methods of mining, and milling, and the uses of feldspar.

**Silica in 1915.** FRANK J. KATZ. Mineral Resources of the United States, 1915, Part II, pp. 55-60. Published June 13, 1916. "Quartz from quartz veins, pegmatite, and quartzite, amounting to 112,575 short tons, valued at \$273,553, was sold in 1915. This was a decrease of 27 per cent in quantity and of 24 per cent in value, as compared with 1914. The decrease was in both crude and ground materials, but greater for the latter.

"The average price of crude quartz in 1915 (exclusive of large quantities for metallurgical purposes, which were valued at 50 to 85 cents per ton) was \$3.30, as compared with \$2.44 in 1914. Prices of ground quartz ranged from \$6 to \$20 per ton and averaged \$10.56, as compared with \$9.09 in 1914.

"So far as can be learned no flint (proper) or chert was produced for consumption as crushed or ground silica or for use as pebbles in grinding mills in the United States in 1915."

The statistics of tripoli and diatomaceous earth are given in more detail in the chapter on abrasive materials.

**Talc and Soapstone in 1915.** J. S. DILLER. Mineral Resources of the United States, 1915, Part II, pp. 61-4. Published June 27, 1916. "The United States leads the world in the production and use of talc and soapstone, and in 1915 the production in this country was greater than ever before.

"The domestic output of talc and soapstone for the last 15 years has ranged from a minimum of 86,901 short tons, valued at \$840,060, in 1903, to 186,891 short tons, valued at \$1,891,582 in 1915, and the development has been approximately uniform.

"In 1915 there were 166,336 short tons of talc produced and marketed in the United States, at a value of \$1,401,197. This exceeded the output in 1914 by 15,248 short tons and \$60,323 in value.

"In the production of soapstone the United States has first rank among all countries. The output in 1915 was 20,555 short tons, valued at \$490,385, a decrease of 653 short tons, or 3 per cent, in quantity and of 6 per cent in value as compared with the production of 1914."

**Abrasive Materials in 1915.** FRANK J. KATZ. Mineral Resources of the United States, 1915, Part II, pp. 65-80. Published June 27, 1916. "The total value of the abrasive materials which are considered in this chapter and which entered trade



increased about 22 per cent in 1915, as compared with 1914. There was an increase in domestic production of natural and artificial abrasives, but a decrease in imports. The value of natural abrasives produced increased about 33 per cent; of artificial abrasives, about 32 per cent; and imports decreased about 26 per cent.

"The value of abrasive materials imported for consumption in the United States in 1915 was

Millstones and burrstones.....	\$ 17,027
Grindstones.....	68,892
Hones, oilstones, and whetstones.....	14,247
Emery and corundum.....	271,649
Diatomaceous earth, tripoli, and rottenstone.....	27,333
Pumice.....	65,691
Diamond dust and bort.....	75,944
Total.....	540,783

"The value of natural abrasives produced and marketed in the United States in 1915 was:

Millstones.....	\$ 53,480
Grindstones and pulpstones.....	648,479
Oilstones and scythestones.....	115,175
Emery.....	31,131
Garnet.....	139,584
Abrasive quartz and feldspar.....	(a)
Diatomaceous (infusorial) earth and tripoli.....	611,021
Pumice.....	63,185
Total.....	\$1,662,055

(a) See chapter on quartz.

"The artificial abrasives here considered include carborundum and crystolon, which are carbides of silicon; alundum and aloxite, which are crystalline aluminum oxides; and crushed steel and steel shot. So far as known to the Survey, these are the only artificial abrasives manufactured in the United States. Artificial abrasives with other names are either special forms of the above-named products marketed under trade names or are imported products. Artificial abrasives sold in the United States in 1915 amounted to 37,684,000 pounds valued at \$2,248,778."

**Graphite in 1915.** EDSON S. BASTIN. Mineral Resources of the United States, 1915, Part II, pp. 81-93. Published June 26, 1916. "The production of natural graphite in the United States in 1915 was approximately 19 per cent, by value, of the graphite imported. In addition to natural graphite, this country produced a considerable quantity of manufactured graphite in the electric furnaces at Niagara Falls. The imports came mainly from the Island of Ceylon."

**Potash Salts, 1915.** W. C. PHALEN. With Simple Tests for Potash. W. B. HICKS. Mineral Resources of the United States, 1915, Part II, pp. 95-133. Published June 30, 1916. "The year 1915 was an epoch-making one in the domestic potash industry. There was produced in this country that year soluble potash salts valued at \$342,000. Quantities are not given for the reason that the product sold came from diverse sources and contained varying proportions of potash. Though this figure for value is of interest as a small beginning in the domestic potash-salts industry, it is practically of no importance in comparison with the total needs of the country, as the quantity it represents is consumed in less than a week in normal time.

"The price of potash salts has increased greatly since the domestic scarcity began to be felt. From a normal price of \$35 to \$40 a ton for high-grade agricultural salts, prices have advanced until in the spring of 1916 chloride and sulfate were quoted at ten times those figures or more. In April, 1916, chloride was nominally quoted at \$425 a ton and sulfate from \$350 to \$400 a ton.

"Experimental work on the production of potash salts from different sources was most active during 1915, and in some places experiment has passed into active construction of works for the production of soluble potash salts."

There are included in this paper brief descriptions of the various methods of potash recoveries as investigated by the Geological Survey and the Bureau of Soils, including recovery

from bittern, Nebraska lakes, alunite, silicates, kelp, cement industry by-product, and numerous miscellaneous sources.

There is also included a section describing simple tests for potash both for qualitative and quantitative determinations.

**Gypsum in 1915.** RALPH W. STONE. Mineral Resources of the United States, 1915, Part II, pp. 151-9. Published July 19, 1916. "Although the output of gypsum mined decreased in 1915, the decrease was only a little more than 1 per cent, and the decrease in value of products marketed was only about 4 per cent. As a matter of fact, the quantity mined exceeded that of all previous years except three, 1912, 1913, and 1914."

This pamphlet includes a summary of the trade and manufacturing conditions, imports, exports, production statistics, methods for preparing gypsum for markets and the uses of uncalcined and calcined products.

**Secondary Metals in 1915.** J. P. DUNLOP. Mineral Resources of the United States, 1915, Part I, pp. 21-8. Published July 15, 1916. "Secondary metals are those recovered from scrap metal, sweepings, skimmings, and drosses, and so called to distinguish them from the metals derived from ore, which are termed 'primary metals.'"

Secondary metals recovered in the United States in 1915 amounted to the following figures:

	Quantity (short tons)	Value
Secondary copper, including that in alloys other than brass.....	99,937	\$33,498,882
Remelted brass.....	137,500	40,788,000
Secondary lead.....	36,400	
Recovered lead in alloys.....	42,500	7,416,600
Secondary spelter.....	52,900	
Recovered zinc in alloys other than brass.....	5,300	14,433,600
Secondary tin.....	5,250	
Recovered tin in alloys.....	8,400	10,554,180
Secondary antimony.....	2	
Recovered antimony in alloys.....	3,100	1,811,568
Secondary aluminum.....	5,700	5,802,100
Recovered aluminum in alloys.....	2,800	
Total.....		\$114,304,930

**Manganese and Manganiferous Ores in 1915.** D. F. HEWETT. Mineral Resources of the United States, 1915, Part I, pp. 29-43. Published July 25, 1916. "The year 1915 was eventful in the manganese industry of the United States. There has been great increase in the production of each variety of ores, although the total quantity is still far below the country's need. New deposits that may become important sources of production have been explored in several states and old mines have been reopened. In the manganese alloy industry several new producers of ferromanganese have entered the field and several companies that have not attempted to make alloys for some years have again become producers.

"The domestic production of manganese ore during 1915 was 9,709 long tons, about four times the production for 1914 and the greatest output since 1901.

"The production of manganiferous iron ores was 801,290 tons, most of which came from established sources. Of this quantity, 69,416 tons contained more than 15 per cent manganese and most of this was used in the manufacture of low-grade ferromanganese, whereas those ores which contained less than 15 per cent manganese were used largely in making high manganese pig iron."

There is also included a discussion of general sources of manganese, data as to the production, imports, and world trade conditions in this industry, and interesting metallurgical sections regarding manganese ores, manganiferous zinc residuals, ferromanganese and spiegeleisen both in this country and abroad.

**Silver, Copper, Lead and Zinc in the Central States in 1915.** J. P. DUNLOP AND B. S. BUTLER. Mines Report, Mineral Resources of the United States, 1915, Part I, pp. 45-137. Published July 28, 1916. "The production of silver in the Central

States in 1915 was 647,553 fine ounces, which, at the average price of 5.07 per fine ounce (4.6 cents lower than in 1914), was valued at \$328,309, as compared with 482,983 fine ounces valued at \$267,089, in 1914. Nearly all the silver that is produced in the Central States is recovered identically in the production of other metals.

"The mine production of copper in the Central States in 1915 was from Michigan and Missouri, the first-named State, as in other years, contributing nearly the entire output, which amounted to 265,685,538 lbs.

"The mine production of lead in the Central States in 1915 was 222,548 short tons, which, rated at the average New York price for the metal for the year of 4.5 cents a lb. (\$.94 a ton), was valued at \$15,899,910 in 1914.

"The production of zinc in the Central States in 1917, based on mine returns with a deduction for separating and smelting losses, was 215,889 short tons, valued at \$53,540,472. The value is computed at 12.4 cents per lb. of spelter (\$248 per ton), the average sales reported by the smelters for the metal."

#### SANITARY LEGISLATION

The following items from the Public Health Reports (on the pages of Volume 31, indicated in parenthesis) relate to recently enacted sanitary legislation of chemical interest:

**Production, Care, and Sale of Milk.** Ordinances covering various phases of the subject and including standards for milk quality or purity are to be found as follows:

San Antonio, Texas, Ordinance adopted June 24, 1915. (1567.)  
Regulation of the Toledo, Ohio, Board of Health, adopted June 10, 1915. (1580.)

Tulsa, Oklahoma, Ordinance No. 1403, adopted July 17, 1915. (1661.)

New York State Legislative Act, Chapter 144, adopted April 6, 1916. (1814.)

West Virginia Public Health Council Regulations No. 43-68, adopted January 25, 1916. (1884-7.)

Bakersfield, California, Ordinance adopted April 3, 1916. (1899-1901.)

**Laboratory Services in Animal Industry.** Chapter 155 of the Massachusetts Legislative Act adopted April 26, 1916, authorizes the State Department of Health to perform necessary services in its laboratory for the Department of Animal Industry under conditions mutually agreed upon by the two departments. (1806.)

#### CONGRESSIONAL COMMITTEES

The following reports rendered by Congressional Committees bear upon subjects of chemical interest.

**Virus, Serum, and Toxin Act.** House Report 814, presented June 9. 7 pp. Paper, 5 cents. Report by the Committee on Agriculture to accompany House Bill 15914, which authorizes the Secretary of Agriculture to license establishments for and to regulate the preparation of virus, serums, toxins, and analogous products for use in the treatment of domestic animals.

**Importation of Virus, Serums, Toxins.** House Report 845, from the Interstate and Foreign Commerce Committee, was presented June 24 to accompany House Bill 199. 2 pp.

**Natural Resources Useful for Chemical Products.** Report of House Committee on Industrial Arts and Expositions on House Bill 10650 to develop and promote the industries utilizing natural resources for chemical products by an exhibit of certain Government bureaus at the Second National Exposition of Chemical Industries. This is the report on the hearings held May 11. The bill has not yet been reported.

**Grain Grades.** Committee on Agriculture and Forestry of the Senate hearings on House Bill 12717 (Agriculture Appropriation Bill) which includes regulations for the grading of grains. The hearings reported in this pamphlet of 86 pages are those held May 19 and 20.

**Coal and Asphalt Deposits.** Two reports, one on hearings and one to accompany House Bill 12544, have been prepared: The first in two parts, one of which was reported in an earlier number. Part 2 of the report on hearings covers 15 pages regarding the sale of coal and asphalt deposits and segregated mineral lands in the Choctaw and Chickasaw nations. The report on this bill was presented June 29 as House Report 888.

**Leases of Oil and Gas Lands.** Report by the Indian Affairs Committee on House Bill 16396, submitted July 14. 3 pp. The Senate Report on the same general subject by the Senate Committee on Indian Affairs in Senate Report 712 submitted July 22 to accompany Senate Bill 638.

**Standard Lime Barrels.** Hearing minutes and report to accompany Senate Bill 5425 have been presented by the Coinage, Weights and Measures Committee of the House. Dated respectively June 1 and June 8.

#### NAVAL CONSULTING BOARD

**Industrial Research Stations.** Senate Document 446, dated May 24. 25 pp. Paper, 5 cents. This is a letter of W. R. Whitney, Chairman of the Committee on Chemistry and Physics of the Naval Consulting Board, transmitting a circular letter to various scientists and including extracts from replies received. The subject discussed is the proposal to establish industrial research stations in connection with land grant colleges in the several states.

#### SMITHSONIAN INSTITUTION

**Annual Report.** 544 pages. Cloth, 85 cents. Publication No. 2410. This report includes among other articles the following three of some chemical interest:

(1)—**Constitution of Matter and Evolution of Elements.** SIR ERNEST RUTHERFORD.

(2)—**Place of Forestry among Natural Sciences.** HENRY S. GRAVES.

(3)—**Vaccine.** L. ROGER.

**Sources of Nitrogen Compounds in the United States.** CHESTER G. GILBERT. Publication No. 2421, issued June 30. 12 pp. Price on application. The same publication which includes as a sub-title "Natural Occurrence of Nitrogen and its Adaptability to Use" is available as Senate Document 471. Dated June 22.

#### NATIONAL MUSEUM

**Handbook and Descriptive Catalogue of Meteorite Collections in National Museum.** GEORGE P. MERRILL. 207 pp. and 40 plates. Bulletin 94. Paper, 55 cents.

#### BUREAU OF FISHERIES

**Fairport Fisheries Biological Station: Its Equipment, Organization, and Functions.** ROBERT E. COKER. Bureau of Fisheries Document 829, issued July 7. 25 pp. and 7 plates. Paper, 20 cents.

#### OFFICE OF PUBLIC ROADS

**The Result of Physical Tests of Road-Building Rock.** PRÉ VOST HUBBARD AND FRANK H. JACKSON. Agricultural Department Bulletin 370, issued July 20. 100 pp. Paper, 15 cents

#### DEPARTMENT OF AGRICULTURE

The following articles in the Journal of Agricultural Research are of chemical interest:

**Rape as Material for Silage.** A. R. LAMB AND JOHN M. EVVARD. Journal of Agricultural Research, 6 (July 3), 527-533.  
**Effect of Autolysis upon Muscle Creatin.** RALPH HOAGLAND AND C. N. MCBRYDE. Journal of Agricultural Research, 6 (July 3), 535-546.

**Digestibility of Very Young Veal.** C. F. LANGWORTHY AND A. D. HOLMES. Journal of Agricultural Research, 6 (July 17), 577-587.

**Influence of Calcium and Magnesium Compounds on Plant Growth.** F. A. WYATT. Journal of Agricultural Research, 6 (July 17), 589-616.

**Digestibility of Hard Palates of Cattle.** C. F. LANGWORTHY



AND A. D. HOLMES. *Journal of Agricultural Research*, 6 (July 24), 641-648.

**Some Properties of the Virus of the Mosaic Disease of Tobacco.** H. A. ALLARD. *Journal of Agricultural Research*, 6 (July 24), 649-672.

#### BUREAU OF MINES

**Report of the Selby Smelter Commission.** J. A. HOLMES, EDWARD C. FRANKLIN AND RALPH A. GOULD. *Bulletin* 98. 538 pp. and 41 plates. Paper, \$1.25. See THIS JOURNAL 7 (1915), 41.

**A Bibliography of the Chemistry of Gas Manufacture.** W. F. RITTMAN AND M. C. WHITAKER. Compiled and arranged by M. S. HOWARD. Technical Paper 120. 29 pp. This is a bibliography of 274 entries (including some duplicates) of articles on carbonization or distillation of coal and various other phases of the gas generating processes in use, together with articles on some of the physical-chemical phases of the subject.

#### BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**Potash Production in California and Potash from Kelp.** THOMAS H. NORTON. Reprint from Commerce Reports. 13 pp. This account gives the summary of the efforts which have been made to relieve the potash shortage in this country.

**Japanese Cotton Goods Industry and Trade.** GEORGE N. WEST. Supplementing the Special Agents Series 86. 12 pp. Paper, 5 cents. This is a collection of recent consular reports on the cotton goods business in Japan.

#### COMMERCE REPORTS—AUGUST 1 TO 29 1916

Exportation of **caustic soda** from Japan, formerly prohibited, is again permitted owing to a great increase in domestic production. (P. 439.)

**Ammonium sulfate**, made from synthetic ammonia prepared by the Haber process, is now being used extensively in fertilizers in Germany. The estimated output for 1916 is 300,000 tons of ammonium sulfate, against 30,000 tons in 1913. By 1917 it is estimated that the German production of nitrogenous fertilizers, *viz.*, ammonia from coke, synthetic ammonia, and calcium nitrate, will be more than equivalent to the normal German import of Chilean nitrate. (Pp. 440-2.)

In spite of increased exports of **matches**, the supply of potassium chlorate in Japan now exceeds the demand. There are 33 match factories in operation. (P. 538.)

The following **dye-producing plants** are found in the Philippines, usually however not in large quantities. Indigo, sappan (which contains the same dye as does brazil wood), mangrove, bandedo, mango, berberine, and turmeric. (P. 566.)

The Japanese production of **gold, silver, copper, antimony, and zinc** shows marked increases. (P. 575.)

The chief fertilizers used in India consist of **oil cake, fish manure, and plant ashes**. (P. 596.)

**Pepsin** is being used in Canada as a substitute for **rennet** in cheese making. (P. 599.)

Arrangements are being made for the development of **bauxite** deposits in British Guiana. (P. 602.)

The Spanish cultivation of **peanuts**, chiefly for oil, is increasing. (P. 613.)

The production of **uranium ore**, and uranium and radium compounds in Bohemia in 1915, shows an increase over 1914. The **radium** compounds in 1915 contained 1.75 g. radium. (P. 627.)

The Argentine government will erect a plant for the production of **aluminum sulfate**, used extensively for clarifying water. (P. 631.)

**Sansevieria fiber**, from Porto Rico and Haiti, is now available for rope, etc., but requires special machinery to handle it. (P. 637.)

Efforts are being made to establish a plant for the extraction of **quebracho wood** in Paraguay, to produce 15,000 tons of extract per year. (P. 643.)

The New Zealand government is to engage in the **kauri gum** industry. Most of this gum is exported to the United States (P. 645.)

Efforts are being made to increase the use of **fish offal** as fertilizer in Canada. (P. 647.)

A study of **kelp** harvesting has failed to show any evidence of damage to fish or shell fish. (P. 655.)

The production of **bleaching materials** in the United States in 1914 including chlorine, chloride of lime, sodium hypochlorite, hydrogen peroxide, sodium peroxide, sulfur dioxide, etc., shows a marked increase (54 per cent) over 1909. (P. 677.)

**Copper mines** in New Brunswick, Canada, that have been idle 16 years, are to be reopened. (P. 683.)

The figures for the United States **production of acids** in 1909 and 1914 are given, showing in most cases an increase in both amount and value in 1914. (P. 694.)

A conference was held in Yorkshire, England, to arrange for textile research in the University of Leeds and technical schools. (P. 700.)

Export of **tungsten and molybdenum ores** from Japan has been subjected to restrictions. (P. 741.)

Extensive deposits of **kaolin** believed to be suitable for china, etc., have been found in Paraguay. (P. 746.)

Various processes for using the residue from the **sulfate paper pulp** industry are discussed. In Germany the waste liquor is neutralized with lime, filtered through coke, and evaporated to a nearly dry pitch-like resin known as "zellpech" (or "celpech"). This material is used as a binder in coal briquets, ore briquets, artificial stone and molding sand; and for filling cotton goods; and impregnating sail cloth, cords, nets, etc. In Sweden **alcohol** is being made successfully from the waste sulfate liquor. (P. 782.)

Production and export of **nitrate** from Chili is increasing though still below former maximum output. (P. 788.)

The use of **copra** (coconut oil in margarin) in Netherlands has increased, owing to shortage of vegetable and animal oils. (Supplement 5b.)

#### SPECIAL SUPPLEMENTS ISSUED IN AUGUST, 1916

GREECE—7a	MEXICO—32a
NETHERLANDS—9b and c	ADEN—49a
SPAIN—15d	CHINA—52c
UNITED KINGDOM, GLASGOW—19i	PORTUGUESE EAST AFRICA—76a

#### EXPORTS TO THE UNITED STATES. (Pp.)

SWANSEA, WALES—(482)	BOLIVIA—(485)	MEXICO—Sup. 32a
Oxalic acid	Tungsten ore	Hides
Nickel salts	Antimony ore	Oil cake
Copper matte	HONDURAS—(651)	Rubber
Hides	Sugar	Sesame
Tin plate	Hides	Copper
GOLD	Rubber	Lead
MALAY STATES—(516)		Zinc ore
Rubber	SPAIN—Sup. 13d	Arsenious oxide
Tin	Copper	Cottonseed oil
Gold	Copper ore	Glycerin
Tungsten ore	Hides	Graphite
ROTTERDAM—Sup. 9c	Iron ore	Sugar
Beeswax	Pyrites	Alcohol
Carbolic acid	Lead	Antimony ore
Formic acid		Beeswax
Tartaric acid	GLASGOW—Sup. 19i	Bones
Cream of tartar	Aluminum	Guayule rubber
Dextrin	Aluminum sulfate	Tin
Fusel oil	Bone char	Vegetable wax
Glycerin	Corundum	Mercury
Gum copal	Creosote oil	Chicle
Gum damar	Tanning extracts	Petroleum
Madder	Magnesite	Onyx
Magnesite	Fire brick	Copra
Artificial musk	Fertilizers	GRECE—Sup. 7a
Potassium cyanide	Hides	Licorice
Sodium cyanide	Manganese ore	Gum mastic
Quinine sulfate	Paper stock	Marble
Fibers	Sperm oil	Olive oil
Glue	Sumac extract	Opium
Hides		Chromite
Rubber	NORTHERN CHINA—	Emery
Manganese ore	Sup. 52c	Magnesite
Oleostearin	Soya bean oil	Paints
Paints	Talcum	Hides
Paper	Hides	Amyl alcohol
Paper stock		Soap
Paraffin	HONGKONG—(760)	Saffron
Saccharin	Tin	MOZAMBIQUE—Sup. 76a
Starch	Cassia	
Tin	Antimony	Mangrove bark

# NEW PUBLICATIONS

By IRRENE DEMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

- Analysis: Elementary Qualitative Analysis; A Laboratory Guide.** A. B. DALES AND O. L. BARNEBEY. 16mo. 205 pp. Price, \$1.25. John Wiley & Sons, New York.
- Centrifugal Pumps and Suction Dredges.** E. W. SARGENT. 8vo. 196 pp. Price, 10 s. 6 d. Charles Griffin & Co., London.
- Cereals: Die Chemie der Cerealien.** F. ROEHMANN. 8vo. 28 pp. Price, M 1.50. F. Enke, Stuttgart.
- Chemical Plants: A Manual of Chemical Plant.** Part V. S. S. DYSON. 8vo. Price, 2 s. 6 d. The Dover Printing & Publishing Co., Dover.
- Earth Pressure, Retaining Walls and Bins.** WILLIAM CAIN. 8vo. Price, 10 s. 6 d. Chapman & Hall, London.
- Economic Geology.** HEINRICH RIES. 4th Ed. 8vo. 860 pp. Price, \$4.00. John Wiley & Sons, New York.
- Engineering: Bibliography on "English for Engineers" with Selected Lists of Technical Books for Graduates in Civil, Electrical, Mechanical and Chemical Engineering.** W. O. SYMPHER. 12mo. 63 pp. Price, \$0.25. Scott, Foresman & Co., Chicago.
- Engines: Practical Handbook of Gas, Oil and Steam Engines, Stationary, Marine, Traction; Gas Burners, Oil Burners, etc.** J. B. RATHBUN. 12mo. 370 pp. Price, \$1.00. C. C. Thompson Co., Chicago.
- Foods: Preservatives and Other Chemicals in Foods.** OTTO FOLIN. 18mo. Price, 2 s. 6 d. Clarendon Press, London.
- Hydraulics: A Textbook of Practical Hydraulics.** JAMES PARK. 8vo. 300 pp. Price, 12 s. 6 d. Charles Griffin & Co., London.
- Illumination: Modern Illumination, Theory and Practice.** 16mo. 273 pp. Price, \$1.00. Frederick J. Drake & Co., Chicago.
- Indicators: Der Indikator und die Indikatorgramm.** W. WILKE. 8vo. Price, M 7.50. Otto Spamer, Leipzig.
- Inorganic Chemistry: Laboratory Manual of Inorganic Chemistry.** L. C. NEWELL. 12mo. 240 pp. Price, \$0.60. D. C. Heath & Co., New York.
- Light and Power Mains: The Localization of Faults in Electric Light and Power Mains.** F. C. RAFAEL. 3rd Ed. 8vo. 217 pp. Price, 8 s. 6 d. "The Electrician."
- Machine Shop Library.** 9 vol. 8vo. McGraw-Hill Book Co., New York.
- Motor Wheels: Das moderne Motorrad, seine Konstruktion, etc.** G. O. CARSAAR. 8vo. 139 pp. Price, M 2.80. R. C. Schmidt & Co., Berlin.
- Organic Compounds: Analyse und Konstitutionsbestimmung organischer Verbindungen.** HANS MEYER. 8vo. 323 pp. Price, M 44.80. Julius Springer, Berlin.
- Petroleum: The American Petroleum Industry.** R. F. BACON AND W. A. HAMOR. 2 vol. 8vo. 975 pp. Price, \$10.00. McGraw-Hill Book Co., New York.
- Plant Physiology: Some Recent Researches.** W. R. G. ATKINS. 12mo. 323 pp. Price, \$2.40. The Macmillan Co., New York.
- Steam Power.** C. F. HIRSHFIELD AND T. C. ULBRICHT. 8vo. 428 pp. Price, \$2.00. John Wiley & Sons, New York.
- Steel: The Heat Treatment of Steel.** HARRY BREARLEY. 2nd Ed. 8vo. 223 pp. Price, \$3.50. Longmans, Green & Co., New York.
- Tables: Electrical Tables and Engineering Data.** H. C. HORSTMANN AND V. H. TOUSLEY. 16mo 331 pp. Price, \$1.50. Frederick J. Drake & Co., Chicago.
- Thermodynamics: Einfuehrung in der technischen Waermelehre.** RICHARD VATER. 8vo. 112 pp. Price, M 1.25. B. G. Teubner, Leipzig.
- Transformers: Fortschritte im Transformatorenbau.** R. EDER. 8vo. 88 pp. Price, M 2.50. Hachmeister & Thal, Leipzig.
- Yeast: Die wirtschaftliche Bedeutung der Hefe als Nahrungs-, Futter-, und Heilmittel.** MAX WINCKEL. 8vo. Price, M 0.70. Carl Gerber, Munich.
- Aluminium: How Aluminium Sheets are Rolled.** *Iron Trade Review*, Vol. 69 (1916), No. 9, pp. 423-424.
- Asbestos: Studien ueber Asbest.** FRITZ BAYER. *Kunststoffe*. Vol. 6 (1916), No. 12, pp. 146-149.
- Blast Furnace: Commercial Considerations Concerning the Blast Furnace.** J. E. JOHNSON, JR. *Metallurgical and Chemical Engineering*. Vol. 15 (1916), No. 5, pp. 235-244.
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- Zinc-Lead Mills of California and Nevada.** L. A. PALMER. *Metallurgical and Chemical Engineering*, Vol. 15 (1916), No. 4, pp. 203-205.



INORGANIC CHEMICALS

Acetate of Lime	100 Lbs	5.00	
Alum lump ammonia	100 Lbs	41	@
Aluminum Sulfate, high grade	Ton	65 00	@
Ammonium Carbonate, domestic	Lb	23 1/2	@
Ammonium Chloride, gray	Lb	10 00	@
Ammonium Phosphate commercial, 98-100%	Lb	14 00	@
Aqua Ammonium, 26°, drums	Lb	8 1/2	@
Arsenic, white	Lb	8 1/2	@
Barium Chloride	Ton	100 00	@
Barium Nitrate	Lb	18	@
Barytes, prime white, foreign	Ton	6 00	@
Bleaching Powder, 35 per cent.	100 Lbs	4	@
Blue Vitriol	Lb	8 1/2	@
Borax, crystals, in bags	Lb	7 1/2	@
Boric Acid, powdered crystals	Lb	11 3/4	@
Brimstone, crude, domestic	Long Ton	35.00	
Bromine, technical, bulk	Lb	1 20	@
Calcium Chloride, lump, 70 to 75% fused	Ton	28.00	@
Calcium Chloride, granulated	Ton		@
Caustic Soda, 74 per cent.	Lb	33 1/4	@
Chalk, light precipitated	Lb	4 1/2	@
China Clay, imported	Ton	18.00	@
Feldspar	Ton	8.00	@
Fuller's Earth, foreign, powdered	Ton	\$35.00	
Glauber's Salt, in bbls.	100 Lbs	6.0	@
Green Vitriol, bulk	100 Lbs	9.5	@
Hydrochloric Acid, commercial, 18°	Lb	17 1/8	@
Hydrochloric Acid, C. P., conc., 22°	100 Lbs	2	@
Iodine, resublimed	Lb	4.25	@
Lead Acetate, white crystals	Lb	15 1/8	@
Lead Nitrate	Lb	15 1/2	@
Litharge, American	Lb	9 1/4	@
Lithium Carbonate	Lb	1.02	@
Magnesium Carbonate	Lb	19	@
Magnesite, "Calcined"	Ton		@
Nitric Acid, 36°	Lb	4 1/2	@
Nitric Acid 42°	Lb	6 1/4	@
Phosphoric Acid, sp. gr. 1.750	Lb	30	@
Phosphorus yellow	Lb	1.20	@
Plaster of Paris	Bbl	1.50	@
Potassium Bichromate, casks	Lb	37	@
Potassium Bromide (granular)	100 Lbs	\$1.35	
Potassium Carbonate, calcined, 80 @ 85%	Lb	50	@
Potassium Chlorate, crystals, spot	Lb	48	@
Potassium Cyanide, bulk, 98-99 per cent.	Mixture	44	@
Potassium Hydroxide	Lb	55	@
Potassium Iodide, bulk	Lb	3.95	@
Potassium Nitrate	Lb	—	@
Potassium Permanganate, bulk	Lb	1.55	@
Quicksilver, flask, 75 lbs.		75.00	
Red Lead, American, dry	Lb	9 3/4	@
Salt Cake, glass makers'	Ton	10.50	@
Silver Nitrate	Oz	41 1/2	@
Soapstone in bags	Ton	8.00	@
Soda Ash, 48 per cent.	100 Lbs	8 1/8	@
Sodium Acetate	Lb	12	@
Sodium Bicarbonate, domestic	100 Lbs	1.65	@
Sodium Bicarbonate, English	Lb	3 1/2	@
Sodium Bichromate	Lb	27	@
Sodium Chlorate	Lb	27	@
Sodium Fluoride, commercial	Lb	—	@
Sodium Hyposulfite	100 Lbs	1.25	@
Sodium Nitrate, 95 per cent, spot	100 Lbs	2.95	@
Sodium Silicate, liquid	100 Lbs	1.00	@
Sodium Sulfide, 30%, crystals, in bbls.	Lb	12 1/2	@
Sodium Bisulfite, powdered	Lb	5 1/4	@
Strontium Nitrate	Lb	48	@
Sulfur, flowers, sublimed	100 Lbs	2.30	@
Sulfur, roll	100 Lbs	1.95	@
Sulfuric Acid, chamber, 66° Be.	Ton	20.00	@
Sulfuric Acid, oleum (fuming)	Ton	45.00	@
Talc, American white	Ton	9.00	@
Terra Alba, American, No. 1	100 Lbs	75	@
Tin Bichloride, 50°	Lb	13 1/2	@
Tin Oxide	Lb	43	@
White Lead, American, dry	Lb	8 1/4	@
Zinc Carbonate	Lb	26	@
Zinc Chloride, commercial	Lb	13	@
Zinc Oxide, American process XX	Lb	9 3/4	@
Zinc Sulfate	Lb	6 1/2	@

ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.	Lb	55	@
Acetic Acid, 56 per cent, in bbls.	Lb	8 1/2	@
Acetic Acid, glacial, 99 1/2% in carboys	Lb	40	@
Acetone, drums	Lb	30	@
Alcohol, denatured, 180 proof	Gal	16	@

Alcohol, grain, 188 proof	Gal	2.64	@
Alcohol, wood, 95 per cent, refined	Gal	63	@
Amyl Acetate	Gal	4.75	@
Aniline Oil	Lb	25	@
Benzoic Acid, ex-toluol	Lb	9.00	@
Benzol, 90 per cent	Gal	60	@
Camphor, refined in bulk, bbls.	Lb	69 1/2	@
Carbolic Acid, U. S. P., crystals, drums	Lb	55	@
Carbon Bisulfide	Lb	7	@
Carbon Tetrachloride, drums, 100 gals.	Lb	16 1/2	@
Chloroform	Lb	48	@
Citric Acid, domestic, crystals	Lb	62	@
Cresol, U. S. P.	Gal	65	@
Dextrose, corn (carloads, bags)	100 Lbs	3.95	@
Dextrose, imported potato	Lb	14	@
Ether, U. S. P., 1900	Lb	15	@
Formaldehyde, 40 per cent	Lb	10	@
Glycerine, dynamite, drums included	Lb	43	@
Oxalic Acid, in casks	Lb	60	@
Pyrallic Acid, resublimed bulk	Lb	2.85	@
Salicylic Acid	Lb	1.50	@
Starch, cassava	Lb	3 1/4	@
Starch, corn (carloads, bags) pearl	100 Lbs	2.65	@
Starch, potato	Lb	7	@
Starch, rice	Lb	8	@
Starch, sago	Lb	3 1/4	@
Starch, wheat	Lb	6 1/2	@
Tannic Acid, commercial	Lb	65	@
Tartaric Acid, crystals	Lb	66	@

OILS, WAXES, ETC.

Beeswax, pure, white	Lb	40	@
Black Mineral Oil, 29 gravity	Gal	13 1/2	@
Castor Oil No. 3	Lb	13 1/2	@
Ceresin, yellow	Lb	10	@
Corn Oil, crude	100 Lbs	\$9.00	
Cottonseed Oil, crude, f. o. b. mill	Gal	normal	
Cottonseed Oil, p. s. y.	Lb	10	@
Croosote, beechwood	Lb	2.75	@
Cylinder Oil, light, filtered	Gal	21	@
Fusel Oil, crude	Lb	4.25	@
Japan Wax	Lb	14 1/4	@
Lard Oil, prime winter	Gal	1.08	@
Linseed Oil, raw (car lots)	Gal	69	@
Menhaden Oil, crude (southern)	Gal	47	@
Naphtha, 68 @ 72°	Gal	33 3/4	@
Neat's-foot Oil, 20°	Gal	1.05	@
Paraffine, crude, 120 m. p.	Lb	5	@
Paraffine Oil, high viscosity	Gal	29 1/2	@
Rosin, "F" Grade, 280 lbs.	Bbl	6.65	@
Rosin Oil, first run	Gal	33	@
Shellac, T. N.	Lb	33	@
Spermaceti, cake	Lb	24	@
Sperm Oil, bleached winter, 38°	Gal	80	@
Spindle Oil, No. 200	Gal	24	@
Stearic Acid, double-pressed	Lb	13	@
Tallow, acidless	Gal	88	@
Tar Oil, distilled	Gal	35	@
Turpentine, spirits of	Gal	46	@

METALS

Aluminum, No. 1, ingots	Lb	61	@
Antimony, ordinary	Lb	14	@
Bismuth, N. Y.	Lb	3.05	@
Copper, electrolytic	Lb	28	@
Copper, lake	Lb	28	@
Lead, N. Y.	100 Lbs	\$7.10	
Nickel, electrolytic	Lb	45	@
Nickel, shot and ingots	Lb	50	@
Platinum, refined	Oz	85.00	@
Silver	Oz	68 1/3	@
Tin	Lb	38 1/2	@
Zinc, N. Y.	100 Lbs	9.70	@

FERTILIZER MATERIALS

Ammonium Sulfate	100 Lbs	3.00	@
Blood, dried F O B Chicago	Unit	3.20	@
Bone, 4 1/2 and 50, ground, raw	Ton	28.50	@
Calcium Cyanamid	Unit of Ammonia	2.55	@
Calcium Nitrate, Norwegian	100 Lbs	—	@
Castor Meal	Unit	—	@
Fish Scrap, domestic dried, f. o. b. works	Unit	3.60	@
Phosphate, acid	Ton	10.00	@
Phosphate rock; f. o. b. mine			
Florida land pebble, 68 per cent.	Ton	2.75	@
Tennessee, 78-80 per cent.	Ton	5.00	@
Potassium "muriate" basis 80 per cent.	Ton	300.00	@
Pyrites, furnace size, imported	Unit	15 1/2	@
Tankage, high-grade; f. o. b. Chicago	Unit	2.90	@

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## EDITORIALS

### MAKING IT EASIER FOR THE MAN WHO WANTS TO KNOW

There is so much to be known about the mechanisms and materials of every business that any short cut to information in any line is sure to be welcome. Especially is this true in the chemical industries where new inventions and discoveries are coming so fast that frequently to be fifteen minutes behind the times is to be completely out of date. Of course, in the very nature of things, workers in this industry will never be able to keep completely abreast of developments. At the very best, a step or two behind the creation of a new method or process to bring about certain results is about all the most progressive engineer or manufacturer can do. Yet, in spite of this constant and rapid change in the building up of this all-embracing industry, there are certain ways and means for keeping posted that are fairly effective.

Most chemical engineers and research chemists, as well as manufacturers, are familiar with the time-honored method of filing catalogues, pamphlets, leaflets, etc., that are sent to them from time to time for their reference library by the patentees and manufacturers of apparatus and materials. This method of preserving such data is, as has been said, time-honored and up to the present has been practical, and, to a certain extent, fairly efficient. But, like a lot of other time-honored things, like the old passenger coach and the copy-book method of preserving records of correspondence, it has, in the light of new developments along these lines, become a bit antiquated.

The new idea for preserving catalogue data and furnishing the profession with a short cut to information on mechanisms and materials in the chemical industries that so ruthlessly shows up the dusty collection of torn and dog-eared catalogues now reposing on the shelves of so many engineers and research chemists, is brought out in the volume of condensed information that has just been issued by the Chemical Catalog Company.

The *Chemical Engineering Catalog* contains in one nine-by-twelve-inch volume most of the information on equipment and supplies that the engineer or research chemist has previously been able to find only after a careful search through his reference library or through the desks of various heads of departments. It is the boiled-down essence of numerous catalogues and pamphlets on subjects that the industry needs to know about.

The original idea of such a compilation was broached some years ago as a duty that the AMERICAN INSTITUTE OF CHEMICAL ENGINEERS might perform for its members. After much study a model was originated. It followed closely a similar catalogue made for the building trades which has earned its success by the

high standards set in text, typography and tone. The Catalogue Committee of the Institute received the support of the American Chemical Society and the Society of Chemical Industry, and a Joint Committee appointed by the three organizations has supervised the methods of handling and classifying the large masses of data available. The catalogue is to be issued annually.

Of course, it is superfluous to point out the direct benefit to the profession of such a volume as this. It saves the information seeker an immense amount of time and gives him in condensed form the real meat of the data he wants. It is the very thing we have all been so long looking for; and although this volume is but a beginning and will undoubtedly be greatly enlarged and improved from year to year, it does so much for the profession that every effort should be made in the way of coöperation.

An extremely interesting feature of the book is the fact that it is loaned for a period of one year, without charge, to persons who have legitimate use for such a work of reference. The publishers are able to do this, owing to the fact that the expense of printing and distributing the book is borne by the firms whose products are illustrated and described in it. The only thing asked for by the publishers in their introductory pages is coöperation among the users of the book with a view to making it more valuable as a work of reference.

No work of this kind can ever be complete or entirely correct without criticisms, suggestions and a certain amount of assistance from users of the volume. Inasmuch as it is distributed gratuitously, for the convenience of those who have the greatest need for such a work, it is evident that its recipients will realize the necessity of coöperation to make the volume more complete.

For instance, when an engineer fails to find the products of any particular firm mentioned in the catalogue pages or in the index, when he fails to find the technical data he desires regarding goods that are mentioned, or when he finds that products interesting to the engineer are omitted entirely, he is urged to write to the publishers calling attention to the omission.

To insure the successful development of this work, the chemical engineer must insist that manufacturers present adequate technical facts regarding what they have to offer and manufacturers must learn what their products are good for and what their mechanisms will actually do. This catalogue should eventually report all houses who have anything to offer to the chemical industry.

The publishers are to be congratulated on their first issue of this catalogue, and it is to be hoped they will be heartily encouraged.

## ORIGINAL PAPERS

THE COMMON REFRACTORY OXIDES<sup>1</sup>

By ROBERT B. SOSMAN

Received July 26, 1916

In discussing the "common refractory oxides" we will confine ourselves to the common rock-forming oxides: silica, alumina, magnesia, lime, and the oxides of iron. These taken together make up practically 90 per cent by weight of the accessible outer shell of the earth, while soda, potash, and water make up most of the remaining 10 per cent.

In comparing the properties of the individual oxides and in discussing their important compounds and mixtures, I hope to bring out certain general principles that will serve to classify and correlate in our minds some of the facts which have already been discovered, and at the same time show where additional research is needed.

## THE PURE OXIDES

One property of the oxides which is of primary importance is the melting point. The melting points of the common oxides are listed in Table I:

TABLE I—MELTING POINTS OF THE COMMON REFRACTORY OXIDES		
Silica.....	SiO <sub>2</sub> (quartz)	Below 1470°
	(cristobalite)	1625°
Alumina.....	Al <sub>2</sub> O <sub>3</sub>	2050°
Magnesia.....	MgO	2800°
Lime.....	CaO	2570°
Ferric oxide.....	Fe <sub>2</sub> O <sub>3</sub>	Unknown
Ferrosoferric oxide.....	Fe <sub>3</sub> O <sub>4</sub>	1580°
Ferrous oxide.....	FeO	Unknown

**SILICA**<sup>2</sup>—Two melting points are given for silica. The explanation of these introduces the very interesting set of allotropic forms that silica exhibits. I have attempted to give a graphic statement of the relations of these forms in one of the diagrams of Fig. II.

Silica possesses to an unusual degree the property of responding very slowly to changes of temperature as regards its melting point and its transitions from one principal form to another. Each of these principal forms, on the other hand, has one or two inversion points of its own, which respond very promptly to temperature change. The principal forms are *quartz*, *tridymite*, and *cristobalite*. Quartz has as reversible inversion at 575°, tridymite has inversions at 117 and 163°; cristobalite is peculiar in having an inversion point whose temperature varies from about 200 to 275°, depending upon the previous history of the crystal. By rapid heating, quartz can be melted before it has had time to transform into tridymite or cristobalite.

The atomic or molecular basis for these interesting relations remains to be worked out.

**ALUMINA**<sup>3</sup>—Two allotropic forms of Al<sub>2</sub>O<sub>3</sub> are known. The common form, known as  $\alpha$ , is the same as the mineral corundum. It was the only form which appeared in the lime-alumina-silica investigation by Rankin and Wright. The magnesia-alumina-silica study (by Rankin and Merwin) brought out a second

or  $\beta$  form. At first it was thought possible that it might be a compound corresponding to magnetite, with the formula Al<sub>3</sub>O<sub>4</sub>, but a chemical analysis by H. S. Washington shows it to be pure Al<sub>2</sub>O<sub>3</sub>. Its relation to the  $\alpha$  form is not yet known.

**MAGNESIA**—Only one crystalline form of MgO is known: it is the same as the mineral periclase. Magnesia has the highest melting point of any of the oxides here described (2800°).

**LIME**<sup>4</sup>—There is only one crystalline form of CaO known at high temperatures. It seems to possess an inversion point, however, at about 420°, which is similar to the 575° reversible inversion point of quartz. The exact location of this point will require further investigation.

Pure CaO is, however, obtainable in two forms.<sup>5</sup> The first, which is probably amorphous, results from the dissociation of calcium carbonate at low red temperatures. On heating for a considerable time at higher temperatures, it changes gradually into the cubic crystalline lime of refractive index 1.83. The latter forms directly from silicate melts or from fused calcium nitrate, and is the stable form at high temperatures. The porous lime ought not, perhaps, to be called a distinct "form," as it is probably not such in the sense in which cristobalite is a "form" of silica.

The porous, probably amorphous, form of CaO is much more reactive than the crystalline. It unites readily with dry carbon dioxide or with water, whereas the crystalline CaO unites only slowly with these compounds. The fundamental reason for this difference is yet to be found.

**OXIDES OF IRON**<sup>6</sup>—The oxides of iron offer a research problem quite different in character from that of the other oxides described above, by reason of the fact that their compositions and properties at high temperatures depend upon the pressure of oxygen in contact with them.

Ferric oxide, Fe<sub>2</sub>O<sub>3</sub>, which occurs in nature as hematite, begins to dissociate, as the temperature rises, into oxygen and a solid solution containing ferrous iron; this may be considered as a solid solution of Fe<sub>3</sub>O<sub>4</sub> in Fe<sub>2</sub>O<sub>3</sub>. At a given temperature the initial dissociation pressure is high, but it drops rapidly as the percentage of FeO in the solid increases, passing through a range in which the pressure falls rather slowly with change of composition, and finally falling rapidly to the dissociation pressure of Fe<sub>3</sub>O<sub>4</sub>, which is very low (less than 0.04 mm. of mercury, at 1200°).

Fe<sub>3</sub>O<sub>4</sub>, in turn, dissociates into oxygen and a mixture of oxides whose character has not yet been determined.

The properties of FeO are still practically unknown. The most of the recorded methods for preparing "ferrous oxide" yield only a mixture of metallic iron

<sup>1</sup> Part of a paper presented before a joint meeting of the local sections of the American Chemical and American Electrochemical Societies at Niagara Falls, April 4, 1916.

<sup>2</sup> C. N. Fenner, *Am. Jour. Sci.*, **36** (1913), 331-384.

<sup>3</sup> Rankin and Merwin, *J. Am. Chem. Soc.*, **38** (1916), 568-588.

<sup>4</sup> Rankin and Wright, *Am. Jour. Sci.*, **39** (1915), 1-79.

<sup>5</sup> Sosman, Hostetter and Merwin, *J. Wash. Acad. Sci.*, **6** (1915), 563-569.

<sup>6</sup> Sosman and Hostetter, *J. Am. Chem. Soc.*, **38** (1916), 807-833, 1188-1198.



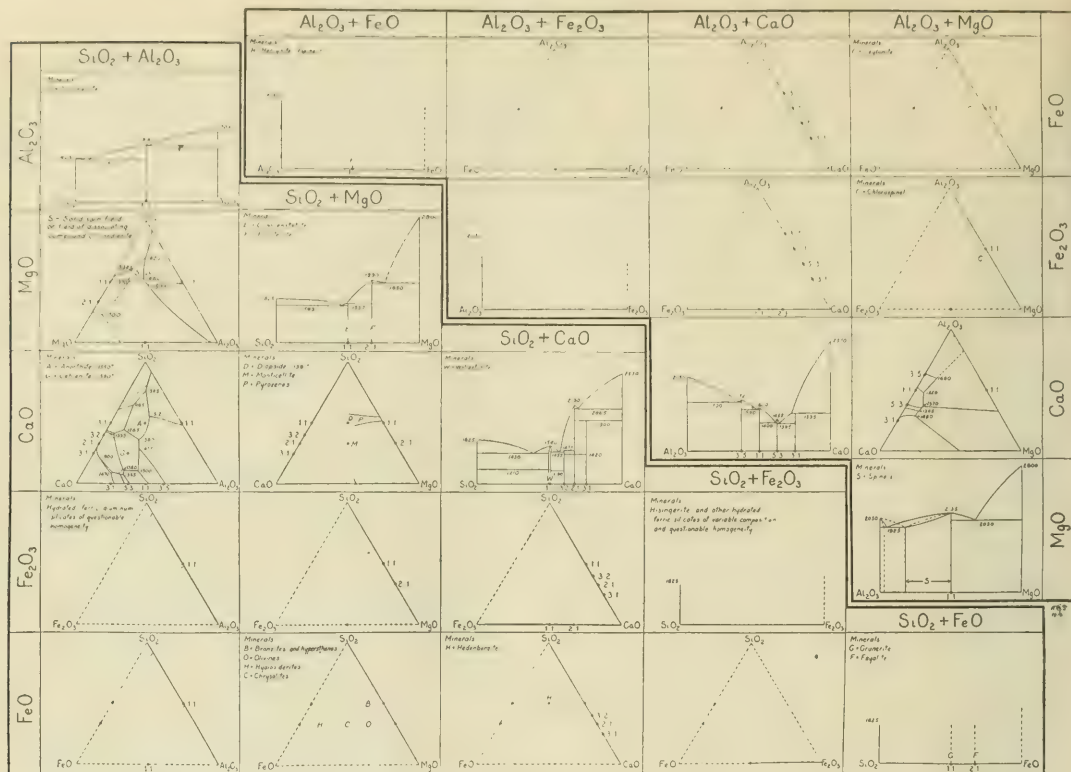


FIG. I

(or iron carbide) with an oxide whose composition falls between FeO and Fe<sub>3</sub>O<sub>4</sub>.

Ferric oxide has an inversion point at 678°, which is sharp and reversible, like the 575° inversion of quartz. This point is marked by an absorption of heat, as the temperature passes 678°, and also by a sudden drop in magnetic susceptibility. According to Honda there is a similar inversion at -40°.

Fe<sub>3</sub>O<sub>4</sub> is said to have a similar magnetic inversion point at about 530°, when it suddenly changes from a "ferromagnetic" to a "paramagnetic" condition. We have not yet investigated this inversion thermally.

The relations of these inversions to one another, and to the similar inversions in pure iron and in steel, offer an interesting field for future study.

#### TWO- AND THREE-COMPONENT SYSTEMS OF THE OXIDES

In order to give a comprehensive and concise view of the relationships of the compounds and mixtures which can be made up from any two or three of the refractory oxides, I have compiled the accompanying diagrams (Figs. I and II). The facts are expressed in the form of phase rule diagrams of all the possible two- and three-component systems which can be made up from the 6 oxides SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, CaO, Fe<sub>2</sub>O<sub>3</sub> and FeO. From these 6 oxides there can be made 15 two-component systems and 20 three-component systems, making a total of 35, all of which are included in the two diagrams.

The larger part of the data upon which the compilation is based are from the results of researches made in the Geophysical Laboratory, individual references to which will be omitted. The dotted curves showing the expansion of tridymite and cristobalite are from measurements by Le Chatelier. The melting points of Al<sub>2</sub>O<sub>3</sub>, MgO and CaO were determined by Knoll at the Bureau of Standards.

All of the compositions have been recalculated to a molal percentage basis, in order to bring out more clearly the regularities and analogies. The temperature scales of the two-component diagrams are all alike, and the base of each diagram is at 1000°. In the three-component diagrams the principal temperatures (quintuple points, etc.) are given in figures opposite the curve-intersections to which they apply. The three-component triangles are of course only projections upon a horizontal plane of the space model of the fusion surface, in which temperature is laid off vertically. Inversion points in the solid phases therefore do not appear; it is also not practicable, on account of the small size of the diagrams, to show the primary phases in each field, and various other important facts for which reference must be made to the original papers. The triangular projections do, however, give a good comparative view of the different systems.

Unfortunately, many of the three-component triangles must be left nearly bare of information, but it

is to be hoped that the next few years will see many of these gaps filled. In these cases, as well as in the completed diagrams, I have indicated by letters the compositions of the principal natural minerals belonging in the system.

A study of the composition of the binary compounds of these oxides brings out an important generalization which may be stated as follows: The stable oxygenated compounds of the elements silicon, aluminum, magnesium, lime and iron with one another

It is interesting to note also that the majority of the compounds which are unstable at their melting points contain a larger number of the individual molecules than do the stable compounds.

A generalization similar to the one stated above for binary compounds applies to the ternary compounds, as far as these are known. It may be stated thus: the ternary compounds of the common refractory oxides are made up of the more stable binary compounds (usually 1 : 1 compounds) in simple propor-

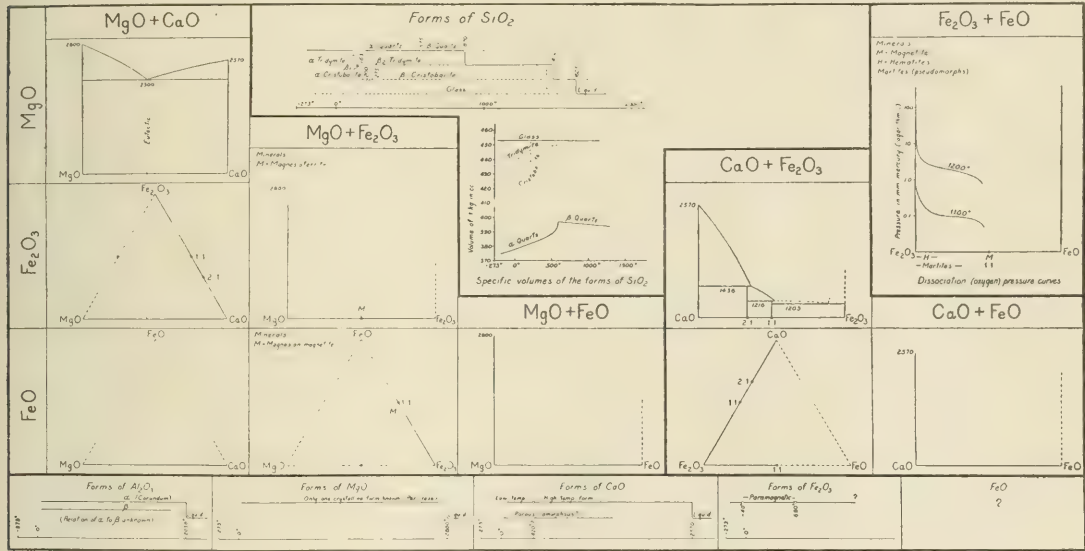


FIG. II

are all made up of the *refractory oxides* of these elements in *simple proportions*, usually 1 : 1 or 2 : 1. This seems to be true quite regardless of what might be expected from valence relations of the elements concerned. The validity of this rule will be evident from Table II, a list of all of the known binary compounds of the common refractory oxides, separated into two classes: (1) those which are stable at their melting points and below, (2) those which dissociate at temperatures below their melting points. Certain mineral compounds, whose properties are not yet well known, are also included.

TABLE II—BINARY COMPOUNDS OF THE COMMON REFRACTORY OXIDES			
SYSTEM	COMPOUND	MINERAL NAME	RATIO OF OXIDES
<i>Stable Compounds</i>			
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> SiO <sub>5</sub>	Sillimanite	1 : 1
SiO <sub>2</sub> -MgO	Mg <sub>2</sub> SiO <sub>4</sub>	Forsterite	2 : 1
SiO <sub>2</sub> -CaO	CaSiO <sub>3</sub>	Wollastonite	1 : 1
	Ca <sub>2</sub> SiO <sub>4</sub>	...	2 : 1
Al <sub>2</sub> O <sub>3</sub> -MgO	Mg <sub>3</sub> Al <sub>2</sub> Si <sub>2</sub> O <sub>12</sub>	Spinel	1 : 1
Al <sub>2</sub> O <sub>3</sub> -CaO	Ca <sub>3</sub> Al <sub>2</sub> Si <sub>2</sub> O <sub>12</sub>	...	3 : 2
	Ca <sub>2</sub> Al <sub>2</sub> Si <sub>2</sub> O <sub>12</sub>	...	2 : 1
Fe <sub>2</sub> O <sub>3</sub> -FeO	Fe <sub>3</sub> O <sub>4</sub>	Magnetite	1 : 1
<i>Mineral Compounds, Stability Unknown</i>			
SiO <sub>2</sub> -FeO	FeSiO <sub>3</sub>	Grunerite	1 : 1
	Fe <sub>2</sub> SiO <sub>4</sub>	Fayalite	2 : 1
Al <sub>2</sub> O <sub>3</sub> -FeO	FeAl <sub>2</sub> Si <sub>2</sub> O <sub>12</sub>	Hercynite	1 : 1
Fe <sub>2</sub> O <sub>3</sub> -MgO	Mg <sub>2</sub> Fe <sub>2</sub> Si <sub>2</sub> O <sub>12</sub>	Magnesioferrite	1 : 1
<i>Compounds Unstable at Melting Point</i>			
SiO <sub>2</sub> -MgO	MgSiO <sub>3</sub>	Enstatite	1 : 1
SiO <sub>2</sub> -CaO	CaSiO <sub>3</sub>	...	3 : 1
	Ca <sub>2</sub> SiO <sub>4</sub>	...	2 : 1
Al <sub>2</sub> O <sub>3</sub> -CaO	Ca <sub>3</sub> Al <sub>2</sub> Si <sub>2</sub> O <sub>12</sub>	...	3 : 1
Fe <sub>2</sub> O <sub>3</sub> -CaO	Ca <sub>2</sub> Fe <sub>2</sub> Si <sub>2</sub> O <sub>12</sub>	...	2 : 1
Fe <sub>2</sub> O <sub>3</sub> -FeO	2FeO.3Fe <sub>2</sub> O <sub>3</sub>	...	2 : 3

tions, usually 1 : 1. This fact is illustrated by Table III, which contains all of the known compounds in two of the ternary systems which have been more or less completely studied:

TABLE III—TERNARY COMPOUNDS OF THE COMMON REFRACTORY OXIDES			
SYSTEM	TERNARY COMPOUNDS	MINERAL	OXIDE RATIOS
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -CaO	CaSiO <sub>3</sub> .Al <sub>2</sub> SiO <sub>5</sub>	Anorthite	(1 : 1) : (1 : 1)
	CaSiO <sub>3</sub> .CaAl <sub>2</sub> Si <sub>2</sub> O <sub>12</sub>	Gehlenite	(1 : 1) : (1 : 1)
SiO <sub>2</sub> -MgO-CaO	CaSiO <sub>3</sub> .MgSiO <sub>3</sub>	Diopside	(1 : 1) : (1 : 1)
	CaSiO <sub>3</sub> .Mg <sub>2</sub> SiO <sub>4</sub>	Monticellite	(2 : 1) : (2 : 1)

An excursion into the field of the alkali silicates furnishes other interesting examples of this principle, as shown in Table IV:

TABLE IV			
SYSTEM	COMPOUND	MINERAL	OXIDE RATIOS
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -Na <sub>2</sub> O	Na <sub>2</sub> SiO <sub>3</sub> .Al <sub>2</sub> SiO <sub>5</sub>	Nephelite	(1 : 1) : (1 : 1) : 0
	Na <sub>2</sub> SiO <sub>3</sub> .Al <sub>2</sub> SiO <sub>5</sub> .2SiO <sub>2</sub>	Jadeite	(1 : 1) : (1 : 1) : 2
	Na <sub>2</sub> SiO <sub>3</sub> .Al <sub>2</sub> SiO <sub>5</sub> .4SiO <sub>2</sub>	Albite (feldspar)	(1 : 1) : (1 : 1) : 4
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> -K <sub>2</sub> O	K <sub>2</sub> SiO <sub>3</sub> .Al <sub>2</sub> SiO <sub>5</sub>	Kaliophillite	(1 : 1) : (1 : 1) : 0
	K <sub>2</sub> SiO <sub>3</sub> .Al <sub>2</sub> SiO <sub>5</sub> .2SiO <sub>2</sub>	Leucite	(1 : 1) : (1 : 1) : 2
	K <sub>2</sub> SiO <sub>3</sub> .Al <sub>2</sub> SiO <sub>5</sub> .4SiO <sub>2</sub>	Orthoclase (feldspar)	(1 : 1) : (1 : 1) : 4

THE SILICATES AS "MOLECULAR COMPOUNDS"

The whole impression left by a review, such as that outlined above, of the silicates and other compounds of the refractory oxides, is that these compounds are really "*molecular compounds*" of the oxides—in Werner's terminology, compounds of second and third order.

Students of the history of chemistry will recognize in this viewpoint something similar to the dualistic system of Berzelius, which flourished over 100 years ago. But it differs radically from Berzelius's system,



in that the idea that there must be a positive and negative part to every molecule is dropped. Long after its electrical basis was shown to be false, Berzelius's system persisted because of its convenience in the classification of chemical substances. The rise of the idea of valence, however, and the remarkable growth of organic chemistry with its basis in the structural formulas of organic compounds, drove Berzelius's system into the background.

Of late years the importance of so-called "molecular compounds" has been gaining increased recognition. It has been realized that the valence theory and the structural formulas based thereon have been inadequate to represent vast numbers of compounds between individual molecules within each of which the valences seemed to be completely "satisfied." It was these compounds that called forth Werner's important work on the ammonia complexes, and his theory of principal and secondary valences, which he has applied to a great number of complex compounds, including crystalline hydrates.

In the meantime, however, the structural formula and fixed valence idea had been extended to the inorganic compounds, including even the little-known silicates. Inorganic chains and rings were more common in the textbooks twenty years ago than they are now, but they still survive. Nevertheless, I think it is a fair statement that little or no good resulted from the inorganic structural formulas, certainly nothing comparable with their yield in the organic field. The most of them represented no real facts about the substance. This is especially true of the silicates, where the attempt to extend the organic idea resulted principally in confusion. Perhaps the climax was reached in a recent book by W. and D. Asch, in which we are provided with structural formulas for window glass and Portland cement.

F. W. Clarke's recent Geological Survey Bulletin on "The Constitution of the Natural Silicates" is based on the structural idea, and some of his formulas do have a defensible basis of fact. But the variance between the facts and the predictions that one might reasonably make from these structural formulas is very wide. One can sit down with a pencil and paper and construct on the valence basis a number of aluminum silicates, for example, of various empirical formulas and various constitutions for each formula, and any one of these would seem just as likely to occur as another. Yet the *only* aluminum silicate that forms at high temperatures, namely, sillimanite,  $\text{Al}_2\text{SiO}_5$ , has to be laid aside by Clarke as possibly a "basic metasilicate," a term that calls to mind the unassorted dump heap of ferric hydrates, lead carbonates, and other muddy mixtures inherited from the days of "basic salts."

This case of aluminum silicate, from the point of view that I am trying to set forth, is comparatively simple.  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , being alike in forming many stable compounds with  $\text{MgO}$ ,  $\text{CaO}$  and other bases, may be expected to form no very stable compounds with each other. If any compound is formed, the one most to be expected is that which contains the simplest ratio of the *oxides*, namely, 1 : 1. This is

exactly the compound that does form. Its small margin of existence, furthermore, is indicated by the very slightly pronounced maximum in the melting curve (see Fig. I), and by the appearance of crystals of its constituent oxides in its melt, suggesting dissociation very near its melting point.

Are the "molecular compounds" drawing us away, then, from the atomic theory and the structural formula? It would be a misfortune if such were the result. The atomic theory need no longer be looked upon as a theory, but rather as an assemblage of well-proved facts, and all chemical theory must rest on the atom. The structural formula, furthermore, has proved too valuable in organic chemistry to be lightly laid aside. At the same time there must be something behind the regularities which appealed to Berzelius, and which form so simple a basis for the understanding of the compounds of the refractory oxides.

There exists a considerable variety of facts which lead unavoidably toward the belief that the simpler molecules retain a certain degree of individuality when they enter into the more complex compounds. Water of crystallization, for instance, shows the same spectral absorption bands as water in solid solution and as liquid water itself. It is not necessary to suppose, however, that there is any sharp division between "molecular" and "atomic" compounds, or between compounds of different "orders." We may rather expect that there is a continuous gradation from compounds in which the physical properties of the constituents have almost completely disappeared, over to the "weakest" of molecular compounds, where the physical properties of the constituent molecules are almost completely retained.

#### THE STRUCTURE OF CRYSTALLINE COMPOUNDS

But no sooner have we convinced ourselves that certain molecules (such as the refractory oxides) retain a considerable degree of their individuality in crystalline compounds, than we are informed by the X-ray analysis of crystal structure that in a crystal the molecule has completely disappeared, or rather, we should say, the crystal itself is one huge molecule. The X-ray spectra of a crystal reveal to us that it consists only of *atoms*, arranged in space in an orderly manner. A crystal of sodium chloride, for instance, is only an assemblage of row upon row and layer upon layer of sodium and chlorine atoms, in which no particular sodium atom is united to any particular chlorine atom. The word "molecule," in the case of crystalline sodium chloride, therefore, no longer represents any concept, as it does in the case of a gas. This apparently unavoidable deduction has been hard for some of the chemists to swallow, and they have sought ways of preserving the molecule in the crystal. Barlow,<sup>1</sup> for instance, believes that a sufficient degree of symmetry to explain the X-ray patterns can be obtained in a sodium chloride crystal by an arrangement of the atoms which still permits a given sodium atom to lie nearer to one particular chlorine atom than to any other chlorine, so that these pairs may still be considered real molecules in the crystal.

<sup>1</sup> *Proc. Roy. Soc.*, **91** (1914), 1-16.

Whether our familiar concept of the molecule will survive, when applied to the crystalline state, is for the future to determine. For the present we may content ourselves with the conviction that the molecule is at least *potentially* present, for let the crystal of sodium chloride be heated to its melting point, then each sodium atom will seize upon a chlorine atom and go whirling away with it into the liquid, like the individuals in a ballroom who have been sitting quietly on orderly rows of chairs until the music starts, when they suddenly group themselves into pairs which go circling about the room.

There is considerable evidence, on the other hand, that certain compounds that exist in the crystalline state are entirely dissociated in the liquid state. The concept of molecule, as applied in the liquid and gaseous states, can therefore have no meaning at all in the case of these compounds. Their formation must be controlled by forces which come into play only when the atoms arrange themselves in orderly patterns; they may be considered to be not the result of chemical affinities or valences between atoms, as we ordinarily understand such forces in a liquid or gaseous molecule, but merely the result of the fact that an orderly arrangement of atoms has been brought about. In other words, the occurrence of a melting point maximum and the other indications of one of these compounds in the phase-rule diagram might have been predicted, not by chemistry, but by geometry. The silicate diopside,  $\text{CaSiO}_3 \cdot \text{MgSiO}_3$ , for instance, may be such a compound. Fig. III gives the curves of specific volume against composition for all mixtures of  $\text{CaSiO}_3$  and  $\text{MgSiO}_3$ , both in the glassy and in the crystalline state. There is no indication of the existence of a compound in the liquid (unordered or glassy) state. Only when the glass is crystallized does the sharp maximum of condensation appear at the composition 1 : 1.

#### PRACTICAL ASPECTS

There are certain principles of practical importance which may be deduced from the facts presented in Figs. I and II. In the first place it will be observed that the maximum melting points in all of the two- and three-component systems are the melting points of pure stable compounds, and the highest melting points of all are those of the pure oxides  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{MgO}$ . This fact is of particular importance to the maker of refractory mixtures. In general, it may be said that the addition of any substance to a refractory will tend to lower its melting point. One principal line of progress in refractories must lie, therefore, in the direction of greater chemical purity in the materials.

Of course, high melting point is not the only desirable feature of a refractory, nor is it always the most desirable. The raw material must be easily molded or cast and easily bonded, and the product must be mechanically strong. In order to get the material bonded and to give it strength and resistance to abrasion, it is customary to add a bonding material. The Norton Company's alundum wares, for instance, contain a variable quantity of a siliceous cement.

The result is a troublesome shrinkage at temperatures far below the melting point of the alumina, which is the principal constituent of the ware; this shrinkage is caused by the combining of  $\text{SiO}_2$  with  $\text{Al}_2\text{O}_3$  and perhaps with other impurities present, and the flowing of the resulting viscous liquid.

An instance of the refractoriness of a pure compound is furnished by the very successful "Marquardt Porcelain" made by the Royal Berlin Porcelain Works. The mineral kaolinite,  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , the principal constituent of fire clay, is not the hydrate of any high-temperature compound, and when it is heated it breaks up. At high temperatures it becomes then simply a mixture of  $\text{Al}_2\text{SiO}_5$  and  $\text{SiO}_2$ , which if heated for a long time will soften and flow at the temperature of the eutectic between  $\text{Al}_2\text{SiO}_5$  and  $\text{SiO}_2$ , which is lower even than the melting point of  $\text{SiO}_2$  or below  $1625^\circ$ . But if  $\text{Al}_2\text{O}_3$  is added to a pure kaolin to make a mixture equivalent in composition to  $\text{Al}_2\text{SiO}_5$ , which is the pure compound sillimanite, then at a high

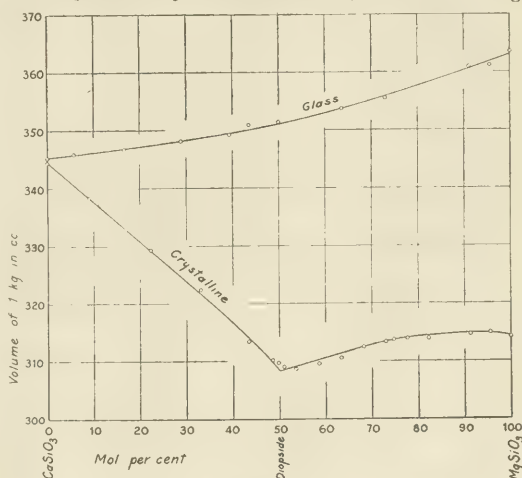


FIG. III

temperature this compound will form. Once formed, it will not melt or flow below  $1815^\circ$ .

This is not, of course, the whole story of Marquardt porcelain. Grinding, mixing, molding, drying, and burning all introduce their difficulties, but the fundamental principle remains that all these processes are directed toward the building of a pure high-melting compound.

An interesting phenomenon exhibited by the refractory oxides is that known as sintering. Any finely powdered substance if held slightly below its melting point will sinter together more or less solidly. The nearer to its melting point an object made of a pure refractory oxide can be burned, therefore, the less binder it will require. There is no reason why a perfectly pure oxide, such as  $\text{Al}_2\text{O}_3$ , cannot be made into a dense hard refractory without the aid of any bond, provided only that the temperature is under good control.<sup>1</sup>

<sup>1</sup> In the discussion of the paper, Mr. Landis stated that in attempting to carry out the Caro process for the oxidation of ammonia, catalyzers of cerium oxide, of thorium oxide, and of various mixtures of these oxides had been tried, and that at a temperature below  $800^\circ$  all of these oxides sintered to an impervious mass on long-time runs.



Another method of bonding a refractory has been already hinted at in the description of Marquardt porcelain. If a pure high-melting compound of two or more oxides be selected as the refractory, it may be made up by thoroughly mixing the component oxides in finely powdered form. The mixture is then molded in the usual way, dried and burned. At a temperature well below the melting point of the compound, the oxides will begin to unite to form the compound, and this chemical reaction will bind the mass together even more effectively than could be accomplished by sintering.

The best example of such a product is magnesium aluminate or spinel,  $\text{MgO} \cdot \text{Al}_2\text{O}_3$ . It has been occasionally used by individual investigators in Germany for crucibles, tubes, and the like, and a similar mixture, probably impure, has also been made up into forms by the Royal Berlin Porcelain Works. As is shown in Fig. I, its melting point is unusually high and its eutectics with its two component oxides melt not much lower ( $1925$  and  $2030^\circ$ ). Particular care need not be taken, therefore, to make it up in the exact proportion to form  $\text{MgO} \cdot \text{Al}_2\text{O}_3$ . It is to be regretted that it is not yet available in this country in forms similar to those of Norton alundum.

Among the other facts represented on the diagrams of Figs. I and II, which find applications in industrial science, we may mention some of the properties of the polymorphic forms of the pure oxides. One of the diagrams of Fig. II represents the volume curves of the forms of silica. The inversion of quartz at  $575^\circ$  is accompanied by a sudden change of volume, an expansion in passing from the low- to the high-temperature form; so a granite wall in a burning building, if it becomes heated to  $575^\circ$ , is seriously shattered by the inversion of the quartz which makes so large a proportion of the stone. The silica brick cap of a glass furnace, as the temperature passes  $575^\circ$ , changes so rapidly in dimensions that a man must be kept at hand with a wrench to "follow up" the cap. No ordinary force is able to resist the change; a pile of 4 or 5 tons of pig iron failed to keep the cap from rising at  $575^\circ$ .<sup>1</sup> Another practical effect is the disintegration of silica brick. Brick made of quartz is likely to be "rotted" or weakened by disintegration if heated and cooled repeatedly past the  $575^\circ$  point.

Fused silica, or "quartz glass," is only stable above the melting point of cristobalite ( $1625^\circ$ ). If used at temperatures below this, it strives constantly to crystallize, and the speed of crystallization is greater, the higher the temperature. Hence the well-known "devitrification" of silica glass. But it happens that the high-temperature form of cristobalite has practically the same density as the glass itself, so that if held at a high temperature the material retains its transparency and homogeneity. Only when it passes the  $\alpha$ - $\beta$  inversion point at  $200$  to  $275^\circ$  does it break up into the familiar chalky, devitrified mass. Whether the cristobalite retains the strength of the glass at high temperatures I do not know, but for some purposes, at least, it might be interesting to see whether the

original advantageous properties of the glass would not be preserved if the furnace were not allowed to cool below  $300^\circ$ .

In 1914 Mr. F. J. Tone, of the Carborundum Company, sent us what seemed to be a new crystalline form of silica, consisting of a chalky mass of fine parallel fibers. The microscope showed that it was really amorphous, and was in fact a *fibrous glass* probably deposited from a vapor. This tendency of amorphous silica to deposit in various fibrous forms is very marked.

Crystalline alumina is now used by the hundreds of tons in grinding-wheels. The crystals are for the most part corundum or  $\alpha$ -alumina, but a certain proportion of  $\beta$ -alumina is also found in the artificial abrasives. One use of this fused alumina which is familiar to all chemists is in the Norton Company's "alundum" articles. We have observed recently that boats made of alundum are extraordinarily constant in weight at high temperatures, much more so than platinum.<sup>1</sup> Platinum steadily loses weight in oxygen at  $1100$ - $1200^\circ$ , especially when iron oxide is heated in it, whereas an alundum boat is constant within  $0.1$  mg. The reason is simple and obvious: platinum is an oxidizable metal and forms a volatile oxide, while alumina is a completely saturated and non-volatile oxide. At  $1100$ - $1200^\circ$  the platinum is oxidized by the oxygen of the air, and the oxide is carried away, while the  $\text{Al}_2\text{O}_3$  remains unchanged.

Many other facts with their practical applications could be brought out by going through the diagrams in detail, but I believe that enough has been said to show that future progress in the application of our knowledge of the common refractory oxides must follow two principal lines: (1) *control of the purity of materials*, and (2) *accurate control of high temperatures*.

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## SOME EXPERIMENTS ON THE CONCENTRATION OF RADIUM IN CARNOTITE ORES

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The investigations<sup>2</sup> of the United States Bureau of Mines have emphasized the fact that the carnotite deposits of Colorado and Utah constitute the principal source of radium in the United States. In recent years these ores have also become one of the main sources of the radium produced abroad. About a year ago the Standard Chemical Company published the statement<sup>3</sup> that in the year 1914 it had produced 18 grams of hydrous radium bromide, equivalent to 9.6 grams of radium element, and that its total production up to March 1, 1915, had reached the handsome figure of 24.3 grams of the bromide.

<sup>1</sup> Hostetter and Sosman, *J. Am. Chem. Soc.*, **38** (1916), 1188-1198.

<sup>2</sup> Moore and Kithil, "A Preliminary Report on Uranium, Radium and Vanadium," Bureau of Mines, *Bull.* **70** (1913); Parsons, Moore, Lind and Schaefer, "Extraction and Recovery of Radium, Uranium and Vanadium from Carnotite," Bureau of Mines, *Bull.* **104** (1915).

<sup>3</sup> Viol, "The Radium Situation in America," *Radium*, **4** (1915), 106

<sup>1</sup> *Trans. Am. Ceramic Soc.*, **15** (1913), 519.

The American carnotites consist of a sandstone with clay binder impregnated with the mineral carnotite, which is probably a hydrous potassium uranium vanadate containing barium and calcium. The valuable constituents of the ore are radium, uranium and vanadium.

The ore on the market is hand sorted and is sold on the basis of its uranium content expressed as the oxide  $U_3O_8$ . The percentage of uranium oxide generally runs between 1.5 and 2.5 per cent, which represents a radium content of 4 to 7 parts per billion ( $4 \text{ to } 7 \times 10^{-9}$  g. radium per g. of ore).

Until recently but little had been published on methods of treating carnotite for the extraction of radium other than a number of patents issued. Practically all of the processes patented involve the extraction of radium by direct chemical treatment. Initial concentration by mechanical means may be in use but the published results are very meager.<sup>1</sup> While the patents describe the processes for the extraction of the valuable constituents of the ore, they afford only scant information as to the quantitative results obtainable.

The value of quantitative experiments conducted on a laboratory scale is well illustrated by the early experiments of Moore and Kithil<sup>2</sup> in which carnotite ore was treated with concentrated hydrochloric and nitric acids. The promising results obtained in the laboratory of the Bureau of Mines have been duplicated during the past two years on a commercial scale in the plant of the National Radium Institute, in Denver. The published results by Parsons, Moore, Lind and Schaefer<sup>3</sup> constitute by far the most comprehensive contribution to the extraction and recovery of radium, uranium and vanadium from carnotite that has appeared.

The experiments of Plum<sup>4</sup> have special scientific value since they present methods of extraction and separation of the other radioactive constituents of carnotite as well as radium. Using 1 kg. of ore, Plum succeeded in extracting 89.9 per cent of the radium by treating successively with sodium carbonate solution, hydrochloric acid, and finally nitric acid.

The investigations of the Bureau of Mines show that equally good extractions can be obtained on a commercial scale by boiling the ore with 38 per cent nitric acid containing a small quantity of hydrochloric acid. After filtering, washing, and partially neutralizing the excess of acid, the radium is removed from the filtrate in the usual way by adding the proper quantities of barium chloride and sulfuric acid. The crude barium sulfates thus obtained generally contain about 1000 parts of radium per billion. The concentration of the radium is increased 150 to 200 times and at the same time nearly all of the uranium and about 50 per cent of the vanadium of the ore are removed.

<sup>1</sup> Fischer outlines a method of initial concentration by grinding the ore and removing the carnotite as slime suspended in water, *Met. and Chem. Eng.*, **10** (1912), 361.

<sup>2</sup> Bureau of Mines, *Bull.* **70** (1913); *Loc. cit.*

<sup>3</sup> *Ibid.*, **104** (1915); *Loc. cit.*

<sup>4</sup> *J. Am. Chem. Soc.*, **37** (1915), 1797.

Our experiments include a study of the following common reagents used in the treatment of carnotite ores with the object of concentrating the radium: (1) concentrated sulfuric acid, (2) sodium bisulfate and salt cake, (3) sulfurous acid, (4) chlorine water, (5) carbonic acid.

#### PARTIAL ANALYSIS OF ORES

In most of the experiments a typical low-grade ore was used containing 1.66 per cent  $U_3O_8$ , 4.03 per cent  $V_2O_5$ , and 4.88 parts of radium per billion ( $4.88 \times 10^{-9}$  g. radium per g. of air-dry ore). A few experiments were conducted with a high-grade ore containing 14.4 per cent of  $U_3O_8$ , 9.7 per cent of  $V_2O_5$ , and 42.68 parts of radium per billion.

The radium values of the ores were determined directly and are approximately 5 per cent higher than the normal equivalent quantities, 4.69 and 40.66 parts of radium, computed by multiplying the uranium content by the equilibrium ratio<sup>1</sup> of radium to uranium ( $3.33 \times 10^{-7}$ ). Differences of this magnitude are not at all uncommon for small lots of ore and have been shown to occur occasionally in ton lots of well sampled ore.<sup>2</sup>

A stock of 250 kg. of low-grade ore was available and 5 kg. of high-grade. Both lots of ore came from the carnotite deposits in the Paradox Valley, southwestern Colorado. The low-grade ore was sampled and ground to pass a 20-mesh sieve in the plant of a commercial ore grinding and sampling firm. The high-grade ore was ground and composited with the ordinary laboratory appliances until it passed a 40-mesh sieve.

The method of analysis followed in the determination of uranium and vanadium in the ores is described in *Bulletin* **70**, U. S. Bureau of Mines,<sup>3</sup> and by Lind and Whittemore in their investigations on the radium: uranium ratio in carnotites.<sup>4</sup> The determination of radium in the ores and radium concentrates separated from them in the course of the experiments was conducted electroscopically by the emanation method. In assaying the ore samples the emanation was generally separated by boiling suitable quantities with nitric acid after the samples had been sealed up for a month or longer to attain equilibrium with the emanation that diffuses away continually under ordinary conditions. Proper measurements of the ionization current produced by the emanation in standardized air-tight electroscopes furnished the data required for computing the quantity of radium.

The determination of radium in the concentrates, crude sulfates, and some of the ore residues (tailings) was conducted for the most part by fusion of weighed samples with mixed carbonates of sodium and potassium followed by solution of the products in nitric acid, or a second fusion, after the lapse of a known period of storage extending over several days. The emanation that accumulates during the interval when collected quantitatively and transferred to a stand-

<sup>1</sup> Heiman and Marekwald, *Jahrb. Radioakt. u. Elektronik*, **10** (1913), 299.

<sup>2</sup> Cf. Lind and Whittemore, *J. Am. Chem. Soc.*, **36** (1914), 2080.

<sup>3</sup> Moore and Kithil, Bureau of Mines, *Bull.* **70** (1913), 88.

<sup>4</sup> *J. Am. Chem. Soc.*, **36** (1914), 2076.



ardized electroscope, can be accurately determined by properly measuring the ionization current produced. From the data thus obtained the quantity of radium in the sample is readily deduced.<sup>1</sup>

In most of the experiments the approximate percentage extraction of radium from the ore was determined by comparison of the  $\alpha$  radiation from equal surfaces of ore and tailings spread out in thin layers on very shallow trays. Extraction values obtained by this method always exceeded the values found by determining the radium content of the tailings by the emanation method, when sulfuric acid or salt cake were used in treating the ore.

This observation was a matter of some moment to us and materially delayed the progress of the experiments. It explains a discrepancy frequently obtained in checking up the recovery of radium. In determining the distribution of radium among the concentrates, tailings and solutions obtained in the course of an experiment, the total radium recovered generally fell short 5 per cent or more (see data 20 to 23, Table I) when the radium content of the tailings was based upon the activity measured by the  $\alpha$  radiation from films of ore and tailings of equal area, even after the latter had stood for a month. For example, an extraction of 92 per cent by the film method would generally correspond to a recovery of only 86 per cent of the radium. This discrepancy disappeared when the determination of radium in the tailings was made by the emanation method in the same way as the carnottites and crude sulfates were assayed. The extraction values were then lower, and the apparent loss of radium was found to be present in the tailings.

At one stage of the work we searched in vain for radium losses in the solutions obtained when liquors of concentrated sulfuric acid containing barium and radium dissolved as bisulfates are diluted with water to precipitate the normal sulfates. The diluted solutions ranged in concentration from 5 to 15 per cent of sulfuric acid. Determinations in this laboratory conducted by J. Underwood, on the solubility of the sulfates of the alkaline earth metals in C. P. sulfuric acid (99.5 per cent  $\text{H}_2\text{SO}_4$ ), indicate that approximately 5 per cent of sulfates remain dissolved when saturated solutions of the bisulfates in concentrated sulfuric acid are diluted with water. For example, after boiling concentrated sulfuric acid containing an excess of finely powdered barium sulfate for several hours to obtain a saturated solution of the bisulfate, the quantities of barium sulfate in samples of 10 cc. each of the clear liquid were found to be 1.957 and 1.850 g., respectively. The higher value represents the residue left when the acid was expelled directly, while the lower result is the weight of barium sulfate obtained by diluting the acid with 10 volumes of water. It will be noted that the direct determination is about 5 per cent higher than the

value obtained by the procedure followed in recovering radium from sulfuric acid liquors.

Moreover, Lind,<sup>1</sup> in his investigations on the determination of radium by the emanation method, points out that very erroneous results may be obtained with solutions containing no barium but an excess of a barium precipitant such as a sulfate or carbonate, which are usually solutions from a radium-barium precipitation.

Our customary procedure of determining the small quantities of radium in the filtrates obtained from the precipitation of radium-barium sulfates by diluting concentrated sulfuric acid solutions was to boil an aliquot part of the filtrate to expel any radium emanation and then store the solution for a definite period in a sealed flask. The emanation that accumulated during the period of storage was then boiled off, collected, and transferred to an air-tight standardized electroscope and the ionization current properly measured. The values thus obtained represented only 0.1 per cent of the radium in ore samples or concentrate—a relatively small fraction of the observed discrepancy. But if radium is precipitated during the period of storage, then the emanation obtained by boiling may be far too low as the radium-barium sulfate precipitates are very low in emanating power.

To ascertain whether considerably larger quantities of radium may escape detection in the filtrates by our procedure, determinations were conducted in some other ways:

(1) A precipitate of barium sulfate was thrown down in the hot filtrate by adding 5 cc. of a 5 per cent solution of barium chloride. After standing 4 days to complete the precipitation and settling of the sulfates, the precipitate was removed, fused with mixed carbonates of sodium and potassium and the radium determined by the procedure outlined above for the assay of crude sulfates and concentrates.

(2) The sulfuric acid of the filtrates to be tested for radium was nearly neutralized with sodium hydroxide and 5 cc. of barium chloride solution added. The radium content of the precipitate of barium sulfate was then determined as in the preceding experiment.

(3) Samples of solutions obtained from some of the ore concentrates were evaporated and the free sulfuric acid expelled by heating. Radium was determined in the residues by the emanation method after fusion with mixed carbonates.

The radium values obtained by precipitating barium sulfate in the filtrates as outlined in (1) and (2) above stood in good agreement with the low radium content of the solution as determined by the usual method followed in our experiments.

However, the radium content of the total residue obtained by evaporating the excess of sulfuric acid was found to be 1.1 per cent of the radium content of the ore samples and concentrates (see Tables I and II). We attribute this higher value to the presence in the filtrate of traces of precipitated radium-barium sulfate that passed through the filter. But

<sup>1</sup> For details of operation, apparatus, and formulas used in the calculation of results, see among other references: Schlundt and Moore, *J. Phys. Chem.*, **9** (1905), 320; Randall, *Trans. Am. Electrochem. Soc.*, **21** (1912), 463; Lind and Whittemore, *J. Am. Chem. Soc.*, **36** (1914), 2062-5; Schlundt, *Trans. Am. Electrochem. Soc.*, **26** (1915), 163.

<sup>1</sup> THIS JOURNAL, **7** (1915), 1024.

inasmuch as the introduction into our balance sheet for radium of 1.1 per cent for radium losses in the solutions still left a discrepancy of nearly 5 per cent for most of the runs we then turned our attention to a more careful examination of the tailings and found there the missing radium.

In this connection we wish to point out that the presence of a relatively large amount of silica in the samples of tailings was not found to interfere in making the radium determinations provided the fused mass is pulverized before it is sealed up for the accumulation of the emanation. If the fusion is not ground up, then the acid fails to penetrate very far into the interior and the results are far too low. The values obtained by removing the silica before fusion with mixed carbonates, as suggested by Lind,<sup>1</sup> were generally somewhat smaller than the direct determinations with silica present.

#### TREATMENT OF ORE WITH SULFURIC ACID

When carnotite ores are treated with sulfuric acid the uranium and vanadium compounds are converted into water-soluble form and their extraction may be made practically quantitative. In the process of Fleck, Haldane and White,<sup>2</sup> the ore is boiled with 15 to 20 per cent acid, which results in leaving the radium with the insoluble residue. The radium may be concentrated by agitating the residue with water and separating the coarse and fine materials by differential sedimentation. In this way most of the radium becomes distributed among the finely divided portion of the residue representing approximately one-tenth of the ore.

McCoy's method<sup>3</sup> of treating carnotites involves roasting with concentrated sulfuric acid till finally a temperature of 300° or even higher is reached. When the solid cake is leached with water, the soluble sulfates are removed and the radium remains with the insoluble residue from which it may be recovered by any known method, the treatment being materially simplified by the absence of vanadium, uranium and iron.

Danforth, Samuels, and Martersteck<sup>4</sup> have devised a method for the treatment of complex refractory carnotites for the purpose of obtaining, especially, vanadium compounds. The crushed ore is first given a plain oxidizing roast at a temperature of about 600°, and is then treated with sulfuric acid of about 1.30 sp. gr. at 80°. The radium and barium which may be present in the ore remain in the residue. To extract the radium, the residue, after removal of soluble sulfates, is treated with mixed solutions of sodium hydroxide and sodium carbonate (the reagents used by Haitinger and Ulrich<sup>5</sup> in working up the residues of pitchblende) to render the sulfates and silicates soluble, and to convert radium and barium compounds into carbonates. After filtering

and thorough washing of the residue, the radium and barium carbonates are removed with dilute hydrochloric acid and recovered from the filtrate by the addition of the proper quantities of sulfuric acid and barium chloride.

When carnotite is boiled with concentrated sulfuric acid in considerable excess, the radium and some of the calcium compounds present are, among others, converted into bisulfates which remain in solution in the hot acid and may then be separated from the insoluble components by filtration followed by washing the residue with concentrated sulfuric acids. From the acid liquors thus obtained the radium is recovered by diluting with water, whereby barium-radium sulfate is precipitated, and calcium sulfate too, if the acid liquor is diluted with an equal quantity of water as proposed by Bredt,<sup>1</sup> but a high-grade crude sulfate relatively low in calcium can be obtained directly by diluting the acid liquor with at least 10 times the bulk of water, as outlined by Schlundt.<sup>2</sup>

When the valuable constituents of the ore—radium, vanadium and uranium—are removed with concentrated sulfuric acid by a single stroke, it is necessary to use about 3 times as much acid as ore.<sup>3</sup> A considerable saving of acid can be effected by conducting the concentration of radium in steps that finally yield crude sulfates of equally good quality. The method involves: (1) digestion or roasting of the ore with a sufficient quantity of concentrated acid to convert the iron, vanadium, and uranium into soluble sulfates, and the barium and radium into bisulfates; (2) leaching of the resulting paste or solid cake with water accompanied by a separation of the coarse and fine portions of the insoluble residue; (3) extraction and recovery of the radium as crude sulfates by treating the radium concentrate with an excess of strong sulfuric acid or some other known method of extraction. The details of the process follow:

Preliminary experiments were conducted in porcelain ware with 100-g. samples of ore in order to determine the amount of acid required and the temperature and period of digestion necessary to obtain a good extraction of radium. Subsequent experiments in cast iron kettles with charges of ore of at least 1 kg., and in one experiment 50 lbs. of ore, gave the quantitative data given in Table I.

When 5 parts of low-grade ore, ground to pass through a 20-mesh sieve, were digested with 4 parts by weight of crude sulfuric acid, 60° Bé., a temperature of 250 to 300°, maintained from 15 to 30 min., was found sufficient to segregate fully 87 per cent of the radium in the finely divided portion of the insoluble residue obtained by leaching with water and differential sedimentation of the products. When the acid was reduced to 1 part by weight of acid to 2 parts of ore, the period of roasting had to be extended to at least half an hour and a final temperature of 300° or higher was necessary in order to have the acid penetrate all parts of the ore and to secure a good ex-

<sup>1</sup> THIS JOURNAL, 7 (1915), 1024; *Loc. cit.*

<sup>2</sup> U. S. Patent 890,584 (1908). The different methods of treating carnotite ores patented in the United States prior to 1915 are described in detail in Bureau of Mines, *Bull.* 104 (1915), 15-27.

<sup>3</sup> U. S. Patent 1,098,282 (1914).

<sup>4</sup> U. S. Patent 1,126,182 (1915).

<sup>5</sup> K. K. Akad. Wissenschaft (Vienna), 117 (1908), 619

<sup>1</sup> U. S. Patent 1,154,231 (1915).

<sup>2</sup> U. S. Patent 1,181,411 (1916).

<sup>3</sup> Schlundt, *J. Phys. Chem.*, 20 (1916), 485.



traction of radium. In treating the high grade ore equal weights of acid and ore were boiled and the digestion period was extended to an hour.

The next step consisted in gradually transferring the ore-acid mass, preferably still hot, to a wooden tank containing a volume of tap water about 3 times that of the ore, and constant stirring to promote interaction and solution. The leaching with water produces precipitation of the radium-barium sulfates in very finely divided form, while the uranium and vanadium, with more or less of the other soluble compounds, pass into solution. The sands and silicates of the ore, being for the most part relatively coarse-grained, settle quite rapidly when agitation of the liquor ceases, while the finer particles, including the radium-barium sulfates, settle relatively slowly, and thus for a time constitute a suspension above the coarse sands. In fact, about a minute after the agitation of the solution ceases, a distinct boundary appears between gray sandy sediment, supernatant blue liquid and nearly white suspension.

Within 2 min. after the last stirring, the liquid with suspended matter was siphoned off or run off

clear liquid was then carefully run off. The sediment or sludge remaining, when dried, constitutes the radium concentrate. Representative data selected from several experiments are incorporated under three series in Table I.

#### TREATMENT OF THE CARNOTITE WITH SODIUM BISULFATE AND SALT CAKE

The decomposition of complex radium ores by fusion with sodium bisulfate was devised by Radcliff,<sup>1</sup> and found suitable in concentrating the radium in the refractory carnotites found in Olary, South Australia. The Australian carnotites contain rare earth and acid earth minerals not found in American carnotites. Hence, to obtain complete decomposition, 10 to 15 per cent of sodium chloride is added to the charge of ore and sodium acid sulfate while the mass is still fluid.

In our preliminary experiments low-grade ore, ground to pass a 20-mesh sieve, was stirred into fused sodium bisulfate in a small iron kettle heated externally. Later, larger quantities of ore were mixed with three times their weight of commercial salt cake obtained

TABLE I—CONCENTRATION OF RADIUM IN CARNOTITE WITH SULFURIC ACID

No.		SERIES A	SERIES B	SERIES C
1	Description of ore.....	20-mesh.	20-mesh.	40-mesh.
2	Weight Used: Ore.....	Low grade	Low grade	High grade
3	Coarse sands (tailings).....	1720 g.	22.68 kg.	500 g.
4		1372 g.	18.58 kg.	270 g.
5	CONCENTRATE.....	79.8 g.	81.9%	54.0%
6		74.19 g.	857.69 g.	50.0 g.
7	ORE DISSOLVED.....	4.31%	3.77%	10.0%
8		348 g.	4.14 kg.	230 g.
9	ACID USED.....	20.2%	18.2%	46.0%
10	Volume of diluted solution.....	1720 g., sp. gr. 1.72	21.05 kg., sp. gr. 1.72	457.5 g., sp. gr. 1.83
11	Barium chloride added.....	12 liters	172 liters	6920.0 cc.
12	TOTAL RADIUM: In ore.....	1.0 g.	5.0 g.	2.0 g.
13	In concentrate.....	$8.39 \times 10^{-6}$ g.	$11.07 \times 10^{-5}$ g.	$2.118 \times 10^{-5}$ g.
14		$7.26 \times 10^{-6}$ g.	$9.61 \times 10^{-5}$ g.	$1.67 \times 10^{-5}$ g.
15	In liquors.....	86.5%	86.8%	79.0%
16		$8.4 \times 10^{-8}$ g.	$1.2 \times 10^{-7}$ g.	$1.7 \times 10^{-7}$ g.
17	In tailings (Em. method).....	1.0%	1.1%	0.8
18		$1.34 \times 10^{-6}$ g.	..	..
19	(Film method).....	15.9%	..	..
20	PERCENTAGE EXTRACTION (Em. method).....	7.9%	8.0%	13.6%
21		84.1%	..	..
22	RADIUM NOT ACCOUNTED FOR BY FILM METHOD (a).....	92.1%	92.0%	86.4%
23	RADIUM PER GRAM: Of ore.....	4.6%	4.1%	6.6%
24	Of concentrate.....	$4.88 \times 10^{-9}$ g.	$4.88 \times 10^{-9}$ g.	$4.235 \times 10^{-9}$ g.
25	Concentration ratio.....	$9.79 \times 10^{-8}$ g.	$11.20 \times 10^{-8}$ g.	$3.39 \times 10^{-7}$ g.
26	Vanadium in tailings, $\text{V}_2\text{O}_5$ .....	20.1 : 1	22.9 : 1	8 : 1
27	Uranium in tailings.....	1.0% of total	1.0%	..
		None	None	..

(a) This datum is the difference between datum 21 and the sum of data 14 and 16.

by opening a series of stopcocks arranged at different levels in the separating tank. Naturally, to complete the removal of the finely divided material still remaining in the sands after the first treatment with water, the sands were given at least three additional washings, preferably with water containing a trace of barium chloride to prevent redissolution of a part of the radium-barium sulfate. The washed sands constituting the tailings rarely contained more than 12 per cent of the radium in the low-grade ores.

The several wash liquors were then united and stirred vigorously for at least 10 min. to promote solution of the sparingly soluble calcium sulfate which formed nearly one-fifth of the suspended matter in the liquor of the first leaching with water. The total quantity of water used for leaching was approximately 10 times the weight of the ore treated. The remaining suspended matter in the combined liquors was then allowed to settle 3 or 4 days in order to complete the precipitation of the radium-barium sulfates. The

as a by-product in the manufacture of nitric acid. The salt cake used was found to contain 33.8 per cent of available acid which represents a product containing nearly 83 per cent as much replaceable hydrogen as in the acid sulfate,  $\text{NaHSO}_4$ .

The final temperature of fusion generally exceeded  $350^\circ \text{C.}$ , and the mixture was kept in a fluid state for at least half an hour and stirred occasionally with an iron ladle. We did not find it necessary to add common salt to the fused charge to complete the decomposition of the ore.

When the fused mass was still hot and somewhat fluid it was slowly poured in a thin stream into 5 times its volume of water which was vigorously stirred to promote interaction and solution. When agitation ceases the coarse sands settle rapidly while the radium-barium sulfates and fine sands remain for a time suspended in the turbid liquid and their separation from the coarse sands is accomplished as pre-

<sup>1</sup> U. S. Patent 1,049,145 (1912).

viously described in the treatment of the ore with concentrated sulfuric acid.

Series F, Table II, gives a typical set of experimental data obtained when low-grade ore was treated with  $2\frac{1}{2}$  times its weight of salt cake as described.

TABLE II—CONCENTRATION OF RADIUM IN CARNOTITE WITH SULFUROUS ACID AND SODIUM BISULFATE & SALT CAKE

No.	SERIES E Sulfurous acid	SERIES F Salt cake
1 Ore used.....	200 g.	1000 g.
2 Coarse sands recovered.....	164.2 g.	828 g.
3 Per cent tailings.....	82.1%	82.8%
4 Concentrate.....	19.19 g.	53.0 g.
5	9.09%	5.3%
6 Ore dissolved.....	35.8 g.	172 g.
7	17.9%	17.2%
8 Volume of diluted solution....	0.2 g.	1 g.
9 $\text{BaCl}_2$ added.....	1 g.	10 liters
10 TOTAL RADIUM: In ore.....	$9.76 \times 10^{-7}$ g.	$4.88 \times 10^{-6}$ g.
11 In concentrate.....	$8.26 \times 10^{-7}$ g.	$4.21 \times 10^{-6}$ g.
12	84.6%	86.1%
13 In liquors.....	$1.92 \times 10^{-8}$ g.	1 g.
14 In tailings (film method).....	1.89%	5%
15 Extraction.....	8.0%	95%
16 Radium not accounted for....	5.5%	7.9%
17 Radium per gram of ore.....	$4.88 \times 10^{-8}$ g.	$4.88 \times 10^{-8}$ g.
18 Radium per gram of concentrate.....	$4.54 \times 10^{-8}$ g.	$7.94 \times 10^{-8}$ g.
19 Concentration ratio.....	11:1	16.1:1

#### TREATMENT OF ORE WITH SULFUROUS ACID

Fleck, Haldane and White<sup>1</sup> suggest the direct extraction of vanadium and uranium from carnotite ores by passing sulfur dioxide into water covering the ore. Burfeind,<sup>2</sup> in addition, describes the concentration of radium in carnotites by treating the subdivided ore with sulfurous acid. The leaching is conducted at room temperatures and presumably at atmospheric pressure. The action of the acid may be hastened by agitation and in the course of a day or two most of the uranium and vanadium are dissolved. Shortly after agitation ceases the coarse gangue settles out and a brown amorphous mud remains for a time in suspension in the supernatant liquid. If the solution and suspended matter are drawn off about a minute or two after agitation ceases, and this operation repeated with fresh portions of dilute sulfurous acid, the radium is carried over and found for the most part in the fine sediment that finally settles out. The uranium and vanadium compounds remain dissolved in the sulfurous acid. The brown sediment constitutes the radium concentrate. Uranium and vanadium are partially recovered by boiling off the sulfur dioxide whereupon basic sulfites of uranium and vanadium are precipitated.

Since the sulfurous acid is oxidized to some extent during digestion, some sulfates are formed, and probably for this reason the precipitation of uranium and vanadium is incomplete when the excess of sulfur dioxide is expelled.

The experimental data given under Series E, Table II, were obtained by giving 200 g. of low-grade ore three leachings each with 400 cc. of saturated sulfurous acid at room temperatures under atmospheric pressure. In each treatment the ore and acid were left in contact for a day in a closed vessel and were well shaken up 6 to 8 times during the first 12 hrs. of the first and second acid treatments, and then allowed to settle for 12 hrs. The clear green liquid was then drawn off. In the third treatment the liquid and suspended

matter were siphoned off after one minute of settling. To complete the separation of coarse and fine sands the ore residue was shaken twice with 400 cc. of water and after one minute of settling, the turbid liquid was drawn off. The coarse gangue material left in three experiments was found to contain from 7 to 12 per cent of the radium in the ore. The sediment of fine sands that settled out from the combined leaches and wash waters after standing 4 days averaged 9 per cent of the weight of ore taken, and contained from 85 to 90 per cent of the radium. From 1 to 4 per cent of the radium was found in the clear solutions. By this process then the radium is concentrated approximately 11 times with an extraction of nearly 87 per cent, whereas in the treatment with concentrated sulfuric acid or salt cake, the extraction is equally good while the concentration ratio is nearly 25 times for the former and 17 for the latter.

#### LEACHING OF LOW-GRADE ORE WITH CHLORINE WATER AND CARBONIC ACID

In view of the statement by Erdman<sup>1</sup> that small quantities of barium sulfate are not precipitated in the presence of free chlorine, it seemed worth while to ascertain whether treatment of carnotites with chlorine water results in a selective extraction of radium. Moreover, the marked solvent action of carbonated waters on compounds of the alkaline earth metals, particularly the carbonates, invited experimentation with carbonic acid.

Experiments were conducted with 100-g. samples of ore in closed vessels at room temperatures and under atmospheric pressure. Ore samples of 20 mesh were given one treatment with 200 cc. of saturated chlorine water (or carbonic acid), respectively. The ore and liquid remained in contact for at least a day and during the first 12 hrs. the contents of the vessels were shaken at least 10 times. After settling some hours, the ore and liquid were separated by decantation and filtration. The extractions of radium obtained in these preliminary experiments ranged from 15 to 30 per cent for the treatment with chlorine water and 30 to 40 per cent with carbonic acid. Although these results were not very promising, further experiments are in progress with the hope of increasing the extraction by having the ore in a finer state of division and extending the period of digestion under different conditions of temperature and pressure.

#### FURTHER TREATMENT OF RADIUM CONCENTRATE

The radium concentrates obtained by treating the ore with sulfuric acid or salt cake as described contain from 80 to 120 parts of radium per billion. The radium-barium sulfates constitute less than 10 per cent of the material, the large bulk being finely divided silica and silicates, which must be removed before refining of the crude sulfates is undertaken.

Two methods of further concentrating the radium were tried with the stock of about 2 kilos of concentrates obtained in the course of various experiments

<sup>1</sup> U. S. Patent 890,584 (1908).

<sup>2</sup> U. S. Patent 1,095,377 (1914).

<sup>1</sup> *J. prakt. Chem.*, **75** (1858), 215.



in which the ore samples were treated with sulfuric acid and salt cake.

The first method used involved selective extraction of the sulfates of barium and radium by boiling the concentrate with concentrated sulfuric acid (sp. gr. 1.82) whereby the bisulfates are formed; these remain in solution in an excess of the hot acid and are then removed by filtration followed by washing the insoluble residue with fresh portions of hot concentrated acid. From the combined filtrates the radium and barium are precipitated by dilution with 6 to 10 volumes of water containing a small quantity of barium chloride. After settling for 3 or 4 days, the diluted acid is run off and the sulfates collected on a filter. The crude sulfates thus obtained generally amounted to about 10 per cent of the concentrate taken; but it should be stated that the amount of crude sulfates obtained depends to a great degree upon the porosity of the filter used in filtering the hot acid liquors. We used for filters asbestos packed in a Buchner funnel, and plates of "Filtros" 4 cm. thick. Filtros plates of medium porosity allowed some of the fine sands to pass, thereby reducing the concentration to 4 or 5.

TABLE III—SECOND STAGE OF CONCENTRATING RADIUM

No.	Extraction with concentrated sulfuric acid	Fusion with mixed carbonates
1 Concentrate.....	50 g.	10 g.
2 Reagent used.....	183 g.	50 g.
3 Crude sulfates obtained.....	6.54 g.	0.596 g.
4 Radium in concentrate.....	$5.60 \times 10^{-8}$ g.	$7.71 \times 10^{-7}$
5 Radium in crude sulfates.....	$5.33 \times 10^{-8}$ g.	$8.42 \times 10^{-7}$
6 Radium recovered.....	95.18%	91.5%
7 Concentration ratio.....	7.64 : 1	16.8 : 1
8 Radium in tailings (film method).....	4.8%	1.0%
9 Radium in solutions.....	1.0%	1.0%

The results reported in Table III were obtained with asbestos filters and the finest grade of Filtros.

The second method of concentration tried was the customary procedure of decomposing silicates by fusion with mixed carbonates of sodium and potassium. When the fused mass was lixiviated with water, the soluble silicates were completely hydrolyzed. The insoluble residue, consisting of silica and the carbonates of radium and barium, was well washed with a 1 per cent solution of sodium carbonate until free from sulfates, and was then digested with dilute C. P. hydrochloric acid for several hours. After filtering and washing, a slight excess of sulfuric acid was added to the filtrate to precipitate the radium along with barium as sulfates. After standing for 4 days, to complete the precipitation of the sulfates, the liquid was run off and the precipitate collected on a filter. The solution of chlorides contained other bases in considerable quantity besides barium and radium, since the sulfates precipitated were found to weigh only one-third as much as the dry residue of chlorides. Typical experimental data obtained are given in Table III.

#### SUMMARY

I—A typical low-grade American carnotite was treated with concentrated sulfuric acid at elevated temperatures whereby radium and barium compounds are converted into bisulfates and the vanadium and uranium compounds are rendered soluble in water. From the resulting product a radium concentrate of fine sands was separated by lixiviating with a large volume of water followed by differential

sedimentation. Approximately 87 per cent of the radium was thus separated and practically all of the vanadium and uranium extracted. The concentration of radium in the sediment of fine sands ranged from 20 to 28 times that of the ore.

II—Low-grade carnotite when fused with sodium bisulfate or salt cake likewise yielded a product from which a radium concentrate was separated by treatment with water accompanied by differential sedimentation. The sediment of fine sand was found to carry approximately 86 per cent of the radium of the ore and its concentration was increased from 15 to 20 times, depending to some extent upon the purity of the salt cake used. Vanadium and uranium passed into solution nearly quantitatively.

III—Digestion of low-grade carnotite with sulfurous acid at room temperatures and differential sedimentation of the products resulted in a segregation of approximately 85 per cent of the radium in the finely divided gangue material at a concentration of 10 to 12 times that of the ore.

IV—The distribution of radium was determined among the solutions, concentrates, and residues obtained by the above methods of treating carnotites.

V—The radium in the concentrates obtained by treating the ore with sulfuric acid or salt cake was separated in the form of crude sulfates by two methods: (1) Digestion with an excess of concentrated sulfuric acid, and (2) fusion with mixed carbonates of sodium and potassium. The crude sulfates thus obtained contain fully 80 per cent of the radium of the ore, and the concentration ranges from 150 to 300 times that of the ore.

VI—Preliminary experiments were conducted on the extraction of radium from carnotites with chlorine water and carbonic acid.

VII—The radium content of the tailings obtained in treating the ore with sulfuric acid or salt cake when determined by the emanation method was found to exceed the values obtained by comparison of the radiation from equal areas of ore and tailings. Hence it is suggested that in the approximate determination of radium in such tailings by the latter method comparisons be made against standardized samples of tailings instead of ore.

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#### ERRORS IN THE DETERMINATION OF ACID VALUES OF BOILED OILS AND VARNISHES

By E. E. WARE AND R. E. CHRISTMAN<sup>1</sup>

Received June 23, 1916

One of the most common analytical constants utilized in the valuation of fats, oils, and varnishes, is the neutralization or acid value. The procedure as outlined in standard texts is quite definite, although it is not ordinarily considered that any appreciable error is introduced by slight variations from recommended practice.

While it is well recognized that the regular pro-

<sup>1</sup> Holder of the Acme White Lead and Color Works Fellowship in Chemical Engineering at the University of Michigan, 1915-1916.

cedure is not satisfactory for the estimation of free fatty acids in alkali soaps, owing to the very decided hydrolysis of such materials in alcohol and ether, apparently no provision has been made for the occurrence of similar hydrolysis of the metallic soaps in the analysis of boiled oils and varnishes.

Ragg<sup>1</sup> does mention the hydrolysis of lead and zinc linoleates by water in discussing the perishability of paint films, but it has not generally been known that these soaps are similarly affected by alcohol.

While carrying out an investigation as to the rôle of metallic soaps in the deterioration of mixed paints during storage the authors were struck by the very evident hydrolysis of the metallic linoleates and resinates during the estimation of the free fatty acids in the vehicle of the aged paints under observation.

Since these salts of linseed oil are so easily hydrolyzed, it is apparent that their presence in the dissolved state would cause an oil to show an acid value which would include the amount of alkali necessary to hydrolyze the soaps present as driers as well as that required to neutralize the free fatty acids. This is a point which we believe has never before been brought to the attention of the oil chemists and is of great importance.

In order to study this influence that the metallic soaps exert on the determination of the acid value in oils, those soaps of linseed oil which are most likely to occur in a boiled oil or varnish, *i. e.*, lead, manganese, cobalt, calcium and zinc, were prepared by precipitation from a neutral solution of the sodium soap, and dried in a vacuum. Using 280 as the molecular weight of the acid radical, the theoretical acid numbers, assuming complete hydrolysis of KOH, were computed as follows:

LEAD	MANGANESE	COBALT	CALCIUM	ZINC
146.2	182.4	181.2	186.8	179.3

On titrating these soaps dissolved in an alcohol-ether mixture, the actual acid numbers found varied only a few tenths from the above figures, except in the case of calcium soap. This showed an acid number of but 79.5, indicating, as might have been expected, only partial hydrolysis. In these titrations the final end-point was taken when the pink of the phenolphthalein would remain for several hours without vanishing. However, the amount of alkali necessary after the first appearance of the fugitive pink color was in no case considerable.

The rosin salts of the same metals were prepared in a similar manner and dried in vacuum. On titrating these in an alcohol-ether solution, they gave the following results. The calculated acid value was computed from the formula  $C_{20}H_{30}O_2$  for rosin:

	APPARENT ACID VALUE	CALCULATED ACID VALUE Assuming Complete Hydrolysis	Per cent Hydrolyzed
Lead salt.....	113.0	139.0	81.3
Manganese salt..	168.3	171.2	98.3
Cobalt salt.....	160.0	170.3	94.0
Calcium salt.....	86.0	175.3	49.1
Zinc salt.....	149.0	168.7	88.3

An oil having an original acid value of 3.05 was

heated with a quantity of lead linoleate to a slightly cloudy solution. This boiled oil had an ash content of 1.15 and an acid value of 10.20. A sample of the same oil run parallel to it but without the drier showed a final ash content of 0.18 per cent and an acid value of 2.31, the decrease in the latter value being due to the volatilization of some of the fatty acid originally present. The difference between the ash content of the oil containing drier and the oil without it indicated the presence of approximately one per cent of lead oxide in solution as the linoleate. This should cause an apparent acid number of 7.1 for the boiled oil, assuming hydrolysis to the same extent as in the previous experiments. The value of 10.20 actually found might indicate that the lead exerted some slight saponifying action on the oil at the high temperature employed in effecting the solution.

This error in the determination of the acid value of oils is in many cases not serious since the amount of soluble metallic soaps is limited. But in varnishes, where the hydrolyzable substance in solution is a metallic soap of rosin or gum, which may be present in considerable quantities, the apparent acid value is but a poor criterion of the conditions actually existing.

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## STORAGE CHANGES IN VEGETABLE AND ANIMAL OILS

By HENRY A. GARDNER

Received October 5, 1916

The writer's attention has recently been called to instances where linseed oil that has been separated from paints has shown low chemical constants. In one instance, several barrels of paint made of pure raw linseed oil stood in a factory yard for a few weeks, exposed in the daytime to the sun. A temperature of 115° F. was probably reached in the middle of the day. Upon analysis, the consumer found the oil that was separated from the paint to have a lower iodine number than that called for by the specifications. The shipment of paint was accordingly rejected. Since pure linseed oil of the proper iodine number was used in the paint, it is apparent that hydrolysis occurred on storage. That such changes are possible should, therefore, be considered by the testing engineer when examining the vehicles of specification paints that have not been freshly used or that have been exposed to high temperatures during storage.

The writer has previously pointed out the degree of change which may be expected to take place in linseed oil when ground with various pigments,<sup>1</sup> and he has also indicated the contributing effects of impurities in oils.<sup>2</sup> Some more recent work has shown that nearly all oils, even when not in contact with pigments, will show changes in their chemical constants when allowed to stand for a period of time. The drop in iodine number is generally accompanied by a rise in specific gravity and acid value.

Quantities of a number of oils were obtained by

<sup>1</sup> The "Effect of Pigments upon the Constants of Linseed Oil," H. A. Gardner, *J. Frank. Inst.*, Oct., 1912, pp. 415-423.

<sup>2</sup> "Changes Occurring in Oils and Paste Paints. Due to Autohydrolysis of the Glycerides," H. A. Gardner, *J. Frank. Inst.*, May, 1914, pp. 533-540.



TABLE 1—ANALYSIS OF OILS

Analyses were made when oils were first obtained and 44 mos. later, at the time they were used in repainting tests. The oils were again analyzed 22 mos. later in September, 1916. Chemical changes occurring in the oils are denoted by the constants.

	Sp. Gr.	Iodine No.	Sapon. No.	Acid No.	Ref. Index
<b>RAW LINSEED OIL</b>					
March, 1911.....	0.931	186	188	2.0	.....
November, 1914.....	0.933	185.4	189.6	2.8	1.4867
September, 1916.....	0.936	176.9	190.2	3.3	1.4798
<b>SOYA BEAN OIL</b>					
March, 1911.....	0.924	129	189	2.3	.....
November, 1914.....	0.925	130.2	193.1	4.7	1.4813
September, 1916.....	0.937	122.0	192.1	7.0	1.4733
<b>MENHADEN OIL</b>					
March, 1911.....	0.932	158	187	3.9	.....
November, 1914.....	0.934	156.3	193.7	16.1	1.4850
September, 1916.....	0.938	144.9	191.4	19.2	1.4768
<b>RAW TUNG OIL</b>					
March, 1911.....	0.944	166	183	3.8	.....
November, 1914.....	0.946	161.5	190.3	5.7	1.5050
September, 1916.....	0.944	158.6	188.7	5.6	1.5138
<b>PERILLA OIL</b>					
March, 1911.....	0.94	180	188	2	.....
November, 1914.....	0.94	172	195.4	7.4	1.4874
September, 1916.....	0.939	160.9	193.3	14.8	1.4767
<b>PERILLA OIL (SPECIAL)(a)</b>					
March, 1911.....	0.94	192	189	3.2	.....
November, 1914.....	0.981	123.8	219.4	20.8	1.4978
September, 1916.....	1.000	122.4	220.9	31.2	1.4840
<b>HEAVY BODIED LINSEED OIL</b>					
March, 1911.....	0.968	133	189	2.8	.....
November, 1914.....	0.992	130.5	200	6.3	1.4966
September, 1916.....	0.974	124.4	206.3	9.0	1.4876
<b>LITHOGRAPHIC LINSEED OIL</b>					
March, 1911.....	0.97	102	199	2.7	.....
November, 1914.....	0.96	103.4	150.9	13.4	1.4778
September, 1916.....	0.974	108.5	137.7	15.2	1.4890
<b>WHALE OIL</b>					
March, 1911.....	0.924	148	191	9.2	.....
November, 1914.....	0.926	138.2	191.2	17.4	1.4820
<b>BOILED LINSEED OIL</b>					
March, 1911.....	0.941	172	187	2.7	.....
November, 1914.....	0.943	170	188	3.1	1.4895
<b>CORN OIL</b>					
November, 1914.....	0.921	124.8	190.1	4.1	1.4800
September, 1916.....	0.924	121.3	191.1	4.6	1.4707
<b>COTTONSEED OIL</b>					
November, 1914.....	0.920	111.7	194.3	0.9	1.4781
September, 1916.....	0.924	110.6	192.9	1.4	1.4681
<b>ROSIN OIL</b>					
November, 1914.....	0.964	68.9	35.5	32.4	.....
September, 1916.....	0.964	66.0	36.6	31.6	.....
<b>TREATED TUNG OIL(b)</b>					
November, 1914.....	0.882	56.4	101.3	7.7	1.4764
September, 1916.....	0.884	53.2	103.2	8.0	1.4660
<b>LUMBANG OIL</b>					
November, 1914.....	0.927	162	189	1.0	1.4789
September, 1916.....	0.926	164.0	188.9	1.9	1.4748
<b>SUNFLOWER OIL</b>					
November, 1914.....	0.924	124.6	189.3	7.5	1.4796
September, 1916.....	0.923	122.2	190.2	9.0	1.4712
<b>HEMPSEED OIL</b>					
November, 1914.....	0.927	149.4	191.1	3.9	1.4822
September, 1916.....	0.930	146.1	191.0	5.0	1.4745
<b>SHARK OIL</b>					
November, 1914.....	0.910	132.8	158.9	5.2	1.4815
September, 1916.....	0.915	127.4	163.3	6.2	1.4722
<b>SARDINE OIL</b>					
November, 1914.....	0.919	134.6	177.3	10.4	1.4800
September, 1916.....	0.962	91.4	180.2	31.1	1.4755
<b>PETROLEUM OIL</b>					
November, 1914.....	0.851	28.2	52.9	1.1	1.4773
September, 1916.....	0.850	28.0	48.6	1.0	1.4669

(a) Has become highly viscous.

(b) Heat treated with driers and thinned with mineral spirits.

TABLE 2—EFFECT OF STERILIZATION ON OILS

Original oil analyzed on November, 1914. Individual portions placed in separate bottles. One set of bottles sealed and heated to 110° C. Both sets again analyzed during September, 1916.

	Sp. Gr.	Iodine No.	Sapon. No.	Acid No.	Ref. Index
<b>RAW LINSEED OIL</b>					
November, 1914.....	0.933	185.4	189.6	2.8	1.4867
September, 1916.....	0.936	176.9	190.2	3.3	1.4798
Sterilized—Sept., 1916.....	0.934	187.1	190.4	3.1	1.4776
<b>SUNFLOWER OIL</b>					
November, 1914.....	0.924	124.6	189.3	7.5	1.4796
September, 1916.....	0.923	122.2	190.2	9.0	1.4712
Sterilized—Sept., 1916.....	0.925	124.6	189.9	6.3	1.4696
<b>MENHADEN OIL</b>					
November, 1914.....	0.934	156.3	193.7	16.1	1.4850
September, 1916.....	0.938	144.9	191.4	19.2	1.4768
Sterilized—Sept., 1916.....	0.937	155.6	192.1	16.3	1.4782
<b>PERILLA OIL</b>					
November, 1914.....	0.94	172	195.4	7.4	1.4874
September, 1916.....	0.939	160.9	193.3	14.8	1.4767
Sterilized—Sept., 1916.....	0.941	174.3	194.2	12.6	1.4788

TABLE 3—RAPID HYDROLYSIS OF LINSEED OIL EMULSIONS

Equal parts by volume of water and oil emulsified with 1 per cent neutral gum. Emulsions kept in incubator at 20° C. for 45 days. At this temperature, in the presence of water, and with a possibility of the accelerating action of enzymes, oils have rapidly developed free acid.

No.	ACID VALUE:	April 1	April 6	April 18	May 4	May 16
1	Raw.....	2.1	3.0	5.6	6.0	8.4
2	Raw—Sterilized.....	2.1	2.5	2.6	4.6	6.2
3	Alkali Refined.....	1.6	2.4	2.4	6.6	.....
4	Acid Refined (Washed)....	15.6	15.8	24.8	35.8	44.8
5	Acid Refined.....	3.0	4.0	15.0	34.0	38.0
6	Boiled.....	4.6	7.4	13.6	22.0	38.8

the writer several years ago for use in some practical exposure tests to determine the wearing properties of such oils when used in paints. Analyses of these oils at various periods are shown in the accompanying tables.

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## THE NITRATION OF TOLUENE TO TRINITROTOLUENE

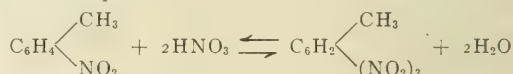
By IRWIN W. HUMPHREY

Received May 6, 1916

Although the nitration of toluene to trinitrotoluene has been carried out on a very large scale since Häusserman started its manufacture in the Chemischen Fabrik Griesheim in 1891,<sup>1</sup> very little has been published on the subject. Its employment as an explosive for military manufacture for this purpose appears to have been taken up next by Italy in 1907 and still more recently by other countries.

Generally it is preferred to make first crude mononitrotoluene (consisting chiefly of the ortho derivative with a small percentage of the paranitro compound) by nitrating toluene with sulfuric acid (1.84) and nitric acid (1.42), and then nitrating the crude mononitrotoluene thus obtained to trinitrotoluene, by separating from the dilute acid and then treating with a mixture of sulfuric acid (100 per cent H<sub>2</sub>SO<sub>4</sub>) and nitric acid (92 to 94 per cent HNO<sub>3</sub>). (Nitration in two steps, first to dinitrotoluene and then to the trinitrotoluene, T. N. T., is also carried out.) The method extensively employed industrially, involving the nitration of mononitrotoluene, was described briefly in 1912 by Langenscheidt.<sup>2</sup>

The following data indicate clearly that the yields of T. N. T., obtainable at a given temperature, are by no means a function of the water concentration of the reaction mixture as has often been assumed from the equation:



It is known that dilute nitric acid (sp. gr. 1.12) at 100° yields principally phenylnitromethane, C<sub>6</sub>H<sub>5</sub>-CH<sub>2</sub>NO<sub>2</sub>.<sup>3</sup> On the other hand, an acid mixture of too low water concentration gives poor yields, owing to oxidation, trinitrobenzoic acid being one of the products. This is well shown by the results tabulated below. In his recent book on the nitro explosives,<sup>4</sup> Escales recommends substantially the method described by Langenscheidt. While the relative cost of toluol, acids, and the alcohol, which may be used

<sup>1</sup> Z. angew. Chem., 4 (1891), 508.

<sup>2</sup> Z. ges. Schiess Sprengstoffw., 1912, 425.

<sup>3</sup> Konowalov, Ber., 28 (1895), 1860, 1861.

<sup>4</sup> "Die Nitrosprengstoffe," Leipzig, 1915, 149.

Exp. No.	KINDS OF ACIDS USED	YIELDS OF TRINITROTOLUENE BY DIFFERENT TREATMENTS					PER CENT CRUDE T. N. T.	CRYSTALLIZED TRINITROTOLUENE Per cent	M. P.	MAXIMUM TEMPERATURE ° C.	Hrs.
		ACID MIXTURE	PERCENTAGES Sulfuric Acid	NITRIC ACID	EXCESS NITRIC ACID Per cent	RATIO ACID MIXTURE TO MONONITROTOLUENE					
15	98%	1.52	2	86	12	32	9.5:1	85.1	79.2°	100-105	3
18	98%	1.52	2	82	16	75	9.5:1	80.8	...	100-105	2.5
17	98%	1.52	2	78	20	31	6:1	77.3	47.0	120-125	1.5
32	98%	1.52	2	80	18	49	7.5:1	73.6	...	120-125	3.5
13	98%	1.52	2	82	16	32	8:1	80.8	...	120-125	1.5
12	98%	1.52	2	86	12	31	9.5:1	81.4	...	120-125	1.5
14	98%	1.52	2	87	11	13	9.5:1	79.1	...	120-125	2
16	98%	1.52	2	82	16	75	10:1	85.9	...	120-125	1.5
23	98%	1.52	2	82	16	75	9.5:1	72.8	79.4	120-125	1.0
27	98%	1.52	2	82	16	75	9.5:1	87.1	76.0	120-125	2.5
30	98%	1.52	2	86	12	27	9.5:1	80.3	57.3	120-125	3
31	98%	1.52	2	85	13	33	9.5:1	81.5	...	120-125	2.5
4	100%	1.50	1	77	23	43	5.5:1	81.0	...	125-130	2
1	100%	1.50	1	75	24	43	5.5:1	81.6	...	130-135	0.5
5	100%	1.52	0	75	25	51	5.5:1	77.6	...	133-136	3
6	100%	1.52	0	74	26	64	6:1	80.3	...	130-135	0.5
10	98%	1.45	6	82	12	33	10:1	83.3	62.2	130-135	0.7
2	100%	1.50	1	74	25	57	5.5:1	72.9	...	140-145	0.5
3	100%	1.50	1	77	22	43	5.5:1	75.7	...	140-145	0.5
7	95%	1.52	4	83	13	51	10:1	70.6	...	140-145	0.5
8	98%	1.52	1	81	18	53	8:1	75.4	62.2	140-145	1
9	98%	1.45	6	82	12	33	10:1	80.8	59.8	145-150	2
34 {	100% with	1.52	7 (SO <sub>4</sub> )	57	36	100	4:1	62.5	44.0	125-120	2
35 {	some 15% oleum	1.52	7 (SO <sub>4</sub> )	57	36	100	4:1	65.5	46.0	100-105	2.5

in the purification of the crude T. N. T., and the value of the final product will largely determine what conditions of nitrating are the most economical, the following data show that better yields of pure T. N. T. are obtained by operating at a somewhat lower temperature than 140°, as prescribed by Langenscheidt, and employing sulfuric acid (98 per cent H<sub>2</sub>SO<sub>4</sub>) instead of the 100 per cent acid, and maintaining the final nitrating mixture at 120-125° for a longer time, namely about 2½ hrs. The proportion of acids and toluene are so chosen that the concentration of water in the final mixture is about 4.4 per cent. In view of the general interest in this subject at the present time these data are here briefly presented.

#### EXPERIMENTAL

It may be pointed out that in Experiment 1 the proportions recommended by Langenscheidt and by Escales were taken. The mononitrotoluene used in these experiments reported in the accompanying table was made in a small Dopp kettle in the usual manner.

Nitrating Mixture	Toluene(a).....	47.5 lbs.
	Sulfuric Acid, sp. gr. 1.84.....	20.0 lbs.
	Nitric Acid, sp. gr. 1.42 (12 per cent excess).....	52.0 lbs.

Nitrating temperature, 22° C., finally raised to 95° C.

Product—68 lbs. (96 per cent of theoretical) crude mononitrotoluene, sp. gr. 1.163 at 22° C.

(a) The purity of the toluene was confirmed by slowly distilling 0.5 liter through a three-bulb Glinisky distilling tube: Distillate below 108.8°, 6 per cent; 108.8° to 109.6°, 90 per cent; 109.6° to 111°, 3 per cent.

After nitrating to the trinitro product, the cooled nitrating mixture was added to five volumes of ice water,<sup>1</sup> filtered, washed with very dilute sodium bicarbonate solution and recrystallized from alcohol containing 10 per cent by volume of benzene.

In conclusion, the author desires to express his indebtedness to Dr. B. T. Brooks, for suggestions given during the course of the work.

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#### REAGENTS FOR USE IN GAS ANALYSIS—V THE RELATIVE ADVANTAGES OF THE USE OF SODIUM AND POTASSIUM HYDROXIDES IN THE PREPARATION OF ALKALINE PYROGALLOL

By R. P. ANDERSON

Received September 15, 1916

The composition of alkaline pyrogallol prepared with potassium hydroxide and the behavior of this reagent in various pipettes has recently been studied

by the author.<sup>1</sup> More recently, Shipley<sup>2</sup> has made a study of the effect of the substitution of sodium hydroxide for potassium hydroxide in alkaline pyrogallol and has made comparisons between the two reagents. While admitting freely the importance of Shipley's work, the author is not entirely satisfied with the comparisons drawn by him and presents herewith a careful comparison of the two reagents based upon the information in the references that have been cited. The points that have been considered are: ease of preparation, time required for analysis, convenience of manipulation, specific absorption, and the cost of materials. The relevant information has been correlated under each heading for the convenience of the chemist who may wish to become familiar with the advantages and disadvantages of each of the two varieties of alkaline pyrogallol.

#### EASE OF PREPARATION

Each solution can be prepared by dissolving pyrogallol in a solution of the proper alkali in water, so that the preparation of either is a matter of little difficulty. To prevent caking of the pyrogallol, Shipley recommends the addition of a little water to it before the addition of the solution of sodium hydroxide.

#### TIME REQUIRED FOR ANALYSIS

The time required for the determination of oxygen with either of the reagents is dependent upon the time consumed in obtaining complete absorption, since the other operations incident to the analysis require about the same amount of time in each case. Shipley has adopted a 4-minute interval<sup>3</sup> for complete absorption with the sodium reagent, while 1-minute contact is sufficient for the potassium reagent. Assuming that the 4-minute interval includes the time necessary for the initial passage of the gas into the pipette and for the final passage of the gas out of the pipette, the corresponding time for the potassium reagent, allowing 15 seconds<sup>4</sup> for each passage of the gas, would be 1½ minutes. This means a saving of 2½ minutes on each determination where the potassium reagent is employed in place of the sodium reagent.

<sup>1</sup> Anderson, THIS JOURNAL, 7 (1915), 587; 8 (1916), 131, 133.

<sup>2</sup> Shipley, J. Am. Chem. Soc., 38 (1916), 1687.

<sup>3</sup> Reagents 3 and 4 on p. 1691 of Shipley's article give complete absorption in 2 min., but elsewhere 4 min. is the minimum time recommended.

<sup>4</sup> See THIS JOURNAL, 8 (1916), 131.

<sup>1</sup> Cf. McHutchison and Wright, J. Soc. Chem. Ind., 34 (1915), 781.



## CONVENIENCE OF MANIPULATION

Three or four transfers of the gas sample to the pipette and return within the 4-minute limit are recommended by Shipley for the sodium reagent. This is perhaps a more convenient method of effecting the absorption of oxygen than shaking for 1 minute, a procedure that is recommended for the Hempel double pipette for liquid reagents in the article of the author's to which Shipley made reference.<sup>1</sup> In subsequent articles<sup>2</sup> 1-minute contact is recommended for the potassium reagent employed in pipettes containing glass tubes. This latter procedure is obviously more convenient than making three or four transfers of the gas as recommended by Shipley for the sodium reagent.

## SPECIFIC ABSORPTION

From data given by Shipley, pp. 1693 and 1700, the specific absorption<sup>3</sup> within the 4-minute interval of the best sodium reagent (No. 9) employed at room temperature in a pipette of Shipley's design on 50 cc. samples of air is 102, and the specific absorption of the potassium reagent recommended by the author for use in the Hempel double pipette for liquid reagents under the same conditions is 20, the sodium reagent thus having more than 5 times the specific absorption of the potassium reagent. The author has found that the specific absorption of the same potassium reagent for 1-minute contact employed at room temperature in the usual form of the Orsat pipette on 100 cc. samples of air is 22. In especially constructed pipettes, a higher concentration of pyrogallol can be employed and the specific absorption of the solution employed in these pipettes was found to be 36, for the same temperature, procedure and source of oxygen as with the Orsat pipette. Thus the ratio of the specific absorptions of the best sodium and potassium reagents is about 3 to 1, rather than 5 to 1. It is somewhat confusing to note that under the topical heading in Shipley's article, "Specific Absorption of Reagents," the values given are obtained by a method closely resembling that of Hempel<sup>4</sup> for "analytical absorbing power," a term representing something entirely different from specific absorption.

## THE COST OF MATERIALS

Shipley's sodium reagent No. 9 (10 g. of pyrogallol, 7.36 g. of sodium hydroxide, 11.62 g. of water, sp. gr. 1.405) contains 0.485 g. of pyrogallol and 0.357 g. of sodium hydroxide per cc. With pyrogallol at \$2.85 per lb. and 74 per cent sodium hydroxide at 4 cents per lb.,<sup>5</sup> this sodium reagent costs 0.309 cent per cc. (pyrogallol 0.305 cent, sodium hydroxide 0.004 cent); and with a specific absorption of 102, 1 cc. of oxygen can be absorbed for 0.003 cent.

Similarly, Anderson's potassium reagent (21.2 g. of pyrogallol and 66.6 g. of potassium hydroxide to 100

cc. of solution) contains 0.212 g. of pyrogallol and 0.666 g. of potassium hydroxide per cc. With pyrogallol at \$2.85 per lb. and potassium hydroxide at 90 cents per lb., and assuming that the potassium hydroxide is 90 per cent pure, this reagent costs 0.28 cent per cc. (pyrogallol 0.133 cent, potassium hydroxide 0.147 cent); and with a specific absorption of 36, 1 cc. of oxygen can be absorbed for 0.008 cent.

At prices current during July, 1914,<sup>1</sup> pyrogallol at \$1.40 per lb., 60 per cent sodium hydroxide at 1.57 cents per lb., potassium hydroxide at 5 cents per lb.—the sodium reagent costs 0.152 cent per cc. (pyrogallol 0.15 cent, sodium hydroxide 0.002 cent); and the potassium reagent, 0.074 cent per cc. (pyrogallol 0.066 cent, potassium hydroxide 0.008 cent). The cost per cc. of oxygen in normal times is thus 0.0015 cent for the sodium reagent and 0.002 cent for the potassium reagent.

## SUMMARY

On the basis of the information that has been presented, the best sodium reagent is superior to the best potassium reagent as regards specific absorption and cost of materials and inferior as regards the time for complete absorption and the convenience of manipulation. The relative importance of the first three of these points of superiority and inferiority can best be shown by computing the saving in expense that could be effected by using the slower reagent and comparing it with the saving of time that could be effected by the use of the more expensive reagent. For example, 150 cc. of sodium reagent No. 9 can be employed for the absorption of 15.3 liters of oxygen at a cost of 3 cents per liter, or \$0.46. To absorb the same amount of oxygen with the potassium reagent will cost 8 cents per liter, or \$1.22—\$0.76 in excess of the cost of the sodium reagent. In normal times, using the prices current during July, 1914, as a basis, 15.3 liters of oxygen can be absorbed by the sodium reagent for 23 cents and by the potassium reagent for 30 cents. To counterbalance the increased cost of using the potassium reagent, we have the saving of time effected by its use, a factor that is influenced by the percentage of oxygen in the gases that are analyzed. Assuming 100 cc. samples of 20 per cent oxygen, 765 analyses would be required in the absorption of 15.3 liters of oxygen. With a saving of 2½ minutes on each analysis, the total saving of time during 765 analyses becomes 317½ hrs. From this must be subtracted the time required for the two extra fillings of the pipette with the potassium reagent necessitated by its smaller specific absorption, for which might be allowed the excess over 30 hrs.

With a choice between 30 hrs. of time and an expenditure of \$0.76 (\$0.07 in normal times) it is difficult to concur with the following statements from Shipley's article. (The italics are the author's.) "Such a reagent as No. 9 should replace in technical gas analysis the use of the more expensive and *less efficient* potassium solution. The *saving of time* and

<sup>1</sup> THIS JOURNAL, 7 (1915), 587.

<sup>2</sup> *Ibid.*, 8 (1916), 131, 133.

<sup>3</sup> Anderson, *Ibid.*, 7 (1915), 587.

<sup>4</sup> "Gasanalytische Methoden," 4th Ed., p. 128.

<sup>5</sup> Wholesale prices in the New York market, Aug. 21, 1916, THIS JOURNAL, 8 (1916), 866.

<sup>1</sup> THIS JOURNAL, 6 (1914), 704.

trouble in using a reagent lasting five times<sup>1</sup> as long should alone decide in its favor." It is hoped that these figures will show that, as long as potassium hydroxide is obtainable even at prices many times the present extraordinary one, true economy dictates that it should be employed in preference to sodium hydroxide for the preparation of alkaline pyrogallol.

#### IN DEFENSE OF THE HEMPEL PIPETTE

During the reading of Shipley's article for the preparation of the comparisons in the preceding pages, the author noted a paragraph of criticism of the Hempel pipette upon which he desires to make brief comment. The paragraph in question follows:

"It is hard to understand why the Hempel pipette should be longer used for any but very special work. It is difficult to fill with any reagent and especially so if the reagent is somewhat viscous. The long bent capillary is a source of weakness in structure and of irregularity in use. The enormous friction of the liquid in the capillary requires, even with comparatively fluid reagents, a considerable excess of pressure to overcome and prohibits entirely the use of many concentrated reagents because of their viscosity. Moreover, the pipette requires a special and expensive stand while shaking has to be resorted to in order to obtain efficient absorption. Should the pipette be broken anywhere only an experienced glass-blower can repair it."

Relative to sentence two, it should be mentioned that an opening<sup>2</sup> between the second and third bulbs of the Hempel double pipette for the insertion of a funnel renders the filling of the pipette with any reagent a simple matter, even if the reagent is somewhat viscous. As regards sentence three, the elimination<sup>3</sup> of the unnecessary U-tube of the original Hempel pipette increases the strength of the apparatus and facilitates its manipulation. With the U-tube removed from the pipette, the pressure required to force viscous liquids such as alkaline pyrogallol through capillary of 1 mm. bore is not unduly large (see sentence four). As to whether shaking has to be resorted to (sentence five) depends upon the style of pipette that is employed. A special form of the Hempel double pipette<sup>4</sup> for solid and liquid reagents is especially adapted for the absorption of oxygen on 1-minute contact with alkaline pyrogallol. A properly constructed frame for these pipettes is extremely long-lived and has proven an economy on account of the protection which it affords the pipette.

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#### RAPID VOLUMETRIC DETERMINATION OF INDIGO

By SAMUEL M. JONES AND WALTER SPAANS

Received July 3, 1916

Of the various methods proposed for the determination of indigo, the one which depends upon the reduc-

<sup>1</sup> Reagent No. 9 has about 5 times the specific absorption of the potassium reagent recommended for use in the Hempel double pipette for liquid reagents to which Shipley refers. This reagent contains 0.136 g. of pyrogallol and 0.715 g. of potassium hydroxide per cc. and, at the present time, costs 0.242 cent per cc. Using 20 as the specific absorption of this solution—Shipley's value—the cost of absorbing 1 cc. of oxygen is 0.012 cent. The cost of absorbing 15.3 liters is then in this case \$1.84, an excess of \$1.38 over the cost with the sodium reagent. Four extra fillings would be required with this reagent, so that the saving in time might be estimated at 28 hrs.

<sup>2</sup> This construction is shown on a special pipette for use with cuprous chloride, designed by the United Gas Improvement Co., in the catalogs of Eimer and Amend and A. H. Thomas Co.

<sup>3</sup> White and Campbell, *J. Am. Chem. Soc.*, **27** (1905), 734; Anderson, *This Journal*, **6** (1914), 237.

<sup>4</sup> Anderson, *This Journal*, **8** (1916), 133.

tion of the sulfonated product by means of a sodium hydrosulfite solution is the one in most general use at the present time. This method, which was first proposed by A. Müller<sup>1</sup> and fully described in the Badische Indigo Book, was a material improvement over the older oxidation methods.

Briefly stated, it consists in comparing the sample with an indigo of known strength by titrating the sulfonated product with a solution of sodium hydrosulfite, also of known concentration, until the solution becomes colorless. By comparing the results, the relative value of the indigo in question may be obtained.

Although the principle involved in this method is correct, there are several factors which render it not only difficult to perform but in many cases inaccurate. In the first place, indigo white, the leuco derivative formed by reducing indigo, is very unstable, and is nearly quantitatively reoxidized to indigo by exposure to air.

Müller tried to overcome this difficulty by performing the titration in the presence of an inert gas, such as coal gas, but, according to our experience, this is not sufficient. In spite of maintaining a constant atmosphere of coal gas, the indigo white reoxidizes very quickly if there is not an excess of hydrosulfite present. Consequently, it is impossible to ascertain the amount of hydrosulfite necessary to produce the endpoint. Moreover, the sodium hydrosulfite, however pure, is like the indigo white, very susceptible to oxidation, as conservation trials of an aqueous solution will readily show. These two factors render the method inaccurate.

Realizing the importance of a rapid accurate method for the determination of indigo, especially in the textile industries, we have succeeded in devising one which produces the desired results.

Like the method of Müller, our new method is based on the reduction of indigo to indigo white. Instead, however, of working in the presence of coal gas, we have found that by using a current of hydrogen, the titration may be carried out the same as any other volumetric titration, without fear of subsequent oxidation. In other words, working with our apparatus in a current of hydrogen, only the amount of hydrosulfite actually necessary to produce the reduction need be used.

We have, in addition to this, substituted formaldehyde sodium sulfoxylate, which is manufactured in a very pure form by the Badische Company under the name of Rongalite C, for the unstable sodium hydrosulfite. Aqueous solutions of formaldehyde sodium sulfoxylate may be conserved for hours or days without suffering the slightest decomposition, which makes it especially suitable as a "standard" to be used for volumetric reduction methods.

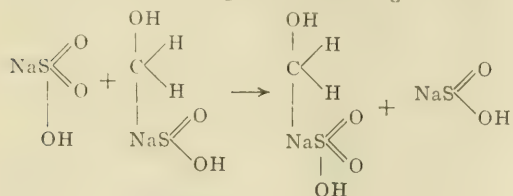
This very stability, however, especially at low temperatures, at first presented considerable difficulty, for on running the solution of sodium formaldehyde sulfoxylate into the sulfonated indigo, no reduction takes place at ordinary temperatures, and only on

<sup>1</sup> *American Chemist*, 128.



heating nearly to the boil is the indigo reduced quickly enough for volumetric purposes.

In order to obviate the necessity of titrating at a boil, we found that in the presence of sodium bisulfite the speed of the reaction may be accelerated, due to the liberation of free sodium sulfoxylate by double decomposition according to the following reaction:



*Formaldehyde*  
*Sodium*  
*Bisulfite*    *Sulfoxylate*    *Bisulfite-*    *Sodium*  
*Sulfoxylate*    *formaldehyde*    *Sulfoxylate*

In making the titration we have found the apparatus illustrated especially suitable (see Fig. 1). The solu-

The standard hydrosulfite-formaldehyde solution is made by dissolving 1 g. of the solid hydrosulfite-formaldehyde (Rongalite C) in 1 liter of distilled water. The sample of indigo to be tested and the standard (C. P.) indigo are sulfonated and prepared for titration in the following manner.

#### PREPARATION OF THE INDIGO SOLUTION BY SULFONATION

If the sample is in powder form, grind up in a small mortar and weigh out exactly 1 g. into a small beaker. Add 15 cc. concentrated sulfuric acid (sp. gr. 1.84) and rub up into an even paste with a glass stirring rod. Wash down the glass rod and sides of the beaker with another 15 cc. concentrated sulfuric acid and then heat on the water bath or oil bath for 2-4 hrs. at 55-60° C., stirring once or twice. Sulfonation should be complete in 2-3 hrs. Allow the sulfonated indigo to cool down and then carefully wash out the beaker with 300 cc. distilled water. Again cool down to 15-18° C. and make up to 1 liter. Filter and the solution is ready for titration.

If the indigo is approximately a 20 per cent paste, use 5 g. for sulfonation, if a 50 per cent paste use 2 g., etc. Add the sulfuric acid slowly so that the temperature does not exceed 50-60° C., for a loss may result by locally carbonizing a part of the indigo and darker solutions will be produced. At the same time and in the same manner sulfonate 1 g. of C. P. indigo for use as a standard.

#### TITRATION

Measure accurately into the small Erlenmeyer flask 50 cc. of the standard (C. P.) indigo carmine solution and add 50 cc. sodium bisulfite solution (60° Tw., 35-36 per cent NaHSO<sub>3</sub>). Connect as shown in the figure, turn on the hydrogen current and heat to 75° C. Then run in the standard sodium formaldehyde sulfoxylate solution from the burette until the blue color disappears. With a good strong current of hydrogen the titration can be carried out slowly without fear of reoxidation of the indigo solution before the final end-point is reached. The first determination will be only approximate and should be repeated until the results coincide. Repeat the titration, using the indigo carmine solution from the sample to be tested.

An example will make clear the method of calculation: 50 cc. of the standard sulfonated indigo solution required 14.50 cc. of the sodium formaldehyde sulfoxylate solution for reduction; 50 cc. of an indigo carmine solution made from 5 g. of an approximately 20 per cent indigo paste required 16.10 cc. of the same sodium formaldehyde sulfoxylate solution. Since the standard indigo contains 1 g. per liter, 1 cc. sodium formaldehyde sulfoxylate equals

$$\frac{(0.001)(50)}{14.50} = 0.003448$$

indigo and 50 cc. of the sample equals (0.003448)(50) = 0.1724 g. indigo paste.

Then,  

$$\frac{(0.003448)(16.10)(100)}{0.025} = 22.206 \text{ per cent indigo in the sample.}$$

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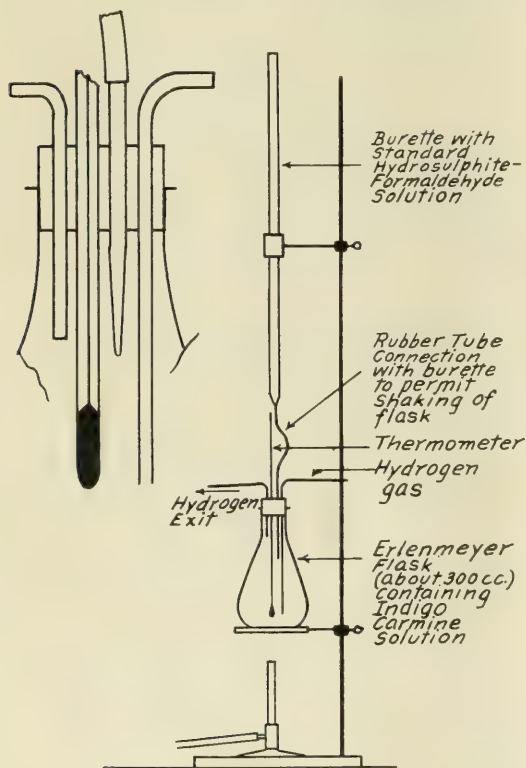


FIG. 1—INDIGO TITRATION APPARATUS

tion of indigo carmine is placed in a small Erlenmeyer flask of about 300 cc. capacity closed with a rubber stopper provided with four holes. Through one of these holes a thermometer is placed, projecting into the liquid in the flask; tubes for the admission and exit of hydrogen gas are provided and a small, tapering tube connecting with the burette closes the fourth hole. A small Bunsen burner and an efficient hydrogen generator of some kind complete the apparatus.

# A METHOD FOR DETERMINING THE STRENGTH OF PAPER WHEN WET

By E. O. REED

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Ordinarily the strength of wet paper is not a matter of importance. Most kinds of paper when wet are very weak and break or tear with the greatest ease. Certain kinds of paper, however, must be handled while wet, and it is essential, therefore, that they have a sufficient wet strength to withstand this service. This is true of photographic paper, especially of blue and brown print paper, of bag and wrapping, of paper textiles and to a less extent of filter paper, and paper which is to be printed while wet. While papers may comply with the specified physical requirements under the usual conditions of temperature and humidity, they may prove entirely unsatisfactory for handling when wet.

It is a well-established fact that the moisture content of the paper has a great effect on paper making and testing, and considerable work has been done to determine the properties of paper under different temperatures and atmospheric moisture conditions. The strength of paper when wet, however, has received little attention. Beadle and Stevens<sup>1</sup> present an article on "The Dry and Wet Strengths of Paper." The exact method of carrying out the wet-strength test is not clearly stated and only the wet strength of papers used in the manufacture of paper yarns is dealt with.

Perhaps one of the most severe conditions to which paper is subjected when wet is in commercial blue and brown print developing. In this work sometimes paper 42 in. wide and 10 or 12 ft. long is handled while thoroughly wet. Much of the so-called blue-print paper will not withstand the necessary wetting without injury even though its other physical qualities may be entirely satisfactory.

The determination of the tensile strength of the wet paper has proved to be the most satisfactory test for indicating the strength required to withstand the washing necessary to insure permanent prints. The wet strength is determined by breaking a strip of paper of a definite width, after it has been immersed in water at a constant temperature for a definite period of time. A Schopper tensile strength machine, calibrated to read from 1 to 1000 g., is used. The jaws of the clamps should open in front, so the ends of the wet strips may be inserted without injury, and are set 10 cm. apart, as a short strip of wet paper can be handled more easily. The test strips are cut 15 mm. wide and sufficiently long to allow for clamping in the machine. Tests are made in both the longitudinal and transverse directions. The strips are placed separately in a water bath at 70° F. for 20 min. After the specified time they are removed one at a time and tested immediately. To obtain accurate results extreme care must be exercised in handling and clamping the wet strips to prevent injury to them.

The wet strength in the transverse direction of

blue and brown print papers upon which most of this work has been done and also of Kraft and rope wrapping is less than 700 g. In the longitudinal direction 1000 g. is an exceptionally high wet strength.

TABLE I—EFFECT OF TEMPERATURE OF WATER ON THE WET STRENGTH (GRAMS) OF PAPER. PAPERS WET FOR 20 MINUTES

L & P No.	KIND OF PAPER	Direction of Strip	Temperature of Water Bath °F				
			50 G.	65 G.	70 G.	75 G.	100 G.
31470	Blue-print paper	Long.	679	610	563	536	346
		Trans.	346	285	282	288	219
31642	Blue-print paper	Long.	1000+	997+	988+	943	731
		Trans.	744	632	634	564	414
28517	Blue-print paper	Long.	1000+	1000+	1000+	1000+	1000+
		Trans.	776	776	738	695	598
12956	BOND:						
	Before sizing	Long.	631	621	604	585	492
		Trans.	300	271	258	258	222
12957	After animal sizing	Long.	918	824	754	754	578
		Trans.	484	412	364	370	293
12914	PARCHMENT BOND:						
	Before sizing	Long.	600	536	464	474	398
		Trans.	270	251	224	228	187
12915	After animal sizing	Long.	850	773	704	674	495
		Trans.	406	329	309	309	240

Table I shows the effect of the temperature of the water on the strength. The length of time of wetting was 20 min. in all cases. From these results it is evident that in order to obtain concordant values the water in which the strips are wet must be maintained at a constant temperature. It will be noted that wide differences exist between results obtained on a paper wet at 50° F. and at 100° F. There is a progressive decrease in strength with rise of temperature of the water in which the papers are wet, and a difference of 5° F. in the temperature of the water makes a significant difference in the wet strength in the longitudinal direction, though the differences in the transverse direction are usually small: 70° F. has been adopted as the most suitable temperature at which to maintain the water bath.

Table II shows the effect of the length of time of wetting on the wet strength.

TABLE II EFFECT OF TIME OF IMMERSION IN WATER ON THE WET STRENGTH (GRAMS) OF PAPER. TEMPERATURE OF WATER BATH 70° F.

L & P No.	KIND OF PAPER	Direction of Strip	Time of Wetting—Minutes				
			10 G.	20 G.	30 G.	45 G.	60 G.
31470	Blue-print paper	Long.	662	591	557	534	495
		Trans.	312	277	277	274	262
31471	Blue-print paper	Long.	487	426	434	438	420
		Trans.	257	236	226	222	222
30857	Bond paper	Long.	539	498	456	456	453
		Trans.	270	258	238	222	213
31632	Blue-print paper	Long.	1000+	908	850	813	793
		Trans.	562	489	464	409	414
28542	Blue-print paper	Long.	935	842	847	812	800
		Trans.	649	592	564	549	537

The figures show that it is necessary to immerse the paper for a definite time to obtain valuable and uniform results. The results obtained on paper immersed only 10 min. indicate, in most cases, that the water has not penetrated uniformly and the individual results are much more erratic than when the paper is immersed for longer periods. After 20 min. immersion, which has been adopted as a suitable period for wetting, the individual results are more concordant though minimum results are not obtained in that time. The transverse strength is but little affected by even longer periods of immersion. In commercial practice blue and brown print papers are seldom in the water bath more than 20 min.

Table III shows the concordance of averages of 5 tests in each direction on the same paper made on

<sup>1</sup> Chem. News, 109 (1914), No. 2843, 242.



different days under the adopted constant conditions of wetting for 20 min. at 70° F. Since the wet-strength tests are registered in grams and difficulty is experienced in handling and clamping the strips

TABLE III—DUPLICATE AVERAGES OF WET STRENGTH MADE UNDER THE SAME CONDITIONS

L & P No.	Papers wet at 70° F. for 20 min.					
	Long. G.	Trans. G.	First Average of Five	Long. G.	Trans. G.	Second Average of Five
28541.....	812	521		829	531	
31632.....	810	408		800	433	
28540.....	690	376		690	395	
31470.....	563	282		591	277	
31471.....	416	224		426	221	

of wet paper in the tester, these averages are considered very close. It is necessary to discard results on strips which have not been properly clamped. Care must also be taken not to put a strain on the strip while clamping.

Wet strength is apparently controlled by the kind of stock, length of fiber, character of beating, kind and quality of sizing and by the formation of the sheet.

Table IV shows that in every case the wet strength was considerably increased by animal sizing.

TABLE IV—EFFECT OF ANIMAL SIZING ON THE WET STRENGTH OF PAPER  
Papers wet at 70° F. for 20 min.

L & P No.	KIND OF PAPER	FINISH	WET STRENGTH		Per cent Increase	
			Long.	Trans.	Long.	Trans.
12956	Bond	Unsize	604	258		
12957		Animal sized	757	364	25.3	41.1
12903	Bond	Unsize	826	432		
12904		Animal sized	981	575	18.8	33.1
12914	Parchment Bond	Unsize	464	224		
12915		Animal sized	704	309	51.7	37.9
12916	Parchment Bond	Unsize	668	323		
12917		Animal sized	873	463	30.7	43.3
12918	Parchment Bond	Unsize	749	370		
12919		Animal sized	983+	483	31.2	30.5
12990	Bond	Unsize	270	162		
		Animal sized	293	158		
12989		Unsize	649	382	121.5	141.8
12991		Animal sized	295	194		
12993	Bond	Unsize	730	415	147.5	113.9
12988		Animal sized				

Owing to the impracticability of obtaining samples of paper made from the same stock by different methods of beating or beaten for different lengths of time or sized with different amounts of rosin or glue or both, it is not possible to show here in figures the effect

physical qualities under ordinary testing conditions or *vice versa*. While this is true, study of the subject has led to the opinion, however, that wet strength is controlled chiefly by beating, sizing, and formation. High wet strength may be obtained with long stock beaten "wet," well matted and so sized as to render the fibers water-resistant.

A detailed study will be made of the effect of different papermaking procedures on wet strength, in order to reach more definite conclusions as to the factors affecting this characteristic of paper. Experience has demonstrated that by means of this test it can be determined whether a blue or brown print paper will withstand the customary washing without tearing.

The method promises to be of even greater utility in predetermining the behavior of bag and wrapping paper when wet, especially of cement and lime bags. Quantities of these materials are being shipped in paper bags, many of which tear readily when damp and offer no protection to their contents against moisture. The method will enable users of such bags to determine whether they will prove satisfactory in service.

#### SUMMARY

Wet strength is an essential property of paper for certain special uses. It is indicated by determining the tensile strength of wet strips, cut longitudinally and also transversely of the sheet. Strips 15 mm. in width and of sufficient length to allow a breaking length of 100 mm. are immersed in water at 70° F. for 20 min. and then tested in a machine calibrated to read in grams. It is important that the paper be immersed for a definite period of time and in water of a uniform temperature, as these factors greatly influence the test. Care must be exercised in making tests as paper is so easily injured when wet.

Wet strength is controlled by the combination of factors which influence other physical properties of

TABLE V—RESULTS OF EXAMINATION OF VARIOUS KINDS OF PAPER—ALL PHYSICAL TESTS MADE AT 70° F. AND 65 PER CENT RELATIVE HUMIDITY

L & P No.	PAPER	STOCK (Per cent)	Rag	Sul- Chem.	Thick- ness	Weight (5000)	Ash	SIZING Per cent	Starch	STRENGTH		TENSILE Break	STRENGTH Stretch	FOLDING ENDURANCE		WET STRENGTH	
										Av. per	Wt.	Kg.	Per cent	Long.	Trans.	Long.	Trans.
31899	Filter	100	...	...	43.5	73	0.2	0.0	0.0	Trace	12.0	0.28	2.6	2.1	0.8	1.3	6
31909	Printing	21	29	50	45.5	50	1.0	0.9	0.0	None	10.0	0.22	2.8	1.9	0.3	1.2	3
31910	Writing	52	48	...	52.5	39	1.2	1.1	0.6	Present	35.5	0.68	8.4	4.1	2.5	4.2	197
30857	Bond	100	...	...	40.0	30	0.8	1.8	4.2	Present	39.5	0.99	8.0	4.4	4.0	6.8	2686
30730	Bond	100	...	...	47.0	36	0.6	1.0	3.6	Present	47.5	1.01	9.0	4.6	3.7	6.3	1798
30856	Bond	53	47	...	46.5	33	0.6	1.6	1.5	Present	33.0	0.71	6.5	3.8	2.9	4.6	400
30858	Bond	...	100	...	48.0	38	2.3	1.2	0.0	None	26.0	0.54	7.6	3.7	1.7	4.0	164
28542	Blue-print	...	...	...	54.0	35	0.5	3.7	1.7	Present	42.0	0.78	6.5	5.4	3.5	7.0	1439
28517	Blue-print	100	...	...	61.5	43	0.6	3.8	2.3	Present	42.5	0.69	9.2	5.3	3.5	4.9	265
31803	Blue-print	100	...	...	62.0	40	0.5	1.8	4.8	Present	76.0	1.23	13.8	7.6	3.9	6.6	3576
31249	Ledger	100	...	...	51.0	36	1.0	1.0	3.5	Present	62.0	1.21	10.7	5.8	4.6	6.6	3489
30855	Ledger	100	...	...	55.0	40	1.2	2.6	4.4	Present	59.5	1.08	10.8	5.9	5.3	7.7	2729
31250	Ledger	...	...	...	47.5	36	3.6	1.5	0.0	Present	28.5	0.60	7.2	3.8	1.3	4.6	270
31922	Kraft	...	100	(sulfate)	57.0	50	0.9	0.7	0.0	None	43.0	0.75	9.4	4.2	1.7	3.7	1312
31921	Rope	...	9	91(Jute)	87.0	90	2.8	2.9	0.0	None	114.0	1.30	14.6	5.8	3.0	6.1	20000+

of each of these factors nor to state exactly the factors and procedures which may produce a satisfactory wet strength.

In Table V are given complete results, including wet strength, on samples representative of various kinds of stock papers.

Examination of these results does not show a definite relationship between wet strength and any of the other characteristics of paper. A paper with a high wet strength will not necessarily exhibit satisfactory

paper such as length of fiber, beating, kind and quality of sizing and formation of the sheet, yet there is no direct relationship between the wet and dry strengths of paper. This test promises to be of value in predetermining the serviceability of paper used for bags, especially for cement and lime, wrapping, photographic, paper textiles and even paper which is to be printed while wet.

THE INSPECTION OF CANNED FOODS<sup>1</sup>

By W. D. BIGELOW

Received August 15, 1916

The first principle in the inspection of any article is that the inspector or analyst should be thoroughly familiar with the normal product. Methods of analysis and data for the interpretation of analytical results should always be standardized by the normal product.

Iron and steel analysts standardize their analytical technique by the examination of standard samples of known composition. That practice is also followed in colleges and universities where instructors often procure for their students samples that have been analyzed by experts in various fields. The same practice must be observed in the examination of canned foods. An analyst who is not thoroughly familiar with a normal product is entirely incompetent to determine whether or not a given sample is normal.

The examination of canned foods may be undertaken to assist in controlling the character and quality of the product; to establish its commercial value and grade; to fix the responsibility for defect in food or package; or in connection with the enforcement of food laws.

Whatever the ultimate object of the work, the immediate purpose is the same—to ascertain as exactly as possible the nature, character and quality of the product under examination. This includes a knowledge of the raw product and method and conditions of manufacture as far as they affect the character and quality of the finished article. In packing and labeling a product, therefore, the canner needs the same information that Federal and State officials need in enforcing the law.

The frequent inquiries received by the writer regarding the examination of canned foods have suggested that an outline of the methods employed by technical laboratories would be of interest. To give such an outline is the purpose of this paper.

## EXTERNAL APPEARANCE OF THE CAN

In the examination of canned foods, the external appearance of the can should be carefully noted. If the can appears "flat," as it is called in the industry (*i. e.*, if the ends are concave), it should be "knocked" with considerable force on one end on a substantial table or block of wood to determine whether a suitable vacuum exists. If the lower end of the can does not remain concave on being struck in this manner, the vacuum in the can is not as great as it should be. The temperature at which the can is examined must be considered in this connection, for it is obvious that if the temperature of the contents were a few degrees higher the can would be a springer.

A lot of cans can be springers in the summer and the ends concave the following fall and winter. They may be springers during a hot wave and "flat" in the same location the following week. Samples of springers sent to the laboratory by a packer during a hot wave have reached us "flat" (with the ends concave) a

couple of days later, because the weather was cooler. The fact that a can does not have a good vacuum or even that it has bulged ends means nothing in itself, but may be significant when considered in connection with other data.

## SWELLS AND SPRINGERS

Cans whose ends bulge ever so slightly are not merchantable and their sale to consumers should not be permitted. The bulged end is a reasonable "warning sign" and should be so regarded. Yet that condition does not usually mean decomposition when found in the retail trade. Very frequent and very serious errors have been made in the inspection of food by assuming that all "swells," as they are popularly termed, are due to decomposition. With non-acid foods, such as peas or corn, swells are usually due to decomposition, be the amount of swelling ever so little. On the other hand, spoilage rarely occurs with acid fruits unless the can be leaky. In this class of products the swelling of the can (in the absence of leaks) is almost invariably due to hydrogen set free by the action of the fruit acid on the metal of the container. The amount of hydrogen liberated in this manner depends to a certain extent on the age of the sample, but to a much greater extent on the conditions of storage. It is influenced little by the method of canning, or by conditions within the control of the packer. A shipment of canned fruit may leave the packer in perfect condition and yet, owing to improper storage, the cans may become springers within a few months or even within a few weeks. A single shipment of California canned fruit may be split, one portion being sent to Texas or Oklahoma and the other to Boston; or one portion may be stored under a hot iron roof and the other in a relatively cool warehouse. Under such circumstances, the goods stored in the cooler location remain in perfect condition long after the others have become springers. This is due solely to the acceleration of the higher temperature on the action of the fruit acids on the metal of the container.

In the inspection of cans with concave ends and apparently normal in every way, the analyst often desires to know whether they are likely to become springers in the near future. In such cases, before opening the can, its vacuum is determined by means of a suitably equipped gauge. The vacuum in the can has no significance in itself, but is often of value when considered in connection with other data.

## VENT HOLES

The number of vent holes appearing in the can is a matter which has occasioned frequent error. No opinion can be formed of the character or history of canned foods by the number of vent holes in the can. The old process of canning many products, including canned beef and salmon, used two vent holes. This was described by the writer as applied to canned beef in Bureau of Chemistry *Bulletin* 13, Part 10, published in 1901. Although the practice is not as prevalent now as it was at that time, it is still found at many plants.

The procedure which gives two vent holes is this.

<sup>1</sup> Read before the Chemical Section of the Association of American Dairy, Food and Drug Officials, August 8, 1916.



The cans are sealed, tipped and given a kettle exhaust—that is, they are heated in the process kettle about half an hour and again vented to permit the escape of air. The new vent hole is then sealed and the cans are again placed in the process kettle and sterilized.

It sometimes happens that the closing of the second vent hole is prevented by a piece of solid material such as meat lying against it. When this occurs, a third vent hole is made in order to have an opening when the second one is closed. If anything lies against the can where the third vent hole is made, the can is vented in still another place and this is continued until a spot is found that is not in contact with the contents of the can.

Even when the method just described is not employed, two or more vent holes are occasionally found in hole and cap cans containing foods of all descriptions. This occurs when the can is not properly closed. At the end of every hole and cap line in the cannery, a man is stationed to inspect the cans as they pass and set out on a table those not properly sealed. Some packers carry the cans on a conveyor through a trough of hot water, when "cap leaks" and "vent leaks" due to defective sealing may be detected by bubbles of air escaping from the top of the can. Whatever the method of sorting, there are often enough cans there that are not properly sealed to keep a man with a hand-soldering iron busy patching them.

These cans can be patched only with an open vent hole to permit the escape of air while the hot steel is on the cap. This is generally accomplished by removing the solder from the old vent hole with a hot soldering iron. Frequently, however, a new vent hole is made. This second vent hole is in no respect a mark of inferiority. The cans are patched immediately and their sterilization is rarely delayed more than a few minutes.

Again, with sanitary cans, there are various reasons why a vent hole may be found. One incident came to the writer's attention a few weeks ago in which, by misunderstanding, the brine was omitted from several hundred cans of shrimp. The workmen understood that they were to be packed "dry." It was the intention of the superintendent to pack them with brine and he could not spare a process kettle long enough to give these cans the process necessary for dry shrimp. What he did was to make two vent holes in the cans, introduce hot brine and close the vent holes again. It was all done in a few minutes and the cans so treated were sterilized in the same process kettle as those that followed them through the sealing machine. The contents of these cans were identical with those of the cans filled and brined before closing.

Again, one crabmeat packer of the writer's acquaintance, buys his sanitary cans with the tops already vented in order that he may continue his former practice of giving the cans a retort exhaust with open vent.

One not familiar with the industry might suspect reprocessing on seeing the cans described in these two illustrations. If he would investigate the matter further, however, he would find that reprocessing

would cook the shrimp to pieces and would darken the crabmeat to such an extent that it would be unmerchandiseable. On the other hand, some foods can be sterilized a second time without materially changing their appearance.

Presence of vent holes is never proof of decomposition. The question of vent holes is merely one of the points that should be noted from the external inspection of the can and considered in connection with data obtained from the examination of the contents.

#### ODOR, FLAVOR AND APPEARANCE

On opening the can, the odor, flavor and appearance of the contents should be carefully observed. In this manner the analyst should be able to determine approximately the quality or commercial grade of the sample. He may thus judge whether the product complies with the grade for which it is sold, or with the representations on the label. The importance of establishing the true commercial grade is not always fully understood. It is not merely a commercial question. A fancy or first quality article, for instance, can be prepared only from a raw product grown under proper conditions, harvested at the best stage of maturity, and canned promptly. Moreover, in many varieties of foods, a fancy or first grade product can be prepared only by experienced and skilled men. If the raw material is not of suitable grade an experienced man will recognize that fact by the appearance or flavor of the finished product. If the raw material is not properly handled, if it is allowed to stand for even a fraction of the time that is customary with fresh vegetables in our city markets, that fact is often apparent in the canned food. It may be suitable for consumption and comply with the law if properly labeled and still not be of the highest commercial grade. For instance, if not handled promptly, peas lose in flavor and asparagus has a tendency to become tough and bitter. To retain a high quality, they must be canned as soon as possible after they are harvested.

A movement is under way to make the commercial grades more uniform and to have the products so labeled that these grades will be understood by the purchaser. As this movement progresses, the importance of holding the products true to label will increase. Even at the present time, this matter is very important and should be considered in the enforcement of food laws.

The importance of odor and taste in the inspection of canned foods cannot be overstated. If the odor and flavor of a sample be not entirely normal, the possibility of delay in manufacture and consequent bacterial change should be considered. In such a case, a microscopical examination is often of value.

#### MICROSCOPICAL EXAMINATION

This method is applied to the liquor if the product has a distinct liquor. If the sample be thick and pasty, enough water may be added to give it a suitable consistency. In either case, water should be added if necessary, so to thin the sample that the number of microscopic particles will not be too great for their

careful study, and this liquid or mixture should be allowed to stand in a beaker or cylinder for a moment until the heaviest particles settle. The proper technique must be worked out with each product.

A mount should then be made and examined microscopically. If bacteria are recognized by size and shape, their presence may be confirmed by bacteriological stains. If either yeasts or bacteria are found in considerable numbers, the analyst should endeavor to find the reason for their presence. Obviously, this method is not applicable to products made by process of fermentation. Kraut, for instance, is prepared by such a process and contains a very large number of bacteria, but should contain few if any yeasts.

The presence of dead bacteria in considerable numbers is merely an indication of the beginning of bacterial change at some time in the history of the product. It may be due to allowing a few cans to stand too long (because of a breakdown in the machine) after filling and before sterilizing, or to storing the raw product for a number of hours in boxes or baskets as is done with fresh vegetables in our city markets. It may be due to any delay in the process of canning. This method may help or mislead an analyst according to his ability and experience. It can be used intelligently only in connection with the other methods described.

The method requires special aptitude, long training and unremitting care. There is no other analytical method applied to foods which is now used so badly and with so little aptitude or judgment as the method for determining the presence of bacteria with the microscope. Mention is made of the importance of special aptitude in judging the odor, taste and flavor of the food. It is necessary to no less extent in a microscopic examination. Both methods are largely subjective. Experience with samples of known character, both fresh and canned, is absolutely necessary. Without such experience, the analyst can be sure only of making serious mistakes.

It should be borne in mind that this is a microscopical and not a bacteriological method. It is used in determining the presence of dead microorganisms. It is therefore widely different from the bacteriological method which follows.

#### BACTERIOLOGICAL EXAMINATION

In the inspection of canned foods, a bacteriological examination is of value only when considered in connection with other methods of analysis. A food that has undergone bacteriological decomposition may be sterile because of the inhibiting action of products of the life functions of the organisms causing the decomposition.

On the other hand, it is believed by some that canned foods may contain aerobic bacteria which cannot develop because of the absence of oxygen and which may therefore remain dormant for a considerable time. It is also believed by some that certain organisms may remain quiescent in some foods because the food does not provide a suitable medium for their growth. The truth of the last two ideas suggested has not been

demonstrated and in fact it is well known that canned foods are almost universally sterile. At the same time, until questions of this nature are settled, bacteriological methods are of more value in research investigations relating to canned foods than in their inspection. In the case of goods very recently packed and to determine whether the process of the plant is sufficient, a bacteriological examination is of value when used in connection with the other methods described above. The results of the bacteriological examination of freshly packed goods can be confirmed by incubating cans for several days and noting the odor, flavor, and acidity of their contents.

#### DETERMINATION OF ACIDITY

This is a method with which relatively little has been done in the examination of canned foods. The laboratories that have used it have not tabulated their results and the data now existing from the titration of normal samples is therefore not available. It is desirable that authentic data of this nature be secured.

The separated liquor should be titrated when practicable. It need not be filtered unless it contain finely divided solids that may obscure the end-point. In the absence of a distinct liquor, the sample should be finely comminuted and a weighted portion placed in a beaker with water. In either case an excess of standard acid should be added, the sample boiled, cooled in water to approximately room temperature and titrated back with standard alkali, using phenolphthalein as indicator.

An abnormally high acidity, or, under some circumstances, an abnormally low acidity, may be of much value when considered in connection with the results of the methods mentioned above.

#### FILL OF THE CAN

When the can is opened, the fill should be carefully noted. If the can be opened by cutting around the side, near the end, it is often convenient to pour the liquor through the opening thus made before turning back the top. It is important that in the examination of a single product a uniform method of separating the drained solids be employed.

If the food under examination consists of insoluble material, such as fruits or vegetables surrounded with water, syrup or brine, the amount of food present should be noted. It may be well to weigh the drained solids and liquor after separation with a suitable screen the size of whose mesh will depend on the product under examination. With some products, a  $\frac{1}{4}$ -in. screen is appropriate; with others a smaller mesh is necessary.

It is often important for the analyst to consider the relation between the drained solids found in the can and the weight of food originally weighed into the can. For instance, with dry pack shrimp, the cut-out weight is less and with wet pack shrimp it is greater than the amount of shrimp originally weighed into the can.

In working with fruit packed in syrup, the specific gravity of the syrup may be determined. Then,



taking into consideration the average sugar and water content of the fruit present and the proportion of that fruit in the contents of the can the analyst can calculate approximately the weight of fruit and strength of syrup that was used originally. The influence of syrup of different strengths on the weight of the drained contents has been worked out by Bitting<sup>1</sup> for a wide range of fruits.

Whether the drained solids and liquor be weighed or not, a record should be made of whether the solid portion of the contents appears to be present in the right amount. In this connection, care should be taken that the analyst be not deceived by the solids floating at the top of the liquor, thus giving the appearance of a good fill, even if the fill be slack. Here again the analyst is not competent to form an opinion unless he knows what is normal with that particular variety of food. Some foods may shrink in processing or become softened so that they settle down, leaving a can which is apparently slack filled although it may have been full at the beginning. Let us take canned shrimp as an illustration. Even if the can be packed so full of shrimp that it will mat together and be unattractive to the eye, the product will often soften on processing so that the fill will appear slack to one not familiar with the product.

The analyst must bear in mind that the examination of one or two cans will often lead to incorrect conclusions. No matter how careful a packer may be, it frequently happens that the amount of brine in the can is either too much or too little. In a well managed corn cannery, for instance, there is always one man whose duty is to open cans at frequent intervals to determine whether the corn is of the right consistency. The character of the corn changes from hour to hour, requiring the relative amount of corn and brine to be changed from time to time in order to give the proper result in the finished product.

#### EXAMINATION OF THE CAN

Cans should be carefully examined to determine whether they are tight. This is more important in constructive work checking up the efficiency of a plant than in the enforcement of food laws. It is just as essential for the canner to know when his cans are defective as when they are not completely sterilized. In both cases he may expect spoilage.

An adequate description of the exact procedure to be followed in determining whether a lot of cans is tight is scarcely practicable within the scope of this paper. Some types of cans may be emptied through a small opening, thoroughly cleansed, again sealed up, air pumped into them under pressure and leaks detected by bubbles of air escaping when the can is held under water. This can may be sealed in a partial vacuum and the vacuum determined after the can has stood a number of days. The crimped edges of sanitary cans may be laid bare by filing and examined with a lens. Soldered seams may be "stripped" (pulled apart) and carefully inspected for possible imperfections of workmanship. If a large percentage

of the cans of a given lot of food is found to leak because of a common fault in their construction, the entire lot of food may have spoiled. Such cases are almost always discovered at the plant and therefore come within the experience of the packer's chemist rather than that of an official enforcing a food law. If they should come to the attention of a food inspection official, the examination of the can is important in that it gives fuller information regarding the nature of the product, and may confirm other data.

Cans containing foods likely to produce pin-holes should be gone over in great detail with a needle. If the analyst has not exceptionally good eyes, a simple lens of reading glass is sometimes useful. The application of the same method of examination to the inside of the can will disclose whether the can is pitting and thus likely to form pin-holes. For this, both ends of the can must be cut off and the body opened by cutting down the side.

In the examination of the can as in the examination of the contents, it is obvious that the results obtained from a single can may be misleading. There are many reasons for this. For instance, small leaks, after admitting contaminated air or contaminated water from the cooling tank, may be closed by particles of food or, as in the case of water pipes, by rusting. If we find leaks in something like half the cans from a lot of swells, we assume that they probably all leaked at the beginning. This explains the fact which so many find it difficult to understand—that a swell may be and frequently is due to a leak in the can.

In such a case, a sample consisting of a single can or a small number of cans is frequently not representative of the lot of goods from which it is taken. After examining a half dozen cans, the writer frequently sends for a case and sometimes several cases. Even then an inspection of the entire lot in the storeroom will often throw additional light on the cause of the difficulty.

#### SUBSEQUENT EXAMINATION

The nature of any further examination must depend on the particular variety of food and, to some extent, on the character of the sample and the reason for the examination. A chemical examination may be made to determine whether certain standards are complied with as the determination of fat and solids in evaporated or condensed milk.

The cause should be understood of various discolorations that are sometimes found on the inside of the can and on the surface of the food. For instance, with some products like kidney beans and, to a certain extent, with peas, the entire inner surface of the can which comes in contact with the food is more or less dark in color, owing to a slight film of insoluble tin sulfide. With peas, the portion of the can which stands uppermost for a few hours immediately after processing and cooling, has a number of spots consisting apparently of iron oxide. These spots gradually become dark until they are quite black, probably owing to the conversion of a portion of the oxide to sulfide. As just stated, these spots on the inside of canned peas are universally present. Apparently they cannot

<sup>1</sup> U. S. Dept. of Agriculture, *Bull.* 196, May, 1915; National Canners Association, *Bull.* 4, February, 1915.

be avoided and they are not in any way objectionable. They sometimes startle a canner who sees them for the first time and the chemist inspecting his product should be able to explain them.

With some products, patches of iron sulfide, apparently in colloidal form and sometimes mixed with particles of food, adhere to the sides of the can. These patches of iron sulfide are not frequent on the whole but have been found in considerable numbers. They vary in size and sometimes their thickness is so great that they become mixed with the food in their immediate vicinity and are objected to by buyers who do not understand their nature. When large, and especially when they become mixed with the food, these patches are unsightly but the amount of iron present is really exceedingly small. The cause of these patches is only partially understood. They always form like the spots just referred to on pea cans on the portion of the can that is uppermost after processing and cooling, which therefore does not come in contact with the food. On storage, the spots gradually become less conspicuous. The conditions leading to their formation are not entirely understood, but it has been determined that they are less numerous and smaller as the can is fuller and freer from oxygen.

Before opening a can of food, it is often of value to determine the vacuum in the can by means of a suitably equipped gauge. This is a matter which has no significance in itself but may be of value when considered in connection with other data.

The amount of tin (or perhaps soluble tin) and iron in acid fruits may be significant when considered in connection with other data. On the other hand, with vegetables, such as asparagus, string beans and pumpkin, whose action on the tin is believed to be due to amino bodies, there is no relation between the amount of tin in the food and the amount of hydrogen in the gas content of the can. We are just beginning to understand this subject and all data bearing on it is of value.

It may sometimes be of interest to determine the composition of the gas in a can with bulged ends. When the can is sealed the air is not entirely removed. Some carbon dioxide is formed in processing and some may be present in the food before processing, especially if it is not sterilized very promptly. Hydrogen is formed by the action of fruit acids on the metal of the container.

It has been pointed out by Baker<sup>1</sup> that hydrogen is not found in the gases of the can until oxygen has disappeared. The composition of the gas present, therefore, may sometimes serve to confirm data obtained by other methods of examination.

NATIONAL CANNERS ASSOCIATION, WASHINGTON, D. C.

### THE CHEMICAL COMPOSITION OF COMMERCIAL GLUCOSE AND ITS DIGESTIBILITY

By J. A. WESENER AND G. L. TELLER

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The term commercial glucose has been applied to a product obtained by the action of certain catalytic agents upon refined starch, until the starch has lost

its identity as such and has been converted into a series of products, consisting of *d*-glucose, maltose and different forms of dextrin. The dilute liquid thus produced is clarified by passing over boneblack and is then carefully evaporated, either to a solid substance or to a syrupy condition known as glucose syrup. The glucose thus produced in this country is made entirely from corn starch and, for this reason, the syrup is designated as corn syrup. It consists of about one-fifth its weight of water, very minute traces of nitrogenous bodies, a very small amount of ash and a group of carbohydrate bodies, consisting of dextrose, maltose and probably several forms of dextrin, and paralleling closely the bodies of a similar nature obtained by the action of malt diastase and other diastases upon starch.

There is apparently a border line between the bodies commonly known as dextrin and that known as maltose, which has led to great confusion in the minds of the chemists who have investigated this subject, largely because of the difficulties attendant upon the separation of such bodies from maltose on the one hand, and the different forms of dextrin, on the other, and the consequent confusion with these bodies and with mixtures of them. This confusion of ideas concerning glucose syrup has been participated in by a large number of investigators, extending in time over a period of 20 or 30 years, and has led to the introduction into the literature of such terms as "gallisin," "iso-maltose," "malto-dextrin" and others.

The voluminous literature on this subject appears to have been reviewed completely by various writers without coming to any definite conclusions as to results. The latest edition of such an authoritative work as Allen's "Commercial Organic Analysis" (4th Ed., Vol. I, 1912), dismisses the matter with the following brief summary:

"Gallisin as hitherto obtained is not a definite compound, and it appears advisable only to retain the term as synonymous with unfermentable matter. The whole question of the structure of starch, the nature of the various dextrins and of iso-maltose still remains a vexed question in carbohydrate chemistry and the utmost confusion exists as regards the subject. [The reader is referred to Ling's article on Starch in Sykes' 'Text-Book of Brewing' (1907).]"

A review of the earlier literature is quite fully set forth in the third edition of the same work, published in 1898, and in Brown's "Handbook of Sugar Analysis" (1912), under the title of Iso-maltose. A clear and concise statement of what appears to be the general understanding of these terms, as they are used, is embodied in the following definitions, as given in the "Century Dictionary and Encyclopedia."

"Gallisin, in chemistry, a substance analogous to dextrin, obtained by fermenting with yeast a solution of commercial glucose or starch sugar and adding to the residual liquid absolute alcohol in excess. Gallisin is precipitated as a white powder, of faintly sweetish taste, hygroscopic, dextrogyrate, incapable of fermentation and yielding dextrose by prolonged heating with dilute sulfuric acid. Probably identical with iso-maltose,  $C_{12}H_{22}O_{11}$ . (Sadtler, "Handbook of Industrial Chemistry," p. 178.)

"Iso-maltose, a substance formed together with maltose from starch on diastatic digestion. It has been produced synthetically from dextrose, does not ferment and is isomeric with maltose,  $C_{12}H_{22}O_{11}$ .

"Malto-dextrin, a variety of dextrine or starch-gum, produced in 'mashing' brewers' malt as an intermediate product between

<sup>1</sup> Original Contributions, 8th Intern. Congr. Appl. Chem., 18, 45.



starch and fermentable glucose. Its claim to be considered a distinct substance is not clearly established."

The presence of so-called gallisin or iso-maltose in glucose has been attributed by some authors to a reversion process brought about by the action of dilute acid upon dextrose during the process of manufacture. This has led to an apparent misconception of the significance of its presence and has brought in question the value of this portion of glucose as an article of food. One recent writer has gone so far as to state that this body is not only unfermentable, but is not hydrolyzable by enzymes,<sup>1</sup> while Allen states:<sup>2</sup> "By heating with dilute sulfuric acid for some hours, gallisin yields a large proportion of dextrose, but its complete conversion has not so far been effected."

It has been the purpose of the work upon which this article is based to clear up some of these points, especially with reference to the assumed presence of an unfermentable body which is not hydrolyzable by enzymes and which consequently would not serve as an article of food.

#### SAMPLES USED IN EXPERIMENTS

In carrying out this work we have made about 600 comparative fermentation tests upon glucoses, starches, foodstuffs and various substances used in control experiments and have supplemented many of these by more or less complete analytical determinations to show the nature of the residual products after the fermentation has been completed. It should be borne in mind in this connection that yeast used for fermentation is necessarily of a more or less variable character, as are also the various diastatic enzymes available for investigations of this kind. While recognizing that there are more or less differences in glucose of different manufacture and also in different lots of glucose of the same manufacturer, we have confined our work largely to a few lots of glucose, purchased in the market,<sup>3</sup> and apparently suitable for this purpose because of fulfilling the conditions exhibited by the glucoses experimented upon by those who have claimed the presence of the unfermentable body known as "gallisin" or "iso-maltose." The solids in the samples examined varied from 79.8 to 83 per cent.

**ASH**—The ash of glucose, while minute in amount, is always present. Its source is partly the grain from which the starch is derived, and partly certain ingredients used in the manufacture of glucose. For these reasons, the composition as well as the amount of ash will necessarily vary. Phosphoric acid is present in small amounts and very probably comes from the grain. The same is true of minute traces of potash and possibly also of the lime. Soda is added during the process of manufacture. Traces of iron are accidentally present. The full analysis of the ash (amounting to 0.34 per cent) of one sample of the glucose is given below.

PERCENTAGE ANALYSIS OF THE ASH OF GLUCOSE			
Soda (Na <sub>2</sub> O).....	0.15	Sulfur Trioxide (SO <sub>3</sub> )..	0.04
Calcium Oxide (lime) (CaO)	0.03	Phosphorus Pentoxide	
Potash (K <sub>2</sub> O).....	Trace	(P <sub>2</sub> O <sub>5</sub> ).....	0.03
Iron Oxide (Fe <sub>2</sub> O <sub>3</sub> ).....	Trace	Carbon Dioxide (CO <sub>2</sub> )..	0.09
		Chlorine (Cl).....	Trace(a)

(a) In the ash, as burned, no chlorine was obtained, in spite of the fact that the ash was distinctly alkaline. When, however, the glucose is burned with the addition of chlorine-free caustic soda, chlorine is found to the extent of 0.16 per cent.

The above ash was absolutely white and contained no traces of copper or other poisonous metals. We made a very extensive examination of glucose for arsenic and were unable to detect the presence of any trace of this material. Sulfites, which during the early history of the manufacture of glucose were used for whitening the product, are now no longer used, and no trace of them was found in the glucose examined.

**NITROGENOUS BODIES**—While starch used in the manufacture of glucose is freed as far as possible from nitrogenous matter, it is practically impossible to remove the last traces, so that very minute amounts of these bodies still remain in the finished product. A careful examination of the glucose examined for nitrogenous bodies gave the following results (percentages):

Ammonia and Amino Nitrogen.....	0.00012
Protein Nitrogen.....	0.00938
Equivalent to Protein (Nitrogen $\times$ 6.25).....	0.058

**CARBOHYDRATES**—The results of the work of various investigators during the past 20 years has been to establish in glucose the presence of dextrose, maltose and dextrans. In our own experiments we have determined the presence of these bodies by methods somewhat different from those used by others. Our fermentation tests were conducted substantially as follows:

A glass bottle of about 500 cc. capacity is used to contain the fermenting mass, and during the process of fermentation is immersed in water in a metal tank having a false bottom and suitable for keeping the fermentation bottle at any desired temperature. The temperature ordinarily used was 35° C. The material to be fermented was dissolved in water so that the amount of water present was 200 cc. The gas developed was collected in a large measuring jar, about 4 in. in diameter and 16 in. high, suitable for collecting 2,000 or more cc. of gas. The top of this jar was connected by glass and rubber connections, with a bottle containing the fermenting liquid. Before the fermentation, the collecting jar was filled with water to the zero mark, or rather slightly above, to provide for the first escape of water, which always takes place to release tension. As fermentation progresses, the water escapes from an opening in the bottom of the jar and passes into a small control bottle of about 4 oz. capacity through a glass tube which extends to near the bottom of the small bottle. It then escapes from the top of the small bottle through another glass tube, thus providing a trap to protect against the entering of air from the outside and to allow for absorption of the gas by water in the collecting jar near the close of the experiment. Used in this way the apparatus is suitable for fermenting 2 to 8 g. of sugar, and collecting the gas produced so that it may be measured with a considerable degree of accuracy. In these experiments 5 g. of sugar were ordinarily used. The amount of gas produced varies from day to day, depending upon the special lot of yeast used for the fermentation. The yeast used was the ordinary compressed yeast as it is sold largely in the markets throughout the country for the use of bakers in the manufacture of bread: the amount of such yeast was large, to produce a rapid fermentation, generally 15 g. The variation is ordinarily greater with different makes of compressed yeast than with the same make as it is

<sup>1</sup> Geoffrey Martin, "Industrial Organic Chemistry," 1913.

<sup>2</sup> "Commercial Organic Analysis," 1 (1898), 361.

<sup>3</sup> The various lots of glucose used were purchased from Bunte Brothers, Chicago, Ill., and were such as they use regularly in the manufacture of high-grade confections. They represent the commercial product of two different glucose manufacturers.

used from day to day. There are some remarkable differences in this respect, which indicate that the results of fermentation are within certain limits due to the special kinds of yeast present, or to certain kinds of bacteria which appear always to accompany the yeast in greater or less amount. The amount of gas ordinarily produced from 5 g. of cane sugar, when 15 g. of compressed yeast were used, varied from 1050 to 1100 cc., and reached its maximum amount in from  $2\frac{1}{2}$  to 3 hours.

The relative activity of the yeast used on different days can be determined by making a series of experiments on fermentation with pure cane sugar. When the work is carefully done, very concordant results can be obtained and this method can be used with a considerable degree of accuracy in estimating the amount of fermentable sugars in a sample of material, calculating from the amount of gas produced from the sample and from the cane sugar used in control, the equivalent amount of cane or other fermentable sugars which the sample contains. It is found that pure dextrose gives substantially 95 per cent of the amount of gas that will be obtained by the same amount of cane sugar fermented under the same conditions. This is as we would expect from the molecular equivalents of these two sugars.

Following out this method of fermentation on glucose, we found that a certain amount of glucose is always fermentable and a still larger amount is not fermentable until it has been converted into some other form of carbohydrates by the use of diastase, either from malt extract or from some other source. In some series of experiments, gas was obtained on the original glucose, equivalent to 28 to 33 per cent calculated as cane sugar. The results of two series of these determinations are shown in Table 1.

TABLE 1

Glucose A: 79.7 Per cent Solids    Glucose B: 81.7 Per cent Solids

Reducing sugars were in all cases determined by Fehling's solution, weighing the resulting cuprous oxide in a Gooch crucible and calculating the results according to the Tables of Munson and Walker (Bureau of Chemistry, U. S. Dept. of Agric., *Bull.* 107).

	A	B
Total Gas Produced from 5 grams Cane Sugar.....	1040 cc.	1100 cc.
Total Gas Produced from 10 grams Glucose.....	690 cc.	720 cc.
GAS EQUIVALENT: to Cane Sugar.....	33.8%	32.7%
to Dextrose.....	35.5	34.6
<b>UNFERMENTED REDUCING SUGARS:</b>		
Calculated as Dextrose.....	6.5	8.2
Calculated as Maltose.....	11.5	14.5
TOTAL REDUCING SUGARS: Calculated as Dextrose.....	31.0	34.6
Calculated as Maltose.....	55.2	61.6
FERMENTED REDUCING SUGARS: Calculated as Dextrose.....	24.5	26.4
Calculated as Maltose.....	43.7	47.1
<b>APPARENT DEXTROSE:</b>		
Calculated from gas and reduction.....	11.7	17.2
APPARENT MALTOSE: Calculated from gas and reduction.....	22.9	16.4
APPARENT DEXTRINS (by difference).....	44.8	47.7

Glucose B, containing 81.7 per cent total solids, gave as much gas as would cane sugar, equivalent to 32.7 per cent of the weight of glucose taken. The unfermented residue contained reducing sugar equivalent to 8.2 per cent of dextrose. The original reducing sugar in the sample, calculated as dextrose, was 34.6 per cent; deducting the amount of unfermented from this leaves a difference of 26.4 per cent dextrose, which was fermented. According to our premises, as stated, if this had been all dextrose, we should have had a production of gas equivalent to substantially 26.4 per cent of dextrose, but we find from our experiments that we have a gas production equivalent to considerably more than this. On the other hand, if we had calculated all our reducing sugars as maltose we should have had 61.6 per cent maltose in the original sample, and 14.5 per cent maltose by reduction after fermentation. This would leave of fermented

sugars, calculated as maltose, 47.1 per cent, which is much higher than we have found by fermentation.

Following out a simple arithmetical calculation, based upon these two series of figures, we can calculate the proportion of maltose and dextrose in the fermented sugars. Thus if the reducing sugars had been all maltose we should have found 20.7 per cent more than if they were all dextrose. Since a considerable part of the fermented reducing sugars of the glucose is maltose and the remainder is dextrose and on taking our gas equivalent of dextrose in comparison with dextrose we have a higher amount of fermenting sugar present than if we take it as cane sugar or maltose, it is well to take the mean between the apparent amount of sugar as dextrose (34.6 per cent), and the apparent amount of sugar as cane sugar or maltose (32.7 per cent), which gives 33.6 per cent.

On this basis, if the fermented sugar had been all dextrose we should have had 7.2 per cent less than we found by fermentation. By using the correct proportion,<sup>1</sup> then, of the amount of reducing sugars present we have  $20.7 : 7.2 :: 47.1 : x$ , which would give 16.4 per cent of maltose. The difference between 16.4 per cent, the apparent maltose, and 33.6 per cent, the total fermented sugars, is 17.2 per cent, as the amount of dextrose fermented. Deducting the amount of fermentable sugars found from the total carbohydrates in the glucose, as previously determined, we find the dextrin to amount to 47.7 per cent. Working in the same manner, we find the dextrose in Sample A to be 11.7 per cent, maltose 22.9 per cent, and dextrin 44.8 per cent.

It is true that if we had used another compressed yeast we would have obtained results a little different from these, but in all cases we found the results to show a large proportion of dextrose to the maltose, and yet the maltose was present in considerable quantity. This is a method which could readily be put into practice for factory control, and in our opinion it would be very satisfactory for the purpose if the proper compressed yeast were used and blank experiments conducted with glucose of known quality. A few slight corrections might be introduced, but for our experimental purposes, they were unimportant.

THE FERMENTATION OF GLUCOSE AFTER DIGESTING  
WITH A COLD WATER EXTRACT OF MALT FOR THE  
PURPOSE OF CONVERTING DEXTRINS  
INTO SUGARS

The malt used for this purpose was a good quality of distillers' malt, selected because of its being rich in diastase. In preparing the cold water extract for use the practice was to grind 200 g. of the malt moderately fine and digest it in 1000 cc. of cold water for a period of 2 to 6 hrs. The mixture was then filtered and the clear water extract taken for use. The amount of solids extracted in this way naturally varies to some extent, depending upon time of extraction and amount of stirring during the time of extraction. Glucose was treated with extracts of this kind under various conditions, at different temperatures, and for different lengths of time, and then subjected to fermentation with compressed yeast. The results of such fermentation were found to depend upon the temperature of

<sup>1</sup> This proportion is based upon the reasoning that if the sugar were all maltose it would be 47.1 per cent, which is 20.7 per cent above the dextrose figure, but we find it by fermentation to be 33.6 per cent which is 7.2 per cent above the dextrose figure. It follows from this that the maltose must be  $7.2/20.7$  of 47.1 per cent.



mashing and upon the kind of yeast used in the fermentation, as is shown in Table 2.

TABLE 2—CC. GAS PRODUCED BY 15 GRAMS OF COMPRESSED YEAST, ACTING UNDER THE SAME CONDITIONS ON 5 G. OF CANE SUGAR, OR GLUCOSE WHICH HAD BEEN DIGESTED FOR 2 HRS. WITH A COLD WATER EXTRACT OF MALT (50 CC.)

Temp. ° C.	Malt Ext.	Glucose & Malt Ext.	Temp. ° C.	Malt Ext.	Glucose & Malt Ext.	Temp. ° C.	Yeast	Cane Sugar	Glucose
40	320	1200	40	220	1100	45	A	1100	1060
50	300	1220	50	200	1140	45	B	1000	940
60	290	1160	60	200	980	45	C	1080	1060

The most favorable temperature for the action of the malt extract was 50° C. When using compressed yeast from different manufacturers the amount of gas produced from the glucose mashed with malt extract is closely related to the comparative amount of gas obtained with the same yeast acting upon cane sugar. This difference in brands of compressed yeast is such as we have found in a large number of gas fermentation tests extending over a period of several years, in studying the comparative strength of yeast in bread-making. Thus it is a general rule that Yeast B, when acting on sugar under conditions in these experiments, will produce less gas than will Yeasts A and C. The probable cause lies in the by-products which are always produced when yeast acts upon sugar and in a complex body like compressed yeast may be brought about by the yeast cells themselves or by certain forms of bacteria which accompany the yeast.<sup>1</sup>

As has been already stated, where yeast acts upon pure cane sugar and upon pure dextrose, the amount of gas produced during the fermentation with like quantities of the same compressed yeast is closely proportional to the amount of sugar present. Some things have been found in our experiments which have shown that where certain starches, or starch products, are acted upon by malt and the result of the mashing is subjected to fermentation, a larger quantity of gas will be obtained than is directly proportional to the amount of sugar which we should expect to be produced from the starch present; thus in treating the prepared starch known as Mazam, with malt extract, a considerably larger proportion of gas is obtained than we should expect from the amount of starch used, assuming that the usual amount of dextrose was eventually obtained from the starch by the combined influence of the malt extract and the maltase secreted by the yeast itself. Mazam is a starchy preparation obtained by hydrolyzing starch much the same as by gelatinizing it with boiling water, except that in the Mazam the starch is subsequently dried and flaked. The amount of gas produced from the dry starch present in Mazam has been found in several experiments to correspond to as high as 122 to 128 per cent of the starch used, calculating on the basis of pure dextrose, to which the starch must be eventually converted before fermentation.

As is well known, most of the cereal foods, corn meal, Quaker Oats, rice, Cream of Wheat, etc., and materials baked from them, like bread, are rich in

<sup>1</sup> It may be mentioned incidentally that while B gives the least amount of gas in fermentation tests, it often, in fact, generally, gives the best results in bread-making, where its influence in softening the gluten of the flour appears to be especially beneficial. This also is probably due to by-products produced during fermentation.

carbohydrates, which consist almost wholly of starch. To show a comparison between the carbohydrates of these several foods and glucose, they were mashed with malt extract as described above, and subsequently fermented. First a complete analysis of the foodstuffs was made and the amount of carbohydrates determined in the usual manner (by difference), after subtracting from the total weight of material the amounts of moisture, ash, protein, fat and crude fiber. Then the same quantity of each material was mashed at a temperature of 50° C. for 2 hrs. with a properly prepared solution of cold water extract of malt, cooled to the proper temperature, 15 g. of yeast added, and the gas resulting from the fermentation collected and measured. The corn meal, Quaker Oats, rice and Cream of Wheat were well cooked, probably more thoroughly than they would ordinarily be as prepared for consumption on the table. The Corn Flakes and Shredded Wheat are breakfast foods prepared for immediate consumption and required no further cooking. Irish and sweet potatoes were baked in the usual manner and the edible portion carefully dried at a low temperature and powdered. The same was done with white bread.

The results of these experiments are given in Table 3, together with the amount of carbohydrates

TABLE 3—GAS PRODUCED BY FERMENTING MALTED CARBOHYDRATES OF CEREAL FOODS COMPARED WITH MALTED GLUCOSE

	Per cent Total Carbohy- drates	Cc. Gas for 5 g. of Material	Cc. Gas for 5 g. Carbo- hydrates in Material
Corn Meal, well cooked.....	78.67	920	1170
Quaker Oats, well cooked.....	66.55	760	1143
Rice, well cooked.....	76.30	870	1140
Cream of Wheat, well cooked.....	75.50	880	1165
Corn Flakes.....	81.52	840	1043
Shredded Wheat.....	75.25	780	1030
Baked Potatoes, dried.....	86.30	945	1095
White Bread, Vienna, dried.....	75.70	840	1110
White Bread, Pullman, dried.....	75.40	820	1090
Bran Bread, dried.....	78.56	640	815
Glucose.....	80.00	880	1100

found on analysis and the total gas calculated to 5 g. of dry carbohydrates. It will be seen that the results obtained from glucose compare favorably with those obtained from several cereal foods and potatoes used, indicating that the dry matter of glucose yields substantially as much food material as many of these cereal foods, especially when allowance is made for the increased sugar content due to the hydration of the starch of the cereal foods.

What has been found to be true of Mazam with regard to an unexpectedly large proportion of gas production has been found to be true in a like manner of other starches and similar carbohydrates present in foodstuffs. Accordingly, to determine to what extent the glucose was converted into fermentable bodies, it was necessary to determine the amount of unfermented matters still present in the fermented solution as well as the nature of these bodies. After fermentation the fermented liquor was made up to a definite volume, filtered and an aliquot part taken for determination of the total solids and the reducing sugars, and in some instances for various other determinations. Typical results in determinations of this kind, using malt extract as the source of the diastase

TABLE 4

(1) Glucose, 10 g., digested in incubator over night at 45° C., with 50 cc. cold water extract of malt, then fermented with 15 g. yeast in comparison with 50 cc. of the malt extract and with 5 g. of cane sugar.

GLUCOSE FERMENTATION IN TRIPPLICATE			
	Cane Sugar	Malt Extract	Glucose and Malt Extract
Solids in the glucose 79.7%			
Total Gas Formation.....	1040 cc.	260 cc.	1980 cc.
Deduct Gas of Blank.....			1720 cc.
Gas equivalent to Cane Sugar.....			82.7 Per cent
Unfermented Solids (corr. for Malt Extract).....			15.4
UNFERMENTED REDUCING SUGARS: Calculated as Dextrose.....			2.5
Calculated as Maltose.....			4.4
Polarization of fermented solution made to 250 cc., 200 mm. tube, 6° Sugar scale.			

(2) Fermentation of 6 g. of glucose after digesting over night at 50° C. with 50 cc. of cold water extract of malt and sufficient water to make 100 cc. Fermented with 15 g. yeast in comparison with 5 g. of cane sugar and with 50 cc. malt extract solution; all in duplicate.

	Cane Sugar	Malt Extract	Glucose and Malt Extract
Total Gas.....	1040 cc.	140 cc.	1140 cc.
Corrected for Blank.....			1000 cc.
Gas equivalent to Cane Sugar.....			80%
Unfermented Soluble Solids.....		1.450 g.	1.950 g.
Unfermented Glucose.....			8.3%
Unfermented Reducing Sugars as Dextrose.....			2.9

(3) Fermentation with 100 g. glucose, digested with 250 cc. cold water extract of malt over night at 50° C., then supplied with 20 g. yeast and fermented as long as fermentation continued. Gas not collected.

Total Solids (corr. for Malt Extract).....	16.4 Per cent
UNFERMENTED REDUCING SUGARS: Calculated as Dextrose.....	3.1
Calculated as Maltose.....	5.5

are shown in Table 4. Evidently a considerable quantity of unfermented solids remains from the glucose after deducting the amount of unfermented solids due to the malt extract and to the water extract used in making the fermentation. The amount of unfermented matter in the tables shown, and in other experiments, is variable, as is also the amount of unfermented reducing sugars.

The conditions are found to be much the same whether a large quantity of glucose (100 g.) is used or a smaller quantity (5 or 10 g.), but the difficulties of manipulation are much greater where larger quantities of glucose are used. In addition to this, with smaller quantities it is possible to measure the amount of gas produced, thus giving further data. For this reason, by far the larger number of experiments which have been carried out have been with small quantities of glucose.

Several experiments with large quantities of glucose were made, but owing to the unsatisfactory results, the details of only one of these are given here: Ten lbs. of glucose were diluted to about 25 per cent of solids with water and digested over night at between 40 and 50° C. with cold water extract of malt. It was then seeded with about 3 oz. of compressed yeast, and fermented as long as fermentation continued (about 5 days). The liquor was then filtered and evaporated to a syrupy condition, after which it was precipitated with 95 per cent alcohol, which was added in excess or until the addition of alcohol produced no further precipitate. The precipitate was allowed to settle, was finally separated by decantation and filtration, and then well washed with fresh alcohol. It must be borne in mind, however, that with a large mass of material of this kind complete separation of insoluble from soluble bodies is difficult, and it is probable that some of the material which would naturally be present in alcohol was carried down with the precipitate. The alcoholic filtrate was next evaporated, then made up to 1000 cc., and divided into two portions, one of which was further fermented by the addition of yeast, which reduced the solids materially, but still left a

large quantity of unfermented matter. The other portion was analyzed and calculated back to the original volume of 1000 cc., and also to the original glucose with the results shown in Table 5. The material precipitated by alcohol was taken up by water and

TABLE 5—UNFERMENTED RESIDUES (PERCENTAGES) FROM 10 LBS. OF GLUCOSE

	PRECIPITATED BY ALCOHOL		IN SOLUTION IN ALCOHOL	
	In the 600 grams syrup obtained	Calc. to glucose taken	In the 1000 grams syrup obtained	Calc. to glucose taken
Total Solids.....	42.95	5.68	33.00	7.73
Ash.....	1.58	0.21	1.12	0.25
Protein (Nitrogen X 6.25).....	3.50	0.46	5.40	1.19
REDUCING SUGARS calculated:				
As Dextrose.....	10.10	1.34	28.64	6.32
As Maltose.....	18.14	2.40	49.00	10.82
APPARENT DEXTRIN when Reducing Sugars are calculated:			(a)	(a)
As Dextrose.....	27.77	3.67	—0.16	—0.03
As Maltose.....	19.73	2.61	...	...
Reducing Sugars as Dextrose:				
After boiling with dilute HCl...	39.70	5.26	...	...
After fermentation.....	1.57	0.21	...	...

(a) This solution evidently contained no dextrin and the reducing sugars present were all dextrose.

filtered, leaving a residue of 600 g. which also was analyzed with the results given in comparison with that of those obtained on the alcohol-soluble matter. A portion of the insoluble in alcohol was heated with 2½ per cent hydrochloric acid in the usual manner, followed in determining starch by treatment with this reagent to convert it into dextrose. That portion of the alcohol-soluble material which had been fermented was also treated with hydrochloric acid in the same manner. Both these solids were subsequently fermented and the reducing sugars found after this fermentation. In that portion of the fermented glucose precipitated with alcohol this unfermented residue of reducing sugars calculated as dextrose amounted to only 3.65 per cent of the dry matter of this residue, which, calculated to the original glucose, amounts to only 0.21 per cent, while the unfermented matter of the alcoholic filtrate amounted to 0.32 per cent of the original glucose. It is very probable that this small amount of unfermented residue when subjected to more favorable conditions for fermentation would also be completely fermented. As it is, the unfermented matter amounts to substantially 0.5 per cent of the glucose taken.

Owing to the introduction of certain products into the fermentation by the use of water extracts of malt and wishing to know the influence of other diastasic ferments, especially those of the body, and such as are used in medicine, experiments along the same line as those given above have been made on glucose, using pancreatin (as described and specified in the "U. S. Pharmacopoeia" and also Taka-Diastase, which is extensively recommended and used for the purpose of assisting in the digestion of starchy foods. Pancreatin, usually obtained from the hog or ox, contains various ferments and is rich in diastase, which, according to the specifications of the U. S. P., "should be capable of converting not less than 25 times its own weight of starch into substances soluble in water." As used, it is a cream-colored, amorphous, dry powder. Taka-Diastase is also a dry powder and contains a ferment said to be isolated from a certain species of mould,



*Euotium Oryzae*, which has been grown on a suitable medium, such as bran, and, according to the manufacturers, is of such a strength that it will in 10 minutes digest 150 times its own weight of starch.

Both of these diastases have been used in a very large number of experiments with glucose alone and in comparison with various kinds of starches, and the resulting products of digestion have been subjected to fermentation with compressed yeast under various conditions in such manner as to determine the amount of gas produced and in many instances the amount of undigested solids and reducing sugars. The outcome of these experiments is fully set forth in Tables 6 to 9. In some instances the completeness of the conversion of starch is naturally indicated by the thoroughness of the fermentation which follows the action of the diastase.

As already noted, in the case of digestion with malt extract, this fermentation is not always uniform with different kinds of compressed yeast. Some compressed yeasts appear to ferment more completely both the reducing sugars and some of the known reducing dextrins than do others. It is to be remembered that yeast is a fungus in a measure similar to that from which Taka-Diastase is obtained, and, as has already been pointed out, compressed yeast is likely to consist of different species of the yeast plant; probably these yeast plants are associated with different forms of enzyme-secreting bacteria, which explains in general why these differences (see Table 6) are likely to occur.

TABLE 6—RESULTS OF FERMENTING GLUCOSE WITH THREE DIFFERENT COMPRESSED YEASTS, AFTER DIGESTING OVER NIGHT WITH 1 G. TAKA-DIASTASE

	Yeast	Cc. Total Gas	Solids Corrected for Blank	Reducing Sugars as Dextrose
Glucose, 6 g. } Yeast, 10 g. } C	A	940	5.34%	1.41%
	B	940	7.50	0.94
	C	940	8.60	0.66
Gas from 5 g. Cane Sugar (Yeast C).....				1100 cc.
Gas from Blank (1 g. Taka-Diastase, each yeast).....				40 cc.
Reducing Sugars.....				None

The influence of different conditions of working of the diastases and different conditions of fermentations is apparent from Table 7.

TABLE 7

Results of fermenting glucose after digesting over night at near 40° C., two lots of 120 g. each made to 500 cc. with water. One with 10 g. Taka-Diastase; the other with 10 g. pancreatin: 25 cc. each, equivalent to 6 g. glucose, taken for fermentation.

	Total Gas Cc.	Per cent Solids Corrected for Blanks	Per cent Reducing Sugars as Dextrose
Taka-Diastase lot.....	1040	14.00	2.60
Pancreatin lot.....	940	23.54	1.20
Cane Sugar (5 g.).....	1100	...	..

It is shown in Table 8 that when the unfermented solids which remain after treatment with both Taka-Diastase and yeast, and pancreatin and yeast, are treated with hydrochloric acid, the unfermented carbohydrates are nearly completely converted into dextrose and that when this dextrose is again fermented with yeast, after properly neutralizing the solution, the entire amount of reducing sugars present is removed by the fermentation.

To make a more thorough study of the nature of the unfermented solids when acting upon glucose by these diastases and by yeast, a parallel series of experiments was conducted as is shown in Table 9.

TABLE 8

Results of fermenting glucose after digesting over night at near 40° C., two lots of 120 g. each made to 600 cc. with water. One with 10 g. Taka-Diastase and one with 10 g. pancreatin, 30 cc. of each, corresponding to 6 g. of glucose, were fermented with 10 g. of yeast and 200 cc. of total liquid. Volume made to 250 cc. after fermentation and clear filtrate taken for examination.

	5 Grams Cane Sugar	Taka-Diastase	Pancreatin Used
Total Gas Produced.....	1100 cc.	900 cc.	880 cc.
Solids after fermentation.....		11.27%	15.0%
Ash in solution.....		1.10	1.34
REDUCING SUGARS AS DEXTROSE:			
After fermentation.....		1.70	1.30
After boiling with 2.5% HCl.....		10.36	9.8
After fermentation of HCl product (60 g. Glucose).....		None	None
300 cc. of above digested glucose solutions were fermented with 20 grams yeast each:			
Unfermented Solids.....		9.22	13.07
Unfermented Reducing Sugars as Dextrose.....		2.04	1.87

Four fermentation tests in each of the two series were carried along in parallel experiments with closely agreeing results as to the amounts of gas produced. The products of each series of the four fermentations were then combined, made up to 1000 cc., and filtered, after which the clear filtrates were used for the subsequent analyses as recorded. A blank test was also made with pancreatin and with Taka-Diastase, but without glucose, so that corrections might be made for solids and other materials introduced from sources outside the glucose.

In these experiments, in addition to the determinations of the amounts of solids and reducing sugars present, determinations were made of the protein and the ash in solution and also the solids introduced and produced by the fermentation, as well as the polarization of the solution after fermentation.<sup>1</sup> The acidity given is expressed in cc. N/10 acid for the volume of liquid, corresponding to 6 g. of glucose. This acid is in part that introduced by the yeast itself and in part that which is produced during the fermentation by the action of the yeast upon the sugars.

Both the pancreatin and the Taka-Diastase contain some milk sugar, which is naturally converted into lactic acid. In some instances not all of the reducing sugar present in these ferments is removed during the process of fermentation, and when such has occurred, the quantity of reducing sugars found in the blank is deducted from the quantity of reducing sugars obtained in the parallel experiment where glucose or starch was used. Succinic acid is a well-recognized product of the action of yeast upon sugars; also a small amount of acetic acid is formed and some lactic acid. The amount of lactic acid is not great, as has been found where the filtered solution has been shaken with ether and titrated after extracting the lactic acid in this way in comparison with the titration where the total amount of acid produced was present.

In both of these series of experiments, shown in Table 9, a portion of the fermented liquor was boiled with 2.5 per cent hydrochloric acid, for the purpose of converting the remaining carbohydrates into dextrose, and it will be seen that for the pancreatin, where 15.3 per cent of unfermented glucose was left in the liquid, reducing sugars were obtained, after boiling with hydrochloric acid, amounting to 13.7 per cent of the glucose used and in case of the Taka-Diastase where 9.5 per

<sup>1</sup> Polarizations were made in a 200 mm. tube of the filtered solution in a Schmidt and Haensch polariscope; the results are given in degrees on the sugar scale as the purpose is to show comparisons rather than absolute amount.

TABLE 9

Results of fermenting 6 g. of glucose in individual fermentation bottles with 0.5 g. of pancreatin, or with 0.75 g. of Taka-Diastase, acting over night at a temperature a little below 40° C.

	Glucose 6 g.	Pan- creatin 0.5 g.	Taka- Diastase 0.75 g.	Glucose 6 g.	Taka- Diastase 0.75 g.	Cane Sugar 5 g.
Total Gas.....	60 cc.	800 cc.	60 cc.	960 cc.	1120 cc.	.....
Unfermented Solids.....	0.560 g.	1.480 g.	0.780 g.	1.350 g.	0.250 g.	.....
Corrected for Blanks.....	.....	0.920 g.	.....	0.570 g.	.....	.....
Unfermented Glucose.....	15.3%	.....	.....	9.5%	.....	.....
Unfermented Sugars:						
As Maltose.....	2.75	.....	.....	1.60	.....	.....
As Maltose.....	4.90	.....	.....	2.80	.....	.....
Protein in 250 cc. solution.....	0.240 g.	0.120 g.	0.096 g.	0.030 g.	0.079 g.	.....
Ash in 250 cc. solution.....	0.080 g.	0.095 g.	0.070 g.	0.078 g.	0.037 g.	.....
Polarization in 200 mm. tube.....	0.1°	2.3°	0.0	1.3°	0.0	.....
Acidity of solution, cc. N/10 Alkali required for 250 cc.....	16.0	42.0	28.0	50.0	24.0	.....
After boiling the filtered solution 2 1/2 hrs. with Hydrochloric Acid 2 1/4%:						
Reducing Sugars as Dextrose.....	13.7%	.....	.....	10.0%	.....	.....
200 cc. of neutralized solution (equivalent to 4.8 g. Glucose) fermented.						
Unfermented Reducing Sugars	None	.....	.....	None	.....	.....
Solids.....	7.160 g.	.....	.....	7.110 g.	0.300 g.	.....
Ash.....	6.480 g.	.....	.....	6.580 g.	0.060 g.	.....
Organic Matter.....	0.680 g.	.....	.....	0.530 g.	0.240 g.	.....
Protein.....	0.240 g.	.....	.....	0.150 g.	0.150 g.	.....
Non-protein Organic Solids.....	0.440 g.	.....	.....	0.380 g.	0.090 g.	.....

cent of unfermented glucose remained after the first fermentation, 10.8 per cent of dextrose was found after treatment with hydrochloric acid.

When the dextroses produced by the use of hydrochloric acid were again subjected to fermentation, they were completely removed. In following out the products which remained after this last fermentation, it will be seen that there is still present in the solution, besides the ash and protein, a small amount of unfermented matter which, in our opinion, may be justly attributed to organic acids produced in one or both of the fermentations. After boiling with the hydrochloric acid, the solution was carefully neutralized with sodium hydroxide before the subsequent fermentation. This would naturally form organic salts with the small amounts of organic acids present from the previous fermentation: these organic acids would appear as part of the organic matter during the burning of the residue to determine the ash present. Then, too, a small additional amount of acids would be added by the yeast used for the second fermentation. It would appear from a study of the results as outlined in this tabulated series of experiments that all the products of glucose are accounted for and that there does not remain any substance which was a constituent of the glucose and which cannot by the process used be converted into substances fermentable by yeast.

FERMENTATION EXPERIMENTS WITH STARCH FOR THE  
PURPOSE OF DETERMINING TO WHAT EXTENT THE  
RESULTS OBTAINED BY THE FERMENTATION OF  
GLUCOSE AFTER ACTION OF THE DIASTASE OF  
MALT EXTRACT, PANCREATIN AND TAKA-  
DIASTASE IS PARALLELED BY THE AC-  
TION OF THESE SAME REAGENTS  
ON WELL-COOKED STARCH

Several series of experiments were made, using different starches in parallel with glucose. The starches used included Kingsford's corn starch, a good sample of wheat starch, ordinary rice starch, arrowroot starch (manufactured by Taylor Bros., London), ordinary potato starch, potato starch made soluble by digesting in the cold with hydrochloric acid (according to the

method of Lintner—the sample used being a product of Merck's) and a sample of Mazam (previously described). In the use of these several starches the quantity taken for the test (usually 5 g.) was put in the fermenting bottle with 100 cc. of water and placed in a water bath, which was subsequently brought to boiling so that the starch in the bottle was maintained at the boiling temperature for at least 15 minutes after it had become thoroughly gelatinized. Great care was taken in gelatinizing the starch to avoid lump formation. This method of preparation gives the starch a more thorough cooking than it ordinarily receives during the cooking of cereals for table use, so that it may be assumed that the starch was in the best possible condition for the working of the diastase.

A parallel series of experiments was made in which starches and glucoses were boiled with dilute hydrochloric acid, as described in the Official Methods of the Association of Official Agricultural Chemists (U. S. Bureau of Chemistry, *Bull.* 107, 53). The amount of hydrochloric acid used in tests of this kind was 2.5 per cent on the liquid used. After boiling with hydrochloric acid, the solution was cooled, exactly neutralized with a sufficient quantity of normal sodium hydroxide, and subjected to the following tests: amount of dextrose present; polarization of the solution in the 200 mm. tube; amount of gas produced in fermentation; and presence or absence of reducing sugars after fermentation was completed. The results of this test are shown in Table 10. The apparent amount of reducing sugars obtained when calculated as actual starch is somewhat less than we should expect from the amount of actual starch present as found by analysis. Whether this is due to the presence of bodies which have not been converted into dextrose or to the destruction of some of the dextrose itself by boiling with hydrochloric acid, or to what extent it may be due to variations incident to the method of analysis, we have not attempted to determine. It is certain, however, that the method of analysis itself is subject to some variations because of the necessity of multiplying any small error introduced in the determination of the dextrose by a large factor, due to the small amount of solution which it is necessary to use for the purpose of reduction: thus the results of the determination are based upon a small fraction of a gram of starch taken. So, too, in the fermentation tests it was possible to use only 200 cc. of the solution, corresponding to 2 g. of the original starch. In determining the amount of starch from dextrose obtained in this way, it is necessary to multiply the dextrose obtained by 0.9 to allow for the water hydration. In the case of the glucose, however, the proper factor to use for this purpose is somewhat uncertain, but may be taken on the average basis of maltose. The factor used was 0.95.

A comparison was made in the fermentation of a number of the starches digested with malt extract, similar to that made on cereal foods, as shown in Table 11. Here, as in the case of Mazam, there is a quantity of gas produced in excess of what we should expect to find when we consider the amount of sugars which



TABLE 10--DEXTROSE PRODUCED FROM STARCH AND GLUCOSE BY BOILING 5 G.  $2\frac{1}{2}$  HRS. WITH 2.5 PER CENT HYDROCHLORIC ACID  
Solution made to 500 cc. after cooling and neutralizing with a measured quantity of standardized sodium hydroxide 200 cc. solution fermented

	PERCENTAGE COMPOSITION OF STARCHES USED				Dextrose Found Per cent of Sample	Starch Equivalent Dextrose $\times 0.9$	Cc. Gas from 200 cc. of Solution	Gas Equivalent of 5 g. of Sample Cc.	Polarization on Unfermented Solution in 200 mm. Tube Sugar Scale
	Moisture	Ash	Protein	Starch					
Wheat Starch.....	8.50	0.23	0.32	90.95	97.3	87.57	360	900	4.0 <sup>a</sup>
Rice Starch.....	9.00	0.69	0.26	90.05	95.1	85.59	400	1000	4.0
Corn Starch.....	8.60	0.22	0.26	90.92	98.2	88.38	370	925	4.2
Mazam (prepared Corn Starch).....	6.30	0.34	0.26	93.24	100.5	90.45	370	925	4.2
Potato Starch.....	10.50	0.26	0.16	89.24	94.6	85.10	370	925	4.0
Soluble Starch (Lintner).....	10.40	0.10	0.35	89.15	92.8	83.50	380	950	4.0
Arrow Root Starch.....	11.00	0.10	0.00	88.90	93.5	84.15	380	950	4.0
Glucose(b).....	18.30	0.35	0.05	81.30(a)	83.1	78.90(b)	320	800	3.7

Total gas from 5 g. cane sugar 1080 cc.

(a) Total carbohydrates.

Reducing sugars after fermentation, none in any of the solutions.

(b) Dextrose  $\times 0.95$  as maltose equivalent.

should normally be produced from the starches by hydrolysis. This is true of all the starches in this comparison except in the case of rice starch where the gas is, for some reason, less.

TABLE 11

Starches fermented with yeast after boiling thoroughly in water, then digesting at 45° C. for 2 hrs. with cold water extract of malt. 5 g. starch or glucose; 50 cc. malt extract; 15 g. yeast.

	Total Gas Produced Cc.	Gas, Corrected for That from Malt Extract	Gas Equivalent to Cane Sugar Per cent
Malt Extract.....	220	1060	103.9
Wheat Starch.....	1280	960	95.1
Rice Starch.....	1180	1050	102.9
Corn Starch.....	1270	1080	105.8
Potato Starch.....	1300	840	82.3
Glucose (Solids 82.1%).....	1060	.....	.....
Cane Sugar (5 g.).....	1020	.....	.....

In the case of the malt extract in Table 11, we have corrected for the amount of gas produced from the malt extract because there is always a certain amount of sugars present in this material. In experiments where Taka-Diastase and pancreatin have been used as the source of the diastase, no correction is made. There is always a small amount of gas apparently produced, even when yeast and water only are used and in most instances with a small amount of Taka-Diastase and pancreatin added as used. In a large number of experiments both of these ferments have been used in excess so as to carry the action of the diastase as far as possible. In many cases one gram of either has been used and allowed to exert its action on the starch or glucose for a period of several hours, generally over night. A comparison of this kind is shown in Table 12. In Table 13, another com-

TABLE 12

Results of experiments in fermenting products of 5 g. of starch and glucose obtained by digesting same with 1 g. of Taka-Diastase for each, over night, at a little below 40° C., and fermenting with 15 g. of yeast in 200 cc. water, later made to 350 cc. and filtered.

Gas Produced Cc.	Polarization of Sol. 200 mm. Tube	Unfermented Solids Per cent	Reducing Sugars as Dextrose (% corr.)	Acidity for 250 cc. N/10 Alkali
Cane Sugar.....	1080	0.0 <sup>a</sup>	.....	28
Wheat Starch.....	1000	1.0	1.50	35
Rice Starch.....	950	1.0	1.68	40
Corn Starch.....	980	0.9	1.60	40
Mazam.....	1000	1.0	2.50	40
Potato Starch.....	950	1.0	2.30	43
Soluble Starch.....	940	1.0	2.30	40
Glucose.....	780	2.0	3.00	43
Taka-Diastase (blank).....	.....	.....	.....	34

parison is shown between Taka-Diastase acting over night and the same quantity acting during the fermentation by yeast only. In this latter instance the Taka-Diastase was added with the yeast and, of course, acted at the same temperature as the yeast, 35° C. It will be seen that with the large amount of Taka-Diastase used (1 g. to each 5 g. of glucose), the action was nearly as rapid and thorough as when the diastase was allowed to act for a longer time. In all of these

instances a considerable quantity of reducing carbohydrates was not removed by the fermentation. The amount is somewhat higher for glucose than for the starches, but, as shown in former experiments (Table 6) in other instances the unfermented products were considerably less than is shown in this instance. This was apparently due to differences in the samples of Taka-Diastase used, as well as differences in the action of the different yeasts, for it was shown with Taka-Diastase, as is more clearly pointed out with pancreatin below, that the diastatic activity of the material became weaker with the age of the sample.

It would appear from the higher proportion of unfermented solids in the case of the glucose and the complex combinations of enzymes of this character, which has been pointed out in an earlier experiment, that there may be in the glucose some form of dextrin which is less readily changed by the enzymes present in this special sample of Taka-Diastase than are those produced in the regular series of changes from the hydrolyzed starch to dextrose. We draw this conclusion from a comparison between the action of the Taka-Diastase and that of malt extract and pancreatin where the hydrolysis is apparently as complete with the glucose as with the starch and from the fact that the different yeasts, which apparently secrete enzymes capable of acting upon starch products less completely hydrolyzed than dextrose, act differently upon the hydrolyzed products of glucose, as already shown. Attention should be called to the acidity of the fer-

TABLE 13

Fermentation with different starches well boiled, 5 g. each, 1 g. Taka Diastase, added at time of adding yeast. Yeast, 15 g. Time of fermentation,  $5\frac{1}{2}$  hrs. No material increase of gas during night. Corrected for blanks.

	Gas Produced Cc.	Polarization 200 mm. Tube	Per cent Solids	Reducing Sugars as Dextrose
Glucose.....	820	1.3 <sup>a</sup>	11.80	3.70
Mazam.....	1020	0.7	8.10	3.10
Soluble Starch.....	920	1.2	9.80	3.20
Corn Starch.....	1000	0.8	9.10	3.00
5 G. Cane Sugar.....	1060	0.0	.....	.....
Same as above, but digested with Taka-Diastase at about 30° C. over night				
Glucose.....	860	1.3 <sup>a</sup>	10.50	3.00
Corn Starch.....	980	0.2	5.20	1.60
Mazam.....	990	0.8	6.00	2.50
Soluble Starch.....	880	1.3	8.40	3.12

mented solutions as shown in Table 12. It will be seen that this is nearly the same for the several starches and the glucose, and is somewhat higher than for cane sugar, and for the blank using Taka-Diastase and yeast alone. Some part of this acidity may be taken as lactic acid, but the amount is not large. With the Taka-Diastase blank, where the total titration for 250 cc. of liquid is equivalent to 34 cc. of decinormal acid, the solution was thoroughly shaken twice with

ether, which would remove any lactic acid present, and the titration after removing the lactic acid in this way was still 31 cc. of *N*/10. In the parallel experiment with the 5 g. of glucose and the Taka-Diastase the total acidity was equivalent to 41 cc. of *N*/10 alkali, and after extracting the ether-soluble acids, it was still 34 cc. It is apparent from this that no considerable amount of the glucose had been converted into lactic acid.

To determine concerning the action of a lesser amount of Taka-Diastase when acting upon starch or glucose, under the conditions of our experiments, two parallel series were run, using Lintner's soluble starch, well boiled, and glucose. The results are shown in Table 14. The total amount of gas produced

TABLE 14  
Experiments with different quantities of Taka-Diastase put in solutions of boiled soluble starch and of glucose at the time of adding the yeast and allowed to act at 35° C. 5 g. glucose or starch and 15 g. yeast. Time of fermentation, 6 hrs. No material change in readings during night.

SERIES	Taka-Diastase Gram	Gas Produced Cc.	Polarization of Solution	Unfermented Reducing Sugars as Dextrose	RATES OF GAS DEVELOPMENT (Cc.)							
					Minutes after Setting							
					40	80	120	150	180	240	300	360
Starch.....	0.000											
	0.025	380	6.3°	4.20%	25	50	120	240	290	350	380	
	0.050	600	4.3		30	120	300	440	500	540	600	
	0.125	840	2.0	2.34	70	380	640	770	800	840	840	
	0.250	860	1.3	2.91	95	490	740	840	850	870	870	
Glucose.....	5.000	1040	0.0		440	980	1020	1050	1060	1060	1060	
	0.000	390	9.0		170	240	300	340	380	380	390	
	0.025	480	3.9	3.89	140	240	320	400	420	440	480	
	0.050	620	2.8		160	290	400	490	530	570	620	
	0.125	700	1.5	3.16	170	420	560	650	680	700	700	
	0.250	770	1.0	2.54	220	520	660	720	750	760	780	

is found to increase steadily with the amount of Taka-Diastase used. Polarization of the solution steadily decreased and there is a perceptible decrease of the amount of unfermented reducing sugars. The total unfermented solids were not determined in this experiment, but are clearly indicated by the polarization. It may also be seen by studying the more detailed results of the gas production, that the action of the yeast is much quicker upon the glucose, even with Taka-Diastase, than upon starch with the small amounts of Taka-Diastase used, thus illustrating the value of sugars in glucose in aiding the more rapid assimilability of the product as compared with that of starch. The table is also of interest as showing the general working of this class of experiments as to gas production.

TABLE 15  
Results of experiments in fermenting products of 5 g. of starch or glucose, obtained by digesting same with 1 g. of pancreatin for each, over night at a little below 40° C. and fermenting with 15 g. yeast, 200 cc. water, and later made to 250 cc. and filtered.

Gas Produced Cc.	Polarization of Sol. 200 mm. Tube	Unfermented Solids (corr.) Percent	Unfermented Reducing Sugars as Dextrose (% Corrected)	Acidity for 250 cc. Equivalent for N/10 Alkali	
Cane Sugar.....	1080				28
Wheat Starch.....	800	3.3°	19.2	5.2	43
Rice Starch.....	790	3.8	22.6	5.8	43
Corn Starch.....	880	2.5	15.4	5.6	43
Mazam.....	800	3.5	20.4	6.0	45
Potato Starch.....	850	3.5	18.6	6.4	43
Soluble Starch.....	880	2.5	15.2	6.3	44
Glucose.....	700	3.0	17.0	5.6	44

Following out a line of experiments on starch and glucose, similar to those given above, using pancreatin as the source of the diastase, we find a series of results as is given in Table 15, where the pancreatin was

allowed to act upon the boiled starches and the glucose over night. The pancreatin was taken from the same bottle as was used in experiment recorded in Table 9, and carried on about 4 weeks earlier. It was that of a standard make in the original container and was in frequent use during the interval; the bottle was kept corked except when a sample was being weighed out.

It will be seen that the activity of the pancreatin had decreased greatly over what it was at the time of experiments recorded in Table 9, so that we may take the results in this experiment as under conditions arising when we have a weakened diastatic ferment. The amount of unfermented solids obtained in this series of experiments is much more than there was with Taka-Diastase under similar conditions. The amount of reducing sugars is more and the polarization of the resulting fermented solution is considerably higher.

Following this, another experiment was made (Table 16), where the same amount of pancreatin was allowed to act upon starches and glucose during

TABLE 16  
Experiments with weakened sample pancreatin acting on boiled starches during time of fermentation. Starch 5 g., pancreatin 1 g., yeast 15 g., water 20 cc.

Gas Produced Cc.	Polarization of Fermented Solution	Per cent Unfermented Reducing Sugars as Dextrose	Reaction with Iodine Solution
Cane Sugar (5 g.).....	1060	0.0°	0.0
Wheat Starch.....	680	5.0	8.11
Rice Starch.....	730	4.5	7.28
Corn Starch.....	560	7.4	8.15
Mazam.....	840	7.4	7.53
Potato Starch.....	440	9.2	8.53
Soluble Starch.....	780	4.5	7.58
Arrowroot Starch.....	560	7.0	8.71
Glucose.....	700	3.2	7.85

the time of fermentation. Here we have a still higher polarization of the resulting fermented liquor and a much larger proportion of unfermented reducing sugars. This, to our minds, is very significant, as it indicates the formation of a large proportion of reducing bodies which partake of the nature of dextrin in that they are not fermented by yeast. It should be noted in this connection that the liquid after fermentation with pancreatin and yeast in this experiment gave an intense violet reaction with iodine for the corn starch, the potato starch and the arrowroot starch, thus showing that a large part of the starch was still in the form of dextrins and that the smaller amount of gas obtained was in no way due to an incomplete gelatinization of the starches acted upon. The other solutions did not give any color with iodine. The proportion of reducing sugars in both these series is fully as high for the starch as for the glucose, showing that these reducing bodies were produced out of the starch as a step in the process of converting the starches into the more readily fermentable sugar, maltose. The amount of gas produced shows that a large amount of maltose also was produced in both cases.

To determine more clearly to what extent this transformation of starches and glucose into unfermentable reducing bodies was due to the nature of the pancreatin used, three other standard makes of pancreatin were obtained in original containers and used in a series of experiments on soluble starch and glucose in connection with the glucose used in the two preceding experiments, which in this series of experiments is marked



M (see Table 17). The unfermented solids were not determined, but the extent of the change from starch of fermented sugars is indicated by the polarization, and in the case of the glucose by the amount of

TABLE 17

Soluble starch and glucose fermented by yeast when treated with different pancreatins added with the yeast. Glucose or starch 5 g., yeast 15 g., pancreatin 1 g.

	Gas Cc.	Polarization	Reducing Sugars as Dextrose
Soluble Starch: Pancreatin A.....	820	2.90	...
Pancreatin C.....	800	2.9	1.63%
Pancreatin D.....	840	2.8	...
Pancreatin M.....	800	4.6	...
Glucose: Pancreatin A.....	700	2.3	1.91
Pancreatin C.....	730	2.3	2.68
Pancreatin D.....	730	2.3	1.69
Pancreatin M.....	710	4.7	4.82
Glucose only.....	360	9.7	...
	360	9.8	...
Cane Sugar.....	1100	0.0	...

reducing sugars still unfermented. In the case of Pancreatin M much more reducing bodies are present and polarization is much higher on both the starch fermentation and the pancreatin fermentation than is the case with the other pancreatins used, all of which points to the same conclusions which we have drawn from the preceding experiments, *i. e.*, that with weakened diastasic action the conversion of the starch into fermentable sugars is not nearly so complete, and the result is the leaving on the way of an increased amount of unfermentable reducing bodies.

Analyses of a large number of malted liquors, including ale, porter, stout, beer, etc., show that in all cases there is a quantity of reducing sugars left in the malted liquor after the fermentation has been completed. This fermentation often extends over a considerable period of time, generally amounting to several weeks. The original wort used for fermentation presumably contains in the neighborhood of 12 to 13 per cent of extracted matter. After fermentation a greater or less quantity of unfermented matter still remains, which is grouped together under the general name of extractives. The average amount of unfermented reducing sugars calculated as maltose, approximates close to 1.5 per cent as is shown in Table 18. While

TABLE 18—UNFERMENTED PRODUCTS IN MALT LIQUORS  
Averages of many compiled analyses by various analysts  
(König, *Nahrungs und Genussmittel*, Vierte Auflage I, Band)

Liquor	No. of Analyses	Per cent Extract	Reducing Sugars as Maltose	Dextrins	Reducing Sugars Total Extract % of
Ale.....	44	5.59	1.07	1.81	17.8
Porter (Stout)....	44	7.97	2.06	3.08	25.8
Weiss Beer.....	33	5.29	1.56	...	29.5

One-half oz. per qt. = 1.5 per cent

this is not large when taken upon the liquor itself it still is sufficient to amount to about 1.5 oz. per quart of malt liquor, and when calculated upon the total extractive matter it is from 18 to 30 per cent of the amount present.

#### DISCUSSION

It is stated by Wahl and Henius<sup>1</sup> that approximately 0.5 per cent of maltose remains in beer, and about twice this amount, or 1 per cent, of so-called malt dextrins, defined as substances that may be considered as in a state of transition from the dextrins to maltose. These authorities apparently base their conclusions, at least part, upon the work of Prior and others,<sup>2</sup> where

<sup>1</sup> "American Handy Book of Brewing and Malting," p. 748.

<sup>2</sup> *Loc. cit.*, p. 537.

they also show that the extent of the fermentation of these so-called malto-dextrins in malted liquors varies within certain limits with the species of yeast which is used, just as we have indicated above, with reference to the results of our own experiments. It will be remembered that in beer-making, the yeasts used are of pure culture, whereas in bread-making, distilling, etc., where compressed yeast is used, such as we have used in our experiments, there may be a mixture of yeast species and an admixture with the yeast of some proportion of different forms of bacteria.

It has been demonstrated by the work of Hanson<sup>1</sup> that certain species of yeast are capable of fermenting maltose because of the presence in them of an enzyme termed maltase, while others are incapable of fermenting maltose because of the absence of this enzyme, but are still capable of fermenting cane sugar after splitting it up into dextrose and levulose by means of the invertase which it secretes. On the other hand, most of the yeasts secrete both these ferments and are capable of fermenting both sugars. In a complex mixture like that obtained from converting boiled starch by the use of diastase, whether from malt, Taka-Diastase or pancreatin, and the subsequent action of yeast, it would be extremely difficult to determine just where the action of the enzymes present in diastase preparation leave off their work and where the enzymes produced by the yeast begin theirs. It is immaterial, however, for our present purpose, because when we have the combined action of these two agents we are able to produce the fermentation and, therefore, have reason to believe that such enzymes are somewhere produced. Malted liquors are recognized and often highly extolled as valuable sources of food and yet it has been shown that a considerable part of the extractive matter which they contain consists of unfermented reducing sugars, of which a considerable part has not progressed to the stage of maltose in the changes which take place between starch and fermentable sugars. It is well recognized that the processes of digestion are more active and energetic as they take place in the body than they can be when they are carried on outside. A considerable number of enzymes have been isolated from the alimentary tract. We do not know to what extent others may be present, but there is evidence to show that all, or nearly all, of the carbohydrates present in glucose are assimilated and used by the body.

It is clearly seen from our own experiments, especially those with pancreatin and with malt extract, that the amount of unfermented reducing sugars is not greater where these diastases have been acting upon glucose in connection with yeast than they are where these combined agents have been acting upon the various starches, and this in spite of the fact that there was originally in the glucose a large proportion of apparently unfermentable reducing sugars already present. It is also seen in several of the experiments that this proportion of apparently unfermentable reducing sugars is largely decreased and in some instances al-

<sup>1</sup> Jorgensen, "Microorganisms and Fermentation," translated by Miller and Lennsholm, 3rd Ed., 1900, p. 167.

most entirely removed by the combined action of yeast and Taka-Diastase, pancreatin and to a less extent with malt extract. It must be borne in mind, however, in this connection, that while these reducing sugars ordinarily present in the glucose are being removed, other apparently unfermentable reducing sugars are simultaneously produced. It is apparent, therefore, that the material which has been classed as gallisin, or an unfermentable sugar in glucose, yields to fermentation when it is acted upon by proper diastases. In this respect it is like similar products produced by the action of diastases, the result of a step in the conversion of starch to maltose. If it so happened that a greater number of the yeasts which are used for fermentation were of those species which do not secrete maltase, we might conclude that maltose also is an unfermentable sugar. Since the reverse is true, it is not so classed.

#### SUMMARY AND CONCLUSIONS

Commercial glucose is a complex body of viscous consistency, running about 42 to 45° Bé. and containing from 80 to 85 per cent solids and 15 to 20 per cent water. It is nearly water-white and possesses a mild, sweet taste. The solids are composed almost wholly of sugars and dextrins, a minor portion consisting of a trace of mineral matter. The ash, present to the extent of mere traces, consists of mineral salts, including phosphates, sulfates, chlorides and carbonates, chiefly of sodium and lime. Tests for arsenic and other poisonous metals show these not to be present. Nitrogenous substances are present as a mere trace, chiefly as protein bodies, amounting to about 0.06 per cent.

It has been quite well-established in the chemical literature that commercial glucose consists of dextrins and reducing sugars. Some authorities hold that the reducing bodies consist almost entirely of maltose, while others hold that they are a mixture of maltose and dextrose, together with some unknown unfermentable substance which has been called "gallisin" by some and "iso-maltose" by others.

In our work we have determined that the fermentable reducing sugars are a mixture of maltose and dextrose by calculations based upon their quantity as determined by reduction and upon the amount of gas developed by fermentation with yeast. The amount of gas thus produced is too large to allow the fermentable sugars as determined by reduction to be calculated wholly as dextrose and too small to allow their being calculated wholly as maltose. With different lots of glucose the relation of the maltose to the dextrose and the amounts of each will vary to some extent. Determinations on two samples show 11.7 and 17.2 per cent of dextrose and 22.9 and 16.4 per cent of maltose, respectively.

Further researches lead to the conclusion that at least three reducing bodies are normally present; namely, maltose, dextrose, and a third, which is less readily fermentable by ordinary bakers' yeast, but which may be made fermentable by the action of certain enzymes, especially those present in pancreatin,

Taka-Diastase and malt, as well as by the hydrolytic action of dilute hydrochloric acid under the influence of heat. These difficultly fermentable reducing bodies amount to about 14 per cent of the total glucose when calculated as maltose, or 8 per cent when calculated as dextrose. The unfermentable carbohydrate residue remaining after removing the maltose and dextrose by fermentation consists of those bodies commonly recognized as dextrins. These, like the unfermentable reducing bodies, when subjected to hydrolytic action by diastase result in products which will under suitable conditions undergo almost complete alcoholic fermentation. When they are subjected to the hydrolytic action of hot dilute acid, applied either to the unfermented glucose or to the residue left after the glucose has undergone alcoholic fermentation, all of these bodies become wholly fermentable.

Cold water extract of malt as the source of the diastase was found less suited for the purpose than pancreatin or Taka-Diastase because of the larger proportion of unfermentable bodies which it contained and introduced into the products of fermentation.

It was found that a good quality of Taka-Diastase converted the unfermentable products into fermentable sugars, leaving only a very small amount of unfermented residue, which contained as reducing sugars less than one per cent of the glucose taken. In the most favorable instances the total unfermented residue amounted to from 4 to 5 per cent and included normal products of fermentation, notably succinic acid and possibly some glycerine, which always results from the fermentation of sugars by yeast. The diastase present in good samples of pancreatin and in the cold water extract of malt in like manner converts the unfermentable residue of the glucose into fermentable sugars, but in some instances less completely than does Taka-Diastase.

In these experiments it was found that the kind of yeast used had a considerable influence upon the completeness of the fermentation of the products produced by the action of the several diastases.

Isolated ferments like pancreatin and Taka-Diastase lose their activity with age and when these weakened ferments act upon glucose the result of the decreased vitality is a decreased proportion of immediately fermentable sugars, with an increased proportion of the unconverted dextrins and of the intermediate unfermentable reducing carbohydrates or reducing dextrins. These conditions are also clearly apparent where weakened pancreatin or weakened Taka-Diastase or a limited amount of diastase acts upon starch of various kinds. The apparent results of such action are an extended row of products, including the well-recognized dextrins, unfermentable reducing bodies (apparently reducing dextrins) maltose and dextrose. The fact that the first bodies in this series are found to a limited extent only when there is a sufficient amount of the active diastase present, but are abundant when there is a limited amount present, indicates that they belong to a natural series of changes between starch and dextrose. The results of our examination of glucose and of the products of the combined action of



diastase and yeast upon glucose, indicate that all the bodies of this series are normally present in glucose which is produced by the incomplete hydrolysis of starch by acids, just as they are present in liquors containing the products of the incomplete hydrolysis of starch by diastase, and that these bodies in glucose yield to further treatment with diastase, just as do those produced by diastase itself. From these facts, it is apparent that the claim for the presence in glucose of unfermentable reducing bodies as reversion products brought about by the action of the acids at a high heat is untenable.

A study of the action of hydrolytic agents and yeast on carbohydrates entering into common foodstuffs, such as potatoes, breakfast cereals, bread, and so forth, and upon pure starches, such as are found in these various food products, has been made in comparison with parallel experiments on glucose. In these experiments it was found that the carbohydrates of glucose agree closely in gas production with the carbohydrates of the more readily digestible foodstuffs, such as white bread, breakfast cereals and potatoes. It was also found that these several carbohydrates when acted upon by isolated ferments and yeast, as in the experiments conducted, yield variable but appreciable amounts of unfermentable carbohydrate products, just as the mashing of cooked starch with malt diastase in the making of malt liquors results in a liquor which after fermentation contains appreciable quantities of such unfermented and apparently unfermentable carbohydrate products.

The fact that commercial glucose, when it is treated with diastase and then subjected to yeast fermentation, is almost wholly converted into alcohol and carbon dioxide goes to prove that it consists of products that are wholly assimilable and, therefore, it furnishes a food to the body of a sugar nature. In this respect it is a more concentrated and at the same time a more readily assimilable food than are most of the carbohydrates belonging to the ordinary foodstuffs which first have to undergo cooking and then complete hydrolysis by the action of the digestive enzymes before they can be utilized by the body. In this respect glucose, pound for pound of dry weight, will furnish at least as much energy as does cane sugar.

RESEARCH DEPARTMENT  
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## VITAMINES AND LIPOIDS IN BUTTER AND MARGARINE

By J. DE RUIJER

Received March 21, 1916

Since Osborne and Mendel found certain substances in milk and butter, apparently of lipid nature, necessary in human food to maintain health and growth, it is interesting to compare butter and margarine as to their respective content of lipid substances.

Of the material tested the butter was taken from one of the cooperative dairying factories in Frisia; "Klappa" and "Planta," both "vegetable butter," from special factories in Amsterdam and Oss, whereas the "margarine proper" was taken from a noted margarine factory. As far as information could be

obtained. Klappa and Planta are made by means of skim milk.

First of all, an easy method was required to find the lipid content of fats and oils. That which the writer used is based on the observation that lecithin is soluble in concentrated acids, but is precipitated again when the acid solution is mixed with water. The first observations were made with lactic acid, but more rapid results could be obtained with hydrochloric acid of 1.19 sp. gr. The lipid precipitate could be separated easily from the diluted acid. Afterwards it was collected on a filter, washed with acid water, dried at 100° C. and weighed.

The lipoids thus obtained, after burning, gave an ash which showed a large phosphorus content on testing with molybdic reagent.

Sesame oil, thus shaken with an equal volume of hydrochloric acid (1.19 sp. gr.) proved to have entirely lost its lipid content.

With the method described the following results were obtained:

GRAMS OF LIPOIDS IN 100 Cc.					
Sesame Oil	0.100	Raffinated		Klappa	0.750
Arachis Oil	Traces	Coconut Oil	Traces	Planta	0.475
Olive Oil	Traces	Filtered Butter Fat	Traces	Margarine	0.975
Cod Liver Oil	Traces	Butter	0.400	"Bran Butter"	1.125

From these figures two conclusions may be drawn: (1) The seat of the lipoids in butter is not the fat itself but the casein solution mixed with it. (2) The lipoids in butter represent only a part of the total lipid content in milk ( $\approx 0.075$  per cent). The remaining part is responsible for the lipid content in margarine and vegetable butter as far as they are made by means of skim milk only. The high figure for "margarine proper" may be due to the use of egg yolk besides skim milk as an emulsifying agent.

In order to enhance the lipid content of "vegetable butter" the albumin-bearing seeds may be turned to account. Just as egg yolk, they contain lipoids in a chemical combination or an adsorption with albumins. So little are they inclined to give up their lipoids to solvents that a sesame oil which was heated with wheat bran at 100° C. afterwards proved even to have lost a great deal of its lipoids.

From this combination or adsorption the lipoids may be set free by treating the seed material with liquors that dissolve the albumins. The "steep liquor" of the corn starch factories, obtained by treating the corn with slightly acidulated water, is an example of such a solution.

To set free the lipoids of wheat bran the bran was treated with diluted lime-water during 24 hrs. The liquor pressed off and separated from the subsiding starch was shaken with a molten mixture of raffinated coconut oil and arachis oil. After that a quantity of skim milk was added, amounting to one-fifth of the emulsion, and the mixture allowed to ripen. Then the fat was separated and worked to a butter-like product, which showed the high lipid figure above (bran butter). The lipid content may be increased by altering the proportion of bran and fat.

Another interesting point in the process described is that the liquor separated from the "bran butter"

may be easily worked to a kind of cheese, in which a large part of the wheat albumins are made available for human food.

The process is in no wise restricted to the use of wheat bran. Maize, peanuts, almonds and many other albumin-bearing seeds and oil cakes await their testing as to the production of palatable food. In fact there is a variety which could never be attained by the dairying industry working with cows' milk only.

SNEEK, HOLLAND

## THE DETERMINATION AND DISTRIBUTION OF MOISTURE IN BREAD

By H. L. WESSLING

Received July 13, 1916

During the past few years the subject of the moisture content of bread has been receiving more and more attention. Excess of moisture is considered much in the nature of adulteration and in certain quarters the advisability of fixing a definite standard for the water content of bread is being considered. It will be necessary in that event, however, to arrive at some understanding as to the method of determining moisture in bread, since this is still a mooted question.

According to Jago,<sup>1</sup> a thin slice should be taken from the center of the loaf, the crust cut off and the interior portion crumbled, these crumbs thoroughly mixed and used for analysis.

Neumann<sup>2</sup> calls attention to the fact that the proportion of crust to crumb, which varies with the size and form of the loaf, must be taken into consideration. He states that the total water content of bread may be known only by determining that of crust and of crumb and finding the relation of crust to crumb. Berman<sup>3</sup> asserts that the results are practically the same whether the moisture is determined on the crust and crumb together (direct method), or on these separately and then calculated for the entire loaf (indirect method). He uses a wedge-shaped slice and takes into consideration the proportion of crust to crumb. Boutroux,<sup>4</sup> like Jago, cuts a slice from the center of the loaf, trims off the crust, crumbles the interior and mixes these crumbs thoroughly. He goes farther, however, in that he determines the moisture on crust and crumb separately. Boutroux also refers to work done along this line by Balland in which he gives the water content of crust, of crumb and of the whole bread.

Wiley<sup>5</sup> uses the entire loaf, which he chops into bits, weighs at once and dries until the bread is reduced to a small bulk. The dried bread is weighed and the loss of moisture determined up to this point. This bread is then ground fine and a further moisture determination made upon a sample thereof.

A very rapid method for the determination of moisture in bread is that described by Wilh. Thörner<sup>6</sup> and recently modified by F. Schaffer.<sup>7</sup>

<sup>1</sup> Wm. Jago and W. C. Jago, "The Technology of Bread-Making," 1911 Edition, p. 834.

<sup>2</sup> M. P. Neumann, "Brotgetreide und Brot," 1914, pp. 436-7.

<sup>3</sup> "Watergehalte van Wittebrood," *Pharm. Weekblad*, **48**, 675.

<sup>4</sup> L. Boutroux, "Le Pain et la Panification," 1897, p. 308.

<sup>5</sup> Bureau of Chemistry, *Bull.* **13**, Part 9 (1898), 1321

<sup>6</sup> *Z. angew. Chem.* **21** (1908), 148.

<sup>7</sup> *Mitt. Lebensm. Hyg.*, **6** (1915), 6.

These are really modifications of Hoffmann's method for the determination of moisture in hops,<sup>1</sup> and the principle underlying them is similar to that used in the well-known Brown-Duvel moisture tester.<sup>2</sup>

According to Schaffer the loaf of bread is cut in two lengthwise and again in two crosswise; from every one of these four portions is cut a slice, from 0.5 to 1 cm. in thickness, which is crumbled fine and these crumbs thoroughly mixed. Of this well-mixed material a 25-g. sample is weighed off and distilled with 200 cc. of heavy petroleum. The water which distills over is collected in a graduated cylinder and the amount calculated to 100 g. of bread. Schaffer refers to the difficulty of getting a fair proportion of crust and crumb but suggests that since the time required for the entire operation is comparatively short, two moisture determinations may easily be made and their average taken.

For the purposes of the work described in this paper, Schaffer's method of taking his sample, from the center of the loaf alone, does not meet our requirements. There is also much opportunity for loss of moisture by evaporation during the operation of sampling and weighing. Finally, the difficulty of obtaining in a 25-g. sample the correct proportion of crust and crumb seems a decided objection.

It is planned later to make use of the Brown-Duvel moisture tester in determining the moisture in bread according to the suggestion of Schaffer, modifying his method of sampling to meet the objections above stated.

For the purpose of studying the variations in the moisture content in different parts of the same loaf this work was undertaken.

The method used for the determination of moisture consists in weighing as quickly as possible in a tared dish, on a torsion balance, the portion of bread selected. This bread is carefully heated at a temperature not exceeding 60° until practically dry. The dried bread is then allowed to stand exposed at room temperature for a few hours, in order to let it come into equilibrium with the air. The loss in moisture up to this point is then determined. The air-dried bread is then immediately ground to a fine meal and the moisture on a 2-g. sub-sample thereof determined in the vacuum oven at the temperature of boiling water. From the per cent of additional moisture lost by this sub-sample, that of the entire sample is calculated and added to the amount lost on heating at 60°. The combined loss gives the total percentage of moisture in the bread.

This method is practically the same as that described in *Arbeiten aus dem Kaiserlichen Gesundheitsamte*, **48** (1915), 605.

Three loaves of different types, and differing in shape as well, were bought on the open market, all being approximately 10 hrs. old and unwrapped. Sub-samples from a slice 2 in. thick, cut from the center of each loaf, were taken in the following order (see Fig. 1):

<sup>1</sup> *Wochschr. Brau.*, **18** (1903).

<sup>2</sup> U. S. Dept. Agr., B. P. I., *Circ.* **72** (1910).



- A—The crust proper trimmed off the entire slice.  
 B—A section about  $\frac{1}{2}$  in. thick, next to the crust.  
 C—A second section  $\frac{1}{2}$  in. thick.  
 D—The innermost portion, in form of a cube.

The moisture was determined on every portion with the results shown in Table I:

TABLE I—PERCENTAGES OF MOISTURE IN PORTIONS OF A SLICE OF BREAD

Bread No.	A	B	C	D
	Crust	Section next to crust	Section next	Inner cube
1.....	25.50	40.78	42.98	42.60
2.....	18.79	32.27	38.42	38.69
3.....	22.31	37.57	41.70	41.67

Loaves similar to the preceding were then used to determine how the moisture varies in slices taken from different portions of the loaf (see Fig. II).

These loaves were sampled as follows:

- A—The end crust, about  $\frac{1}{2}$  in. thick.  
 B—A slice immediately adjoining A and about  $\frac{1}{2}$  in. thick.  
 C—A slice  $\frac{1}{2}$  in. thick cut about half-way toward the center.  
 D—A slice  $\frac{1}{2}$  in. thick directly from the center of the loaf.

The moisture content of every slice (crumb and crust together) was determined with the results shown in Table II:

TABLE II—PERCENTAGES OF MOISTURE IN DIFFERENT PARTS OF COMMERCIAL BREADS

Bread No.	A	B	C	D
	Crust	Slice next to crust	Slice half-way to center	Slice from center
1.....	22.63	35.12	35.41	36.01
2.....	27.77	35.74	36.26	36.23
3.....	17.11	30.68	37.38	37.77

Having shown in this experiment that the water content varies depending upon the section of the loaf from which a slice is cut, the next step was to determine the moisture of the loaf as a whole compared with that of these slices. Loaves of bread similar to



FIG. I

FIG. II

the preceding were used. These were cut in half and the moisture determined on slices cut from one half in a manner similar to that indicated in Fig. II. The other half, E, was used entire, crust and crumb together, for a total moisture determination. These results are shown in Table III:

TABLE III—PERCENTAGES OF MOISTURE IN DIFFERENT PARTS OF A LOAF OF BREAD COMPARED WITH THAT OF THE ENTIRE LOAF

Bread No.	A	B	C	D	E
	Crust	Slice next to crust	Slice half-way to center	Slice from center	Half loaf or total
1.....	26.85	36.59	37.70	37.45	35.14
2.....	20.03	32.75	35.65	35.93	33.09
3.....	23.50	35.32	38.18	38.00	34.99

As a final experiment the moisture of the entire loaf as well as of different portions thereof was determined as follows: The loaf (which was a crust-covered one) was cut in half, and one half divided into two quarters. The total moisture was determined on one quarter, and the moisture of the crust and of the crumb separately on the other quarter. From the remaining half loaf was cut a thick slice, as in our first experiment, and the different portions trimmed off as indi-

cated in Fig. I, moisture being determined on every portion. These results are shown in Table IV:

TABLE IV—PERCENTAGES OF MOISTURE IN PORTIONS OF A LOAF OF BREAD COMPARED WITH THAT OF THE ENTIRE LOAF

A	B	C	D	E	F	Total in
Crust	Section next to crust	Section next	Inner cube	Crust of 1/4 loaf	Crumb of 1/4 loaf	1/4 loaf
26.84	39.72	43.10	43.08	29.18	41.44	37.17

## DISCUSSION OF RESULTS

It is very evident that the moisture content of the crumb varies considerably, depending upon its proximity to the crust or to the center of the loaf. It might be supposed that there would be a more or less regular increase in moisture as the sample approaches the actual center, but this does not seem to be the case. In fact, the results indicate that there is no appreciable difference in moisture content in slices of bread taken a reasonable distance from the end of the loaf or in the crumb of any individual slice taken a reasonable distance from the crust. Therefore, after one gets fairly within the loaf, it seems to matter little whether the crumb be taken directly from the center of the loaf or not, since the variation is not great until rather near the end or crust of the loaf. There is a great difference, however, between the moisture in the whole bread (as determined on one-half or one-quarter of a loaf),<sup>1</sup> and that in either the crust or crumb taken separately or in one entire slice. This shows that in reporting the moisture content of bread it is necessary to state what portion of the bread was used, as well as how the moisture was determined.

Another point that seems to deserve attention is the age of the loaf. It is known to every one that bread loses moisture from the moment it leaves the oven. Consequently some idea of the freshness of the loaf should be given. When bread is baked in the laboratory it is usually weighed from 1 to 2 hrs. after leaving the oven. When loaves are bought on the open market it is not always possible to know how long the time since baking, but this will almost always be less than 24 hrs.

In conclusion, to determine the moisture in bread use one-half or one-quarter of a loaf, depending upon the character of the crust, and follow the method described on page 1021. This is a far more simple as well as more accurate method than to find the proportion of crust to crumb and to determine the water content of each separately.

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## A POLARISCOPIC DETERMINATION OF SUGAR IN "CONDENSED MILK"

By R. O. BROOKS

Received September 20, 1916

In the legal analysis of "condensed milk," two items are of paramount importance, *viz.*, the percentage of fat and the percentage of milk-solids. For the estima-

<sup>1</sup> When the loaf is crust-covered, one quarter of it, obtained by cutting the loaf in half crosswise and this half in two lengthwise, is sufficient to represent the entire loaf. When the loaf lacks crust on one side, by reason of having been baked in contact with another loaf, one half of the loaf is required for analysis.

tion of the fat we have an almost perfect method in that of Gottlieb, as variously modified by different analysts. For milk-solids in *unsweetened* condensed milk (formerly incorrectly called "Evaporated Cream") it may be safely said that the determination of total solids is sufficient. But in the determination of milk-solids in *sweetened* condensed milk, there is presented a far more difficult problem.

The Official methods of the A. O. A. C.<sup>1</sup> (now being revised and published in the journal of that association) have prescribed a determination of milk-solids in condensed milk by the lengthy and very questionable method of estimating the fat, lactose, proteins (nitrogen  $\times 6.38$ ), and ash and taking the sum of these. These four items do not comprize all the constituents of milk-solids and although the determinations of fat and lactose may be quite correct, the estimation of proteins ( $N \times 6.38$ ) is a mere guess and the ash a mere residue of various mineral salts originally present.

Sugar is determined in the Official methods by subtracting the above "milk-solids" from the total solids. The last item can be determined fairly closely and it is obvious that a far more logical and rapid method of estimating milk-solids in sweetened condensed milk is to reverse the procedure and get the milk-solids by subtracting the sugar from the total solids.

Various methods, gravimetric and polariscopic, have been proposed for the direct estimation of the sugar, but the problem cannot be regarded as satisfactorily solved hitherto. A tedious gravimetric method, utilizing copper reductions before and after citric acid inversion, has been tried out by the A. O. A. C., with some success, but of course a polariscopic method would be much more preferable in every way.

Polariscopic methods have been proposed, including one by Knight and Formanek in the January, 1916, issue of *THIS JOURNAL*. They have quite fully reviewed the faults of the past efforts along such lines and give a bibliography that would be a waste of valuable space to repeat here.

Their own method seems somewhat lengthy and cumbersome to the writer, who has used the simple method given below, in his consulting practice, for over a year, without his results failing to agree with factory data, even once. However, factory calculations on a large scale cannot be considered an exact check; in fact, the only exact check is to add an exact proportion of pure, dry sugar to some unsweetened condensed milk and see how much the proposed method of analysis shows.

#### TEST OF METHOD

Therefore pure granulated sugar was further purified, as described in revised *Bulletin* 107, 40, for standardizing saccharimeters, and then thoroughly dried. A normal weight of this gave a reading of 100 on the sugar scale of the latest model of the Schmidt and Haensch sodium light polariscope.

To the appropriate quantity of a well-known brand of *fresh* unsweetened condensed milk and also to some *canned* unsweetened milk (processed at a higher tem-

perature than the *fresh* product) the above purified sugar was added, to yield sweetened condensed milks containing exactly 45 per cent sucrose.

On account of the lowering of the degree of concentration in commercial condensed milks (due to over-liberality in lowering the government standards) it has been the writer's custom to dilute 50 g. of the sample to 100 cc., thus making the measuring and calculation of aliquots simpler and quicker. With aliquots representing 6.5 g. of each of the above-standardized, sweetened condensed milks, the method of analysis gave, respectively, 45.07 per cent and 45.32 per cent sucrose. Using aliquots representing 13 g. (half-normal weight) of the two products, the method gave 45.11 per cent and 45.18 per cent sucrose, respectively.

Although the quarter-normal weight (6.5 g.) of the sweetened *fresh* condensed milk happened to give the closest result (45.07 per cent), yet the writer is constrained to favor the use of a  $N/2$  weight (26 cc. or 13 g.) so as to use smaller multiplying factors, as he is convinced that the only possible error of the method is the personal one in taking the polariscopic readings.

#### DESCRIPTION OF THE METHOD OF ANALYSIS

Therefore the method as used is as follows: Weigh out exactly 50 g. of the *well-mixed* sample, dilute with water to exactly 100 cc. and carefully shake or stir until completely dissolved. Pipette<sup>1</sup> exactly 26 cc. (13 g.) into a beaker, dilute with water to about 40 cc. and add Fehling's copper sulfate solution drop by drop, stirring meanwhile, until the proteins and fat are precipitated (about 1.5 cc. is sufficient).

Filter on a paper similar to the E. & A. qualitative analysis filter paper and wash the precipitate with water until the filtrate measures exactly 100 cc. Stir filtrate until of a uniform faint blue color and take the direct reading in a 200 mm. tube of the polariscope, noting temperature, which should be between 20 and 30° C. To exactly 50 cc. of the filtrate add 5 cc. of concentrated hydrochloric acid, mix and allow to stand over night at the above temperature range.

Add a few drops of phenolphthalein indicator solution, exactly neutralize with strong alkali solution and acidify with one drop of dilute (10 per cent) hydrochloric acid to discharge the red color. Make up to 100 cc., filter and take the invert reading in 200 mm. tube at same temperature as that of the direct reading. Multiply the direct reading by 2 and the invert reading by 4 and calculate the sucrose by Clerget's formula, using the factor 141.7, thus:

$$\text{Sucrose} = \frac{100 (\text{Direct reading} - \text{Invert reading})}{141.7 - \frac{\text{Temp.}}{2}}$$

The precipitate of proteins and fat on the filter paper (from first filtration) can be used for an estimation of proteins by Leach's method (drying, weighing, ashing and subtracting the ash and finally correcting

<sup>1</sup> Shake or stir again just before measuring out the 26 cc. to avoid any formation of a cream layer. Of course an exact 10 cc. portion of this diluted sample can be used for the Gottlieb fat determination and another 10 cc. portion for the determination of total solids and "ash."

<sup>1</sup> Bureau of Chemistry, *Bull.* 107, revised, U. S. Dept. of Agr.



for fat present) and it is probable that the fat could be determined on the dried precipitate by powdering and extracting with ether in a Soxhlet apparatus, similar to a method proposed by A. E. Paul.

Milk sugar (lactose) can be determined directly (by copper reduction gravimetric or by volumetric methods) on the filtrate before inversion, so we have here an outline for a "complete" analysis of sweetened condensed milk, using at the most but three aliquots of the original diluted sample.

The use of copper sulfate as a precipitant of proteins and milk-fat is a well-known procedure and the writer finds that the filtering off of the precipitate presents no difficulty, being rapid and the filtrate coming through clear from the first. Many samples can be started in a day, and the next day all invert readings taken. The actual working time on each sample is quite brief, and the results very close to the truth. Factory samples ranging from 35 per cent sugar to over 50 per cent sugar have been tested in the writer's consultation and analytical practice and, as said above, the results have always agreed with factory data.

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## ESTIMATION OF SUGAR IN MEAT PRODUCTS, PARTICULARLY EXTRACTS<sup>1</sup>

By W. B. SMITH

Received July 12, 1916

The best precipitants for the nitrogenous bodies in meats and meat extracts which interfere with the reduction of Fehling's solution by sugar, are mercuric nitrate, mercuric acetate, and picric acid, followed by phosphotungstic acid, with or without hydrochloric acid. For polarimetric work the excess of mercury does not have to be removed, but for copper reduction this is absolutely necessary. Irrespective of other qualities this fact makes the use of mercuric salts tedious and difficult. The removal of the excess of mercury is troublesome; although it has been performed with ease under certain conditions, which appear to be distinct acidity, sufficient rapidity of the current of  $H_2S$ , and not too concentrated solution, several chemists have found difficulty with it, especially when meat extracts containing high percentages of sodium chloride are being tested. If this part of the clarification is not well done, the succeeding steps cannot be carried out successfully. This criticism applies particularly to the nitrate of mercury; not only is the acetate of mercury more efficient as a precipitant, but the nitric acid greatly hinders the formation of mercuric sulfide.

For these reasons picric acid, when used in place of mercuric salts, not only is easier of manipulation, but saves a very great proportion of the time required. Folin states,<sup>2</sup> "in the presence of copper, alkaline picrate solutions are not reduced by sugar," and this has been confirmed by the experience of the writer. The sugar can, moreover, be estimated by the picramic

acid reaction recently published by Benedict,<sup>1</sup> Bernhard,<sup>2</sup> and Myers.<sup>3</sup>

### ESTIMATION OF SUGAR

In this work the sugar was determined by reduction of Fehling's solution and estimation of the copper in the precipitate by Low's iodide method. As described in a former paper,<sup>4</sup> difficulty is sometimes experienced (with the mercuric salts filtrate) in filtering off the cuprous oxide, which comes down yellow and more or less soluble in water. Less difficulty has been found when picric acid is used. The Munson-Walker method usually gives good results, especially when the percentage of sugar is high. Out of 150 tests of various methods the following are representative:

PRODUCT	PER CENT SUGAR Munson-Walker	FOUND BY Bertrand
Cured Meat Extract.....	4.27	4.31
Bouillon Cubes.....	1.77	1.88
Extract from Spleens and Livers.....	1.81	1.82

There are indications, however, that Bertrand's method is more tolerant of impurities than the Munson-Walker. The following tests were made on a single solution, clarified by the picric acid method from extracts of beef:

	Percentages	
Sugar by Bertrand method.....	0.09	0.13
Sugar by Munson-Walker: using 50 cc. of sugar solution	0.28	0.39
using 25 cc. sugar solution and 25 cc. water.....	0.20	

The results by Munson-Walker are not concordant and were affected by the amount of sugar solution taken. In this instance the high figures were due to a gummy residue which contained copper. The Munson-Walker method is superior in its definition of the time for bringing to boiling, but Peters' suggestion<sup>5</sup> of a temperature limit is timely. The bulk of the reduction takes place before the mixture boils. On the whole, Bertrand's method of reduction is preferred. As Bertrand's tables did not reach below 10 mg. sugar, the factor 0.49 was used to convert copper percentages into sugar when necessary.

### REMOVAL OF NITROGENOUS BODIES

Bertrand's method having been adopted as giving nearly accurate results for the purpose, various methods of removing the nitrogenous bodies which interfere were tested. Nearly all the work was done on meat extracts, which have more of the interfering bodies than any other kind of meat product, and hence give the most severe tests of any method.

It is well to point out that unclarified meat products give little or no precipitation of copper because the cuprous oxide is held in solution by the protein substances present. When these are partially removed a point is reached at which the holding of cuprous oxide in solution is reduced to a minimum and high results are obtained, owing to the presence of creatinin and similar substances which themselves cause a reduction of Fehling's solution. While it cannot be said of any sample in advance which of these errors

<sup>1</sup> "Estimation of Sugar in Blood," *J. Biol. Chem.*, **20** (1915), 67-69.

<sup>2</sup> *Chem. Abs.*, **10** (1916), 1230.

<sup>3</sup> *J. Biol. Chem.*, **24** (1916), 147.

<sup>4</sup> *Jour. Assoc. Official Agr. Chemists*, **1**, No. 2, Aug., 1915, pp. 176-181.

<sup>5</sup> *J. Am. Chem. Soc.*, **34** (1912), 930.

<sup>1</sup> Published by permission of the Secretary of Agriculture.

<sup>2</sup> *J. Biol. Chem.*, **22** (1915), 327-9.

will occur, in general it is the case with meat extracts that abnormally high precipitation of copper results. Hence with the methods here studied the lowest results are usually the most accurate. The details developed by the writer for the use of either mercuric acetate or picric acid are as follows:

#### METHOD I—MERCURIC ACETATE

**MEATS**—Boil 40 g. sample (fairly free from fat) with 150 cc. water 15 or 20 min.; cool, add 10 to 20 cc. twice-normal mercuric acetate (slightly acid with acetic acid), then add strong sodium hydroxide carefully until nearly neutral to phenolphthalein, and make up to 200 cc., exclusive of fat. Filter through a large folded filter as quickly as possible. To 120 cc. of the filtrate add 2 cc. glacial acetic acid, and saturate with  $H_2S$  in the cold. Remove excess of  $H_2S$  with a current of air, and restore volume to 120 cc. Filter, take 80 cc., add 5 cc. (or an excess) of 20 per cent aqueous phosphotungstic acid and 5 cc. concentrated  $HCl$ , and make to 100 cc. Filter and determine dextrose at once; 20 cc. of filtrate equal 3.20 g. sample.

Invert another portion of filtrate according to Bureau of Chemistry *Bull.* 107, p. 41, revised, and determine total reducing sugars. The hydrochloric acid already added is not sufficient for complete inversion in the time stated.

**MEAT EXTRACTS**—Dissolve 5 g. extract in 100 cc. water, add about 35 cc. mercuric acetate solution, and proceed as with meats. Ten cc. or more of phosphotungstic acid solution should be used instead of five.<sup>1</sup> Twenty cc. of final filtrate before inversion contains 400 mg. of sample.

#### METHOD 2—PICRIC ACID

**MEATS**—Boil 50 g. finely divided sample (fairly free from fat) with about 150 cc. water for 15 or 20 min.; cool, add 1 to 5 g. picric acid (solid) and 15 to 20 cc. of 20 per cent aqueous solution of phosphotungstic acid, and make up to 250 cc., exclusive of fat. Filter and take 150 cc. of filtrate. Make up to 160 cc. with 8 cc. concentrated  $HCl$  and 2 cc. water, mix, and filter. The filtrate in each case should be clear. Determine reducing sugar at once, 20 cc. of solution being assumed to contain 3.75 g. sample. Invert and determine total reducing sugars.

**MEAT EXTRACTS**—Dissolve 5 g. meat extract in about 25 cc. of water, add an excess (4 to 6 g.) solid picric acid and an excess (40 to 60 cc.) of a 20 per cent aqueous solution of phosphotungstic acid.<sup>2</sup> Mix and make up to 100 cc. Filter, take 60 cc. (or more) of filtrate, add 3 cc. (or more, if necessary) concentrated  $HCl$ , make up to 66 cc. and filter quickly. The filtrate should be perfectly clear, but will have a light yellow color due to picric acid in solution. Determine reducing sugar in the filtrate at once. Twenty cc. equal 0.909 g. sample.

Take another portion of the filtrate and invert, adding more  $HCl$  according to one of the methods in

<sup>1</sup> An excess of both mercuric acetate and phosphotungstic acid is required.

<sup>2</sup> An excess of both picric and phosphotungstic acids is required, but the hydrochloric acid should be kept as small in amount as the nature of the solution will permit.

Bureau of Chemistry *Bull.* 107, p. 41. Determine invert sugar.

Results obtained by these methods are given in Tables I and II. Only a few representative figures are given, the others being entirely similar. The amounts of sugar recovered when known amounts of sucrose were added to the sample before clarification indicate that the methods as a whole are correct, the errors being no greater than might be obtained on pure sugar solutions. It must be remembered that very small amounts of sugar are being dealt with and that any error is apt to appear relatively large. In some cases one drop of thiosulfate solution was equivalent to several hundredths of a per cent of sugar.

When dextrose was added to the filtrates after clarification, the errors inherent in the clarification were avoided. The figures show that practically the same amount of sugar was recovered as was added, indicating that, on the one hand, no cuprous oxide is held in solution, and on the other that no nitrogenous or other substance is present which causes increased reduction.

		TABLE I				
SAMPLE	Clarifier used	PER CENT SUGAR				
		in Meat	Added	Total	Recover-	Error
SUGAR ADDED TO ORIGINAL SAMPLE:						
Sausage.....	Hg acetate	0.29	0.11	Sucrose	0.40	0.42 +0.02
						0.41 +0.01
Fresh Meat Extract.	Hg acetate	1.77	4.9	Sucrose	6.67	6.67 =0.00
						6.62 -0.05
						6.83 +0.16
Fresh Beef Extract...	Picric acid	0.65	10.0	Sucrose	10.65	10.60 -0.05
						10.88 +0.23
						10.62 -0.03
SUGAR ADDED TO CLARIFIED FILTRATE:						
Diluted Beef Extract	Hg acetate	0.58	7.44	Dextrose	8.02	7.95 -0.07
Fresh Meat Extract.	Hg acetate	1.24	3.72	Dextrose	4.96	4.99 +0.03
Cured Meat Extract	Hg acetate	3.81	7.27	Dextrose	11.08	10.99 -0.09
Cured Meat Extract	Hg acetate	3.97	3.72	Dextrose	7.69	7.69 =0.00
Fresh Meat Extract.	Hg acetate	1.12	0.96	Dextrose	2.08	2.06 -0.02

The preceding results having indicated that sugar is quantitatively recovered by these procedures, commercial samples of meats and meat extracts containing sugar were examined for reducing sugar before and after inversion, with the results shown in Table II:

TABLE II—COMPARISON BETWEEN MERCURY AND PICRIC ACID METHODS

SAMPLE	BEFORE INVERSION		PER CENT SUGAR FOUND		AFTER INVERSION	
	Hg Method	Picric	Hg Method	Picric	Hg Method	Picric
Extract of cured meat.....	2.36	2.68	2.36	5.23	5.32	5.20
Extract of cured meat.....				6.84	7.05	6.85
Sugar cured ham.....				6.85	7.10	6.96
Sugar cured bacon.....	0.11	0.12	0.45			0.46
Extract of spleens, livers, etc.....	0.22	0.24	0.60			0.60
	2.34	2.50	2.34	2.85		2.90

These figures indicate that the same results may be obtained by both the mercuric acetate and the picric acid methods. As the latter is very much shorter, its superiority is shown.

In order to make as severe a test as possible of the relative values of the various precipitants, 100 g. of extract which was known to be chiefly from muscular tissue of fresh beef, and hence nearly free from sugar, were dissolved in water and several portions clarified as indicated in Table III. At first the clarification was not made complete, in order to test the necessity for the use of hydrochloric acid, and to some extent, of phosphotungstic acid.



METHOD 1—Mercuric acetate (already described)

METHOD 2—Picric acid (already described)

METHOD 3—Mercuric nitrate (otherwise same as 1)

METHOD 4—A modification of Neuberg & Kerb's method.<sup>1</sup> The solution was made alkaline to phenolphthalein with strong solution of sodium carbonate and strong mercuric acetate added in excess. Considerable difficulty was experienced in ascertaining this point, more sodium carbonate being added once or twice. After filtering off the precipitate, the excess of mercury was removed and the solution treated as in Method 1:

TABLE III—EFFICIENCY OF CLARIFYING AGENTS

Test No.	Per cent Sugar	Method	Phosphotungstic Acid	HCl
7	0.19	4	None	None (excess Hg not removed)
11	2.01	3	None	None
4	0.67	4	None	None
6	0.63	4	Partial	None
1	0.69	2	Partial	Partial
12	1.14	3	Partial	Excess
COMPLETE CLARIFICATION				
13	0.74	1	Excess	Excess
2	0.45	2	Excess	Excess
5	0.60	1	Excess	Excess
3	0.50	2	Excess	Excess
9	0.58	4	Excess	Excess
10	0.56	4	Excess	Excess

0.59 Average of completely clarified solutions  
0.48 Average by Method 2

The results show the need of complete clarification, Method 3 giving especially high results. The other methods give comparable results, the error of the conditions worked under being probably more than 0.1 per cent. Test No. 7 was run without the removal of mercury, and was of no value. Methods 2 (picric acid) and 4 (sodium carbonate and mercuric acetate) gave the best results, the picric acid method being much the easiest and shortest of the four. From the experience of the writer, it is thought that the average of Tests 2 and 3 was nearly the true amount of sugar in the extract (0.48 per cent). Dextrose was then added to unused portions of solutions and the total reducing sugar determined. The results (Table IV) are perhaps more conclusive than those in Table III, as it is easier to estimate correctly the larger amounts of sugar. Three tests using no phosphotungstic or hydrochloric acid showed errors of 0.20 to 0.55 per cent. Four tests, using some phosphotungstic acid but no HCl, gave errors from 0.10 to 0.50 per cent. Three tests (one by each method except the mercuric nitrate), using excess of both phosphotungstic and hydrochloric acids, gave errors of only 0.01 to 0.10 per cent.

TABLE IV—RECOVERY OF ADDED DEXTROSE FROM BEEF EXTRACT

No.	In Extract	Added	Total	Sugar Found	Error	Clarifier
(a) No phosphotungstic or hydrochloric acids						
18	0.48	12.47	12.95	13.50	+0.55	Na <sub>2</sub> CO <sub>3</sub> + Hg acetate
23	0.48	3.17	3.65	3.45	-0.20	Hg nitrate + NaOH
24	0.48	5.09	5.57	5.10	-0.47	Hg acetate + NaOH
(b) Insufficient phosphotungstic acid: No HCl						
15	0.48	13.61	14.09	13.59	-0.50	Picric acid
19	0.48	3.36	3.84	3.65	-0.19	Na <sub>2</sub> CO <sub>3</sub> + Hg acetate
20	0.48	3.36	3.84	3.33	-0.49	Na <sub>2</sub> CO <sub>3</sub> + Hg acetate
21	0.48	3.36	3.84	3.94	+0.10	Na <sub>2</sub> CO <sub>3</sub> + Hg acetate
(c) Excess phosphotungstic acid and HCl						
17	0.48	2.11	2.59	2.58	-0.01	Picric acid
22	0.48	4.06	4.54	4.48	-0.06	Na <sub>2</sub> CO <sub>3</sub> + Hg acetate
25	0.48	2.66	3.14	3.24	+0.10	Hg acetate + NaOH

As these figures are entirely in accord with all others obtained, they appear to indicate that these methods give accurate results. Sodium carbonate is better in conjunction with mercuric acetate than sodium hydroxide, on account of the action of the CO<sub>2</sub>.

<sup>1</sup> Biochem. Z., 40 (1912), 498-502.

One important difference between mercury salts and picric acid should be noted. After recovering the mercury it is convenient to add the phosphotungstic acid and the hydrochloric acid together. With picric acid, however, the reactions are somewhat different, three precipitates being formed:

(1) Pierates of protein substances, precipitated in solutions containing organic acids.

(2)—Phosphotungstates insoluble in solutions containing no free mineral acids.

(3)—Phosphotungstates soluble in neutral solutions or in the presence of organic acids, but insoluble in hydrochloric or sulfuric acid.

The first two precipitates are not antagonistic to one another, but are more or less dissolved on the addition of hydrochloric acid. For this reason it is best to add the picric and phosphotungstic acids together, filtering off the precipitate before the hydrochloric acid is added.

Nitrogen determinations show that about five-sixths of the total nitrogen is removed by this process. As the nitrogen remaining is in compounds of low molecular weight such as ammonia and mon-amino acids, in reality nine-tenths or more of the nitrogenous substances are removed. Two extracts gave the following results:

Original nitrogen.....	7.32%	Original nitrogen.....	7.59%
After mercuric acetate, phosphotungstic acid and HCl.....	1.21%	After picric acid.....	5.40%
		After phosphotungstic acid	2.18%
		After hydrochloric acid....	1.28%

#### ERROR IN REDUCING SUGAR RESULTS DUE TO INVERSION OF SUCROSE

The methods herein described are open to the objection that the hydrochloric acid inverts the cane sugar so rapidly as to make the reducing sugar results too high. While this objection does not appear to have good grounds, yet even if it were true the methods would have value owing to the facts that the total sugar estimation is very accurate and that the natural sugars in meat products are reducing. However, some careful tests of the amount of inversion have been made. It is well known that even in neutral solutions sucrose reduces Fehling's solution. The minimum amount of hydrochloric acid for complete precipitation of the phosphotungstates is about 1/20th the total volume of the solution. When this amount is employed it appears to be all used up in reactions with the other substances in the solution. Five cc. of one solution required 40 cc. of N/10 alkali for neutralization, but the volatile acid distilled from a similar portion required only 0.8 cc.

Comparisons of the percentages of reducing sugar obtained from meat extract solutions before and after the addition of cane sugar gave these results:

Reducing sugar found in absence of sucrose	Reducing sugar found in presence of sucrose after adding
Sample 1 1.64	Sucrose 5.0% 1.67
Sample 2 0.49	Sucrose 6.5% 0.47
Sample 3 1.54	Sucrose 7.5% 1.49
Sample 4 0.20	Sucrose 10.0% 0.20

In these cases the copper reduction was begun in 2 or 3 min. after the addition of the hydrochloric acid. The sugar was added to the original product.

When cane sugar has been added to the solution after clarification some increase of reduction has been

observed, but not more than would be obtained on aqueous solutions of sucrose. It is only necessary to give one out of several series of tests. Meat extract solutions containing about 4 per cent of total sugar, mostly reducing, were each treated with 40 mg. sucrose (about 5 per cent) and allowed to stand a few minutes before neutralization. Reducing sugar was then determined on this solution and also on a control solution identical except that no sucrose was added.

A blank test on 40 mg. cane sugar showed reduction equivalent to 0.21 per cent sugar on the amount of sample used. The extract solutions gave the following results (percentages):

Time of standing Minutes	Sucrose present	REDUCING SUGAR FOUND		Increase
		In control	In sucrose solution	
1	5.27	3.95	4.16	0.21
4	5.00	4.22	4.35	0.13
2	4.94	4.28	4.41	0.13
3	4.92	4.30	4.46	0.16
Reduction of aqueous sucrose solution.....				0.21

The temperature of the room during this experiment was about 25° C., which was favorable to inversion. The above figures show that the estimation of reducing sugar in the presence of sucrose is quite practicable by this method, the increased reduction being within the limits of error of ordinary sugar methods.

It should be remembered also that the solution is acid before the addition of hydrochloric acid, so that although inversion is slow, in the presence of sucrose the whole process should be carried through without too much delay. After the addition of the hydrochloric acid the filtrate should be neutralized immediately. Where only total invert sugar is desired, the solutions do not change for several days. Clarification becomes more complete as the solution stands.

It is believed that the methods outlined in this paper offer accurate means of determining reducing sugars in meat extract before and after inversion.

#### SUMMARY

I—Clarification of meat extract solutions for estimation of sugar by Fehling's solution is best accomplished by an excess of picric and phosphotungstic acids, followed by a minimum amount of hydrochloric acid.

II—In the presence of sucrose, reducing sugar may be determined within 0.1 or 0.2 per cent, provided proper precautions are observed.

III—Total reducing sugar may be determined within 0.1 per cent.

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#### LIGNOCERIC ACID FROM ROTTEN OAK WOOD

By M. X. SULLIVAN

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In the study of the origin of organic soil constituents a chemical study of rotten wood was undertaken in these laboratories in the year 1908. A large amount of dead oak wood was collected from a woody section near Washington, D. C. Since vanillin had long been reported<sup>1</sup> as a constituent of wood, the ground-up wood was extracted with alcohol, the alcohol extract freed

from alcohol and the residue treated with ether. From the ether extract, by the customary methods of testing for aldehydes, a small amount of an aldehyde-containing resin of a vanillin odor was obtained which gave the color reactions of vanillin.

Since vanillin is sublimable, about 200 g. of wood were heated between large watch-glasses to obtain sublimate matter, and though vanillin was subsequently found in wood and other vegetable material by appropriate methods,<sup>1</sup> practically all the material sublimed from the wood was insoluble in hot water and was of a fatty nature. To obtain a large amount of this sublimable fatty matter, about 20 lbs. of rotten wood were placed in a retort, connected with a Liebig condenser, and subjected to heat. As a result of regulated heating with Bunsen burners a steady stream of material varying from tarry matter to a yellowish white crystalline solid distilled over through the condenser.

The material obtained was soluble in hot alcohol. On cooling, crystalline matter separated out of the alcohol. On filtering while the alcohol was still warm and washing with cold alcohol, most of the coloring matter went into the filtrate. The crystalline matter was then placed on a porous plate and treated with cold petroleum ether until colorless. The purified substance recrystallized from alcohol melted at 73–75°. The compound was soluble in ether, hot alcohol, warm petroleum ether, and was insoluble in water.

Subsequently, by much the same method, lignoceric acid<sup>2</sup> was obtained from peat soil. Lignoceric acid has the elementary composition of C, 78.2; H, 13.0; O, 8.8. As determined by Dr. E. C. Shorey at the time he was working on the lignoceric acid of peat soil, the elementary composition of the substance obtained by me from wood was C, 78.6; H, 13.35; O, 8.5. It was thought at the time (1909) that the substance from the wood might be identical with lignoceric acid which Hell<sup>3</sup> found in beech wood tar. The elementary composition and melting point, however, were suggestive to me of cerotic acid from beeswax, which has a percentage composition of C, 78.78; H, 13.13; and melts at 78°.

No further work was done on the identification of the compound from the rotten wood until very recently, when the question of the identity of the wood substance was revived by the finding of cerebrosides<sup>4</sup> in mold from soil and by the work of Levene and West, who found that lignoceric acid is an oxidation product of cerobronic acid derived from cerebrosides of brains by hydrolysis.

Lignoceric acid forms a lithium salt insoluble in hot methyl alcohol. Accordingly, the material from the wood was dissolved in methyl alcohol and the resulting solution was treated with a methyl alcohol solution of lithium acetate as long as a precipitate formed. In this way the material collected from the

<sup>1</sup> Sullivan, *THIS JOURNAL*, **6** (1914), 919.

<sup>2</sup> O. Schreiner and E. C. Shorey, U. S. Dept. Agr., Bureau of Soils, *Bull.* **74** (1910).

<sup>3</sup> *Ber.*, **13** (1880), 1709.

<sup>4</sup> Sullivan, *Science*, **38** (1913), 678.

<sup>5</sup> *J. Biol. Chem.*, **15** (1913), 193.

<sup>1</sup> Singer, *Monatsh.*, **3** (1882), 395.



dry distillation of the wood was divided into two portions, the one, the major portion with a lithium salt insoluble in hot methyl alcohol; the other, small in amount, with a lithium salt soluble in methyl alcohol. The acids were liberated by boiling with dilute sulfuric acid and extracting the cooled mixture with ether. Recrystallized from alcohol, the respective acids melted at 78 and 85°. The acid from the lithium salt insoluble in methyl alcohol, melting at 78°, was further purified and the melting point rose to 80–82°.

This latter acid, presumably lignoceric acid, was compared with cerotic acid made from beeswax according to the method employed by Marie.<sup>1</sup> The acid obtained from the wax melted at 78–79°; mixed with the acid from rotten wood melting at 80°, the melting point of the mixture was 72–74°. The lowering of the melting point of the mixture shows that the acid from the wood is not identical with cerotic acid. The wood acid mixed with lignoceric acid from peat soil gave a mixture melting at 79–81°, so these acids are probably identical.

Lignoceric acid forms a lead salt melting at 117°,<sup>2</sup> and a lithium salt decomposing about 190–195°. The acid from the rotten wood gave a lead salt melting at 116–117°, a lithium salt decomposing at 195° and gradually liquefying to 210–215°, at which temperature it formed a brown liquid.

From the solubility of the acid and its salts the percentage composition, the decomposing point of the lithium salt, the melting point of the lead salt, and the non-lowering of the melting point when mixed with lignoceric acid from soil, it may be concluded that the acid derived from the rotten oak wood by dry distillation is lignoceric acid identical with the lignoceric acid obtained by Hell<sup>4</sup> from beech wood tar and from "carnaubon" from ox kidneys by Rosenheim and MacLean.<sup>5</sup>

The lignoceric acid, or a closely related substance, exists in the wood, for it has been obtained by extraction with alcohol. To obtain this acid the finely ground wood was extracted with hot alcohol and the part which separated on cooling was saponified with alcoholic soda. Part of the sodium salt was insoluble in hot alcohol. The filtrate from the hot alcoholic soda was freed from alcohol, with replacement by water. The hot water mixture was filtered hot. The filtrate treated with sulfuric acid gave a crystalline acid which was purified by crystallization from alcohol and ether. The free acid gave a lithium salt insoluble in methyl alcohol. The acid freed from lithium melted at 80–82° and was found to be identical with the acid obtained from wood by dry distillation.

The second acid obtained in the dry distillation of wood, the acid melting at 85° with a lithium salt soluble in hot methyl alcohol, is believed to be the inactive cerebronic acid described by Levene and West.<sup>4</sup> It is a white, easily pulverizable, non-hygroscopic substance soluble in ether and warm alcohol.

On cooling the alcohol it separates out in round masses, often in thick lamellae, which show a fine radiating structure. It is free from nitrogen and burns with the smell of burning fat. Its sodium salt is insoluble in water and not very soluble in hot alcohol, especially in hot alkaline alcohol. On rubbing, it becomes electrified.

The general properties of the acid, its solubility, the solubility of the sodium and the lithium salts suggest the inactive form of cerebronic acid described by Levene and West. A further indication that cerebronic acid exists in rotten wood is that from a sodium alcoholate extract of the rotten wood material resembling cerebronic acid has been obtained. The alkaline alcohol solution was filtered hot and cooled in an ice box. The precipitate which formed was slightly soluble in boiling water. The part insoluble in hot water was recrystallized successively from 95, 80 and 60 per cent alcohol. The nearly colorless material made a fine suspension in hot 50 per cent alcohol and the turbid mixture passed through filter paper. On concentrating the solution, white matter settled out in mamillary masses, which on drying melted at 106–108°, the melting point of active cerebronic acid. This material was soluble in warm glacial acetic acid, from which it settled out as a jelly on cooling. The part most soluble in cold glacial acetic acid melted at 90–94°.

Cerebronic acid, as described by Levene and Jacobs,<sup>1</sup> has three forms: (1) the optically active form melting at 106–108°; (2) the inactive form melting at 82–85°; and (3) a mixture of these melting about 92°.

All in all, it is believed that cerebronic acid exists in rotten wood, though absolute proof was not obtained. A pleasing hypothesis is that cerebrosides exist on the living tree and that from the cerebrosides there forms in the rotting of the wood, under the action of molds, bacteria, and the processes of oxidation, cerebronic acid and lignoceric acid. Of the presence of cerebrosides in wood no tests have been made; of the presence of cerebronic acid in rotten wood there are indications; and of the presence of lignoceric acid, a close relative of these, there is a satisfactory proof.

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#### METHOD OF EXTRACTION AS AFFECTING THE DETERMINATION OF PHOSPHORIC ACID IN SOILS

By HARRISON HALE AND W. L. HARTLEY

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While determining the phosphoric acid in soils during some work done in coöperation with the Missouri State Fruit Experiment Station, occasion was also taken to compare O. L. Brauer's<sup>2</sup> method of extracting the phosphoric acid 2 hrs. with 2 *N* HNO<sub>3</sub> with the official method of the Association of Official Agricultural Chemists<sup>3</sup> of extracting 10 hrs. with HCl (sp. gr. 1.115).

The soils were taken by Mr. A. D. Kilham of the

<sup>1</sup> *Ann. chim. phys.*, [7] **7** (1896), 145.

<sup>2</sup> *Hell and Hermann, Ber.*, **13** (1880), 1713.

<sup>3</sup> *Meyer, Brod, and Soyka, Monatsh.*, **34** (1913), 1113.

<sup>4</sup> *Loc. cit.*

<sup>5</sup> *Biochem. J.*, **9** (1915), 103.

<sup>1</sup> *J. Biol. Chem.*, **12** (1912), 381.

<sup>2</sup> *This Journal*, **6** (1914), 1004.

<sup>3</sup> *Bureau of Chemistry, Bull.* **107**, 14.

Station from plots near Marionville, Mo., which were used for growing strawberries, and to which fertilizer had been added as follows, per acre:

SAMPLES 2 & 3	SAMPLES 6 & 15	SAMPLE 13	SAMPLE 16
Check Plot	375 Lbs. Bone Meal	300 Lbs. Sheep Manure 375 Lbs. Bone Meal	500 Lbs. No. 2 Manure

According to Marr<sup>1</sup> the check plots show the following analysis:

No.	Volatile Matter	Alumina	Ferric Oxide	Magnesia	Lime	Potassium Oxide	Insoluble Matter	TOTAL Per cent
2.....	3.64	2.22	1.99	0.12	0.55	0.10	90.78	99.40
3.....	4.41	2.10	1.98	0.17	0.43	0.11	90.80	100.00

At first an effort was made to precipitate the phosphoric acid with ammonium molybdate, dissolve the precipitate in ammonium hydroxide, reprecipitate with magnesia mixture, ignite and weigh as  $Mg_3P_2O_7$ . However, owing to the small amount of phosphoric acid present, accurate results could not be obtained. Thereafter, the determinations were made volumetrically by adding an excess of standard NaOH to the phosphomolybdate precipitate and titrating the excess with standard  $H_2SO_4$ .<sup>2</sup>

The following results show that the 2-hr. digestion with 2 N  $HNO_3$  extracts as much phosphoric acid as the 10-hr. digestion with HCl (sp. gr. 1.115). The 10-hr. diges-

<sup>1</sup> Master's Thesis, Drury College, 1915.

<sup>2</sup> Bureau of Chemistry, *Bull.* 107, 16.

PER CENT  $P_2O_5$  FOUND IN SOILS  
Brauer's Method: 2 hrs. Extraction with 2 N  $HNO_3$   
A. O. A. C. Method: 10 hrs. Extraction with HCl (sp. gr. 1.115)

Sample No.	GRAVIMETRIC DETERMINATIONS		VOLUMETRIC DETERMINATIONS	
	Brauer's Method	A. O. A. C. Method	Brauer's Method	A. O. A. C. Method
2.....	.....	.....	0.052	0.048
3.....	0.0532	0.0435	0.048	0.053
6.....	.....	.....	0.061	0.061
13.....	0.0511	0.0580	0.060	0.063
15.....	0.0638	0.0638	0.0551	0.050
16.....	0.0700	0.0600	0.0435	0.062

tion with HCl brings down considerable organic matter which it is very difficult to remove completely with  $HNO_3$ . This organic matter produces a precipitate when the excess of acid is neutralized with ammonium hydroxide in preparing to add the ammonium molybdate, which requires considerable  $HNO_3$  to redissolve, whereas the reaction with 2 N  $HNO_3$  brings down no interfering substances.

#### CONCLUSIONS

I—The 2-hr. digestion with 2 N  $HNO_3$  extracts as much phosphoric acid as the 10-hr. digestion with HCl (sp. gr. 1.115).

II—The 10-hr. digestion with HCl (sp. gr. 1.115) brings down very much more interfering substances than the 2-hr. digestion with 2 N  $HNO_3$ .

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### THE FLAME ARC IN CHEMICAL MANUFACTURE

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Photo-chemistry has developed into an increasingly important science with an extensive, scientific literature; however, but little progress has been reported on the use of light in the practical manufacture of chemicals—probably because of the lack of a powerful, constant light source. In the search for such a light source, to accelerate the chlorination of natural gas in the manufacture of chloroform, it was found by one of the authors (C. W. B.) that the high-amperage, white flame arc far excelled all other sources of light for this special work. As its advantages are so great, a discussion of its main features may be of interest and value to others engaged in studying the effect of light on chemical reactions.

It is well established that photo-chemical reaction is proportional to the absorbed light energy.<sup>1</sup> Since chlorine is yellow (absorbing blue light) and bromine is red (absorbing blue and green light) so the maximum chemical power of light for these materials occurs in the short wave (blue, etc.) region of the spectrum. Chlorine and bromine are transparent in the far ultraviolet as shown by Mr. N. P. Peskov.<sup>2</sup> For this reason, far ultraviolet light (*i. e.*, beyond 3000 Å.) is unsatisfactory for causing chlorination and bromination. Among others, Baskerville and Riederer<sup>3</sup> have shown that the blue end of the visible spectrum is

more suitable than ultraviolet light for the chlorination of methane. As was to be expected, they found that the presence of light of other wave lengths does not practically interfere with the action of the blue and violet so that light filters or sources of pure light are unnecessary. Our experience in the chlorination of methane hydrocarbons has led to similar conclusions and a few experiments in the chlorination of aromatic hydrocarbons gave the same results.<sup>1</sup> The snow-white flame arc, as will be shown below, is especially rich in blue light which is best for chlorination work.

In the reaction, hydrogen uniting with chlorine under light to form hydrochloric acid ( $Cl_2 + H_2 = 2HCl$ ), the more active region of the spectrum is from about 5160 Å. to 3700 Å. according to the experiments of Bunsen and Roscoe.<sup>2</sup> The maximum action is exerted with the solar spectrum in the region of the Fraunhofer lines G (4308 Å.) and H (3968 Å.) according to Fabre and Silberman.<sup>3</sup> Draper says that the maximum action in the indigo region is 700 times stronger than in the extreme red.<sup>4</sup> Bunsen and Roscoe found that reaction power decreased gradually beyond line J.<sup>5</sup> Peskov<sup>6</sup> shows that chlorine absorption ex-

<sup>1</sup> In the chlorination of methane, pure light is unnecessary because the products of the reaction are transparent to ordinary light to about 3000 Å. The absorption spectrum of chloroform and carbon tetrachloride lies in the ultraviolet beyond about 3000 Å. (See W. N. Hartley, *7th Int. Congress Appl. Chem.*, 9 (1909), 88. The other product, hydrochloric acid, is still more transparent, being so to beyond 2500 Å. (See E. J. Evans, *Phil. Mag.*, 6, No. 31 (Jan., 1916), 55.)

<sup>2</sup> See Sheppard, "Photo-Chemistry," page 118.

<sup>3</sup> *Ann. Chem. Phys.*, [3] 37, 297.

<sup>4</sup> See Eder's "Handbuch der Photographie," p. 323.

<sup>5</sup> The E. I. du Pont de Nemours Powder Co., French Patent 453,406, Jan. 21, 1913, used in chlorinating hydrocarbons, glass tubes with daylight or the blue light of the quartz lamp

<sup>6</sup> *Loc. cit.*

<sup>1</sup> P. Lasareff, *Ann. Physik*, 24 (1907), 661.

<sup>2</sup> "Quantitative Light-filter for the Ultraviolet Part of the Spectrum," *J. Russ. Phys. Chem. Soc.*, 47 (1915), 918.

<sup>3</sup> *This Journal*, 5 (1913), 5.



tends to 5400 Å.; then toward the violet, it has a space of diminished absorption, but finally shows a marked increased absorption in the spectral region from 4000 Å. to 3000 Å. The absorption of bromine extends from 5400 Å. to 3800 Å., hence the mixture of bromine and chlorine gives an excellent screen for getting far ultraviolet radiation beyond 3000 Å.

Ultraviolet light up to about 3000 Å. may be expected to be useful but with extreme ultraviolet light (beyond 3000 Å.) from a quartz mercury arc, Plotnikov<sup>1</sup> has shown a marked decomposition of hydrochloric acid. This fact is confirmed by the experiments of D. Berthelot and H. Gaudechon,<sup>2</sup> who propose the theory that decomposition by increasingly shorter waves of light is parallel to decomposition at increasingly higher temperatures by heat. Our experiments show extremely little ultraviolet in the spectrum region beyond 3000 Å. with the light of the snow-white flame arc which in this respect is very similar to sunlight plus blue skylight. Some of the proofs of this statement follow. The ultraviolet light of the snow-white flame arc gives no ozone odor which is so very marked with the quartz mercury arc. Also there is far less coagulation of egg-albumen than with the light of the yellow flame *bare* arc. Spectrum plates taken by one of us (W. R. M.) with a concave grating spectroscope show a marked decrease in photographic effect in the region of about 3000 Å. compared with other flame carbons or the open carbon arc. Although special flame carbons have been designed to give much far ultraviolet light in the region from 3000 Å. to 2000 Å. where the quartz mercury arc has some of its most powerful lines, the white flame arc is designed to have a spectrum extending into

of the reaction mixture by its heat of reaction. The lower the temperature, the greater is the actinic power of the light necessary to maintain a speedy reaction with small percentages of chlorine, and so in the search for a light of high intensity in the blue and violet, we finally came to an arrangement using the snow-white flame carbon arc light which we consider worthy of description.

The choice of the white flame arc was also made because of its extensive use in photo-engraving, photography, blue-printing, and other photo-chemical reactions.<sup>3</sup> Some photo-chemical reactions call for a special spectrum distribution. This can be readily attained with flame carbons having chemicals giving differently colored light.

#### COLOR RESOURCES OF FLAME CARBONS

The manufacturer of flame carbons uses,<sup>4</sup> as is well known, calcium fluoride for yellow light. Correctly described, the yellow flame arc is equally rich in red and green light but deficient in the blue and in spectrum yellow. The sensation yellow is produced by the combination in the eye of red and green light. The yellow flame arc has also a fair amount of violet and ultraviolet. Strontium fluoride is used for the red flamer, which is rich in red light and spectrum yellow with a fair amount of blue and ultraviolet.<sup>2</sup> Here, as well as in Plotnikov,<sup>3</sup> there is given the following Table I, a list of materials and the color of their arc light.

The white flame carbons are of special manufacture and their composition is kept secret except that it is known that rare earths are used.<sup>4</sup> The light of the snow-white flame arc is the closest approach to sunlight plus blue sky of any known illuminant,

TABLE I—ARC LIGHT COLOR OF SEVERAL CHEMICALS

MATERIAL: LIGHT:	Copper Blue	Silicon or Iron Reddish Violet	Titanium Blue	Lanthanum Oxide Pure White	Didymium Oxide Pure Violet	Thorium Oxide Reddish	Ceric Oxide Pure Blue
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ultraviolet like sunlight. The solar spectrum<sup>3</sup> extends into the ultraviolet to about 2910 Å. Hence, not only in quantity of light but also in quality of light is the flame arc the most suitable.

The enclosed arc lamp, quartz mercury arc, mercury vapor lamp or incandescent light sources are quite limited in the maximum quantity of light obtainable from a single unit compared with the flame arc. Also the flame arc by a shunt control which is described later, can be gradually varied over a range of several fold increase in light. This is a matter of great importance in experimental work.

#### NEED FOR GREAT INTENSITY OF BLUE LIGHT FOR CHEMICAL ACTION

In our work, it was found desirable to be able quickly to bring about the complete reaction of a small amount of chlorine diluted with a large amount of the substance with which it was to react. In other words, the reaction should be carried out at comparatively low temperatures, having at no time sufficient chlorine present to increase greatly the temperature

considering either the visible or the ultraviolet spectrum. The spectrum shows in every part closely crowded lines with no appreciable blank spaces. In passing, it is interesting to note that daylight itself has not strictly a continuous spectrum but has its dark spaces due to the Fraunhofer lines.

#### CHEMICAL ACTION WITH DIFFERENTLY COLORED FLAME CARBONS

The chemical action with differently colored flame carbons has been compared below, as to (a) bromina-

<sup>1</sup> In the photo-engraving field about 95 per cent of the light used in the United States is the white flame arc. The chief reaction in the photo-engraving field depends on the reaction of hardening gelatine and albumen by chromates under the influence of blue light. Potassium bichromate with gelatine has its maximum effect in the blue, gradually extending into the green but is weak in the ultraviolet (see Eder, *Loc. cit.*, p. 319). A similar demand for blue light is found in the reaction of light on ferric oxalate, silver bromide, etc. In the case of silver chloride, the maximum effect comes in the ultraviolet but where glass is used only that kind of ultraviolet that can pass glass can be useful. This is favorable to the white flame arc which allows over 80 per cent of its effect on solio paper to take place through ordinary glass. There are, however, other reactions, as in color-photography, that call for a different spectrum distribution. For instance, red or yellow flame carbons are very good for panchromatic photography.

<sup>2</sup> For a discussion of this and references, see W. B. v. Czudnochowski, "Das elektrische Bogenlicht," p. 539.

<sup>3</sup> "Photochemische Versuchstechnik," p. 40.

<sup>4</sup> See recent paper of Dr. W. C. Moore, on "The Flame Arc," *Trans. Am. Electrochem. Soc.*, 27 (1915), 435.

<sup>1</sup> "Photochemische Versuchstechnik," p. 205.

<sup>2</sup> *Compt. rend.*, 156 (1913), 889-892.

<sup>3</sup> See work of Freer, *Philippine Jour. Sci.*, 5 (1910), B. 14; Miethe and Lehmann, *Sitzb. Akad. Wiss. Berlin*, 8 (1909), 268.

tion, (b) effect on solio paper, and (c) effect on paraphenylenediamine. In these tests, a 10 mm. lower flame carbon was the positive and a  $1\frac{1}{2}$  in. enclosed arc core carbon was the upper negative. These tests were made with a Macbeth 220 volt flame lamp using 25 amperes with 90 arc volts. The most recent arrangement for using flame arcs on 220 volts is to use two or four arcs in series. For the solio paper and paraphenylenediamine tests, the inverse of the average time required to cause equal color effect was used.

**BROMINATION**—The effect of different lights on a 10 per cent solution by volume of bromine in toluol was tested at 2-ft. distance from the arc. The time was observed for the bromine color to disappear, using the solution in a glass test-tube (0.6 in. diam., 6 in. long, glass thickness 0.025 in.) which was cooled by an air blast and so kept at an average temperature of 36 to 39° C. With the quartz flask similar tests were made. This had the disadvantage of not having as much area exposed to the light in proportion to the amount of chemical as in the case of the glass test tube. There are, of course, several variables difficult to control in the reaction of bromine on toluol and the effective spectrum region is further toward the longer wave lengths than with chlorine.<sup>1</sup> For instance, there is great influence of dissolved oxygen in chlorination and bromination, as is well known.<sup>2</sup> Also the brominated products of the reaction have marked absorption of light<sup>3</sup> at about 2760 Å. The results here obtained did not check with chemicals from different sources for unknown reasons. However, the same chemicals were used in the same table and both tables show the same order of effect of the different light sources.

TABLE 2—AMOUNT OF TIME (SECONDS) FOR BROMINATION BY DIFFERENT LIGHT SOURCES

ARC LIGHT	GLASS TEST-TUBE	BLUE GLASS TEST-TUBE	QUARTZ FLASK
White Flame.....	60	100	100
Yellow Flame.....	50	90	55
Red Flame.....	170	400	115
"Blue" Flame.....	240	220	160
Pure Carbon Arc.....	280	210	130

Another set of samples of toluol and bromine from other sources gave faster results under these same conditions. However, the relative order of the results is about the same. With the glass test-tube, the yellow flame was the most efficient, the white flame next and then, in order, red flame, "blue" flame and pure carbon arc. The light was at 2 ft. in each case.

TABLE 3—BROMINATION TIME (SECONDS) WITH ANOTHER SET OF CHEMICALS

ARC LIGHT	GLASS TEST-TUBE	QUARTZ FLASK
White Flame (25 amp., 90 arc volts)	36	36
Yellow Flame (25 amp., 90 arc volts)	25	24
Red Flame (25 amp., 90 arc volts)	170	21
"Blue" Flame (25 amp., 90 arc volts)	210	60
Pure Carbon Arc.....	280	58
750 Watt N filled clear bulb incandescent.....		274
1000 Watt N filled blue bulb incandescent.....		235
Mercury Vapor Lamp, 3.3 amp. 110 v.....		610

In fairness to the flame arc it should be mentioned that a single flame arc at 25 amperes with 90 arc volts (on 220 volt line) has been improved upon from 50 to even over 100 per cent in some cases by using

two or four flame arcs in series on 220 volts in the more recent flame lamps. For 110 volt lines, many high-amperage flame lamps are now being designed with two arcs in series.

**EFFECTS ON SOLIO PAPER**—In the reaction on solio paper, the snow-white flame arc gives a greater effect by far than the light of any of the other flame carbons. This applies also as regards the light through glass.

TABLE 4—PHOTOGRAPHIC POWER ON SOLIO PAPER

ARC AT 25 AMP.—90 ARC VOLTS	NO GLASS	WITH GLASS
White Flame.....	100% (S)	80%
Yellow Flame.....	35	17
Red Flame.....	30	22
"Blue" Flame.....	60	30
Pure Carbon Arc.....	40	24

The inverse of average time to equal coloration of solio paper is the basis of the above figures which are referred to the most efficient result with the white flame as standard (S).

The glass, referred to in the above table, was ordinary window-glass 0.090 in. thick. This would probably transmit ultraviolet light<sup>1</sup> up to perhaps 3500 Å. The white flame gives a light, passing glass, which light is over three times as effective on solio paper as any other flame carbon of those tested except the "blue" flame and here the white flame is 2.6 times stronger.

**EFFECT ON PARAPHENYLENEDIAMINE**—To obtain a better idea of the ultraviolet, some tests were made with paraphenylenediamine and nitric acid. This makes a very good test because it is sensitive only to ultraviolet light.<sup>2</sup> Rays from gas, Auer, electric glow and Nernst lamps do not affect it.<sup>3</sup> In our tests, we used white blotting paper which was impregnated with this compound in nitric acid solution [1 g. of paraphenylenediamine, 3 cc. distilled water, 2 cc. nitric acid (sp. gr. 1.21)]. The blotting paper was then dried<sup>4</sup> in a steam oven for about one-half hour. On exposure to the light, the treated blotting paper turns green or blue-green and with long exposure it may turn to a bronze color. Tests were compared only under like conditions with the same strip of paper prepared and divided. The best test results were obtained with the 25 ampere arc at 2 ft. distance and exposing in increments of one-half minute without glass. With glass, because of the absorption of the ultraviolet beyond about 3500 Å., the exposures were made in steps of 5 minutes each.

TABLE 5—PHOTOGRAPHIC EFFECT ON PARAPHENYLENEDIAMINE

25 AMP.—90 ARC VOLTS	Total Ultraviolet No Glass	Part through Ordinary Window Glass	Transmission Ratio
White Flame.....	50%	12%	1 to 4
Yellow Flame.....	40%	0.8%	1 to 50
Red Flame.....	30%	0.15%	1 to 250
"Blue" Flame.....	100% (S)	4.0%	1 to 25
Pure Carbon Arc.....	20%	1.0%	1 to 20

The "blue" flame with no glass was taken as the standard of reference (S) giving the maximum of effect of these particular carbons. The white flame arc again shows the best glass transmission. The "blue" flame carbon was designed to have a rich far

<sup>1</sup> See S. E. Sheppard, "Photochemistry," p. 261

<sup>2</sup> C. Schall, "Eder's Jahrb. of Phot." 1906, p. 39.

<sup>3</sup> Phot. Work, 33 (1907), 321; see also pages 330 and 642, Eder's "Handbuch der Photographie."

<sup>4</sup> If dried over night the paper blackens and is useless. Ordinary newspaper is useless.

<sup>1</sup> See ref. Beilstein's "Organische Chemie," 2, 56.

<sup>2</sup> See Plotnikov, "Photochemische Versuchstechnik," p. 105.

<sup>3</sup> See J. E. Purvis, J. Chem. Soc. Lond., 99, 1700.



ultraviolet, and in this respect, it is shown by the above tests to have the most ultraviolet (with no glass of course) of all these flame carbons.

#### USES OF FLAME ARC FOR CHEMICAL CHANGE

All the uses of the flame carbons are being extended very rapidly because they offer the highest candle power and best efficiency and the widest choice of color and control of the amount of light. There are nearly a million white flame photographic carbons being used annually in the United States for photographic and similar purposes. One of the recently developed photo-chemical uses<sup>1</sup> has been tests for dye fading by flame arc light because tests showed that at 10 in. (25 cm.) from a 28 ampere white flame arc, the chemical effect in causing dye fading is four or five times as great as that of the best June sunlight plus blue sky.<sup>2</sup> This result is supplemented by the reliability of the flame arc *versus* the daily and seasonal extreme changes in sunlight.

Some idea of the efficiency of the high-amperage white flame arc can be gathered from the following table giving *mean spherical candle power*.

TABLE 6—MEAN SPHERICAL CANDLE POWER OF WHITE FLAME LAMPS

LIGHT SOURCE	LINE VOLTS	ARC VOLTS	AMP.	M. S. C. P.
White Flame Single Arc (D. C.)	115	63	28	5130
White Flame Twin Arc (D. C.)	115	90(a)	30	6700

(a) This is the total arc voltage of the two arcs in series. On A. C. for same line power much greater photo-chemical effect is obtained.

Until the recent development of the high-amperage flaming arc, the chief artificial sources of light for photo-chemical work were the enclosed carbon arc and various kinds of mercury arcs. Another new source has been found in the gas-filled incandescent lamp. A brief mention of these light sources as to their value for photo-chemical reactions may not be amiss.

#### CHEMICAL ACTION WITH ENCLOSED CARBON ARC

The enclosed carbon arc was the best source of blue light for chemical purposes until the introduction of the high-amperage white flame arc only a few years ago. The low operating cost, long life, ruggedness and rich cyanogen bands with very long arcs<sup>3</sup> (by 220 line volts) were the reasons for its general use. The flame arc presents the following advantages over the enclosed arc:

(1) The composition of the light with the enclosed arc changes vertically because of the difference in color of arc stream and arc crater. The light of the flame arc is essentially of the same color in all directions.

(2) The enclosed arc secures its increased photo-efficiency over the open pure carbon arc by decreasing the air supplied to the arc and so allows of increased intensity of the cyanogen spectral bands. For this reason, the maximum actinic efficiency of the enclosed arc (especially with large globes) is not reached until the oxygen of the air has been largely burnt up. This

<sup>1</sup> See paper, W. R. M., "Use of the Flame Arc in Paint and Dye Testing," *Trans. Am. Electrochem. Soc.*, **28** (1915), 371.

<sup>2</sup> It is calculated that two to five days' continuous operation with the flame arc will give fading results requiring a year of daylight under the usual conditions of test for dye fading with daylight in this latitude and climate (Cleveland, Ohio).

<sup>3</sup> See papers for comparison with flame arcs, V. A. Clarke, *Electrical World*, **64** (1914), 956; W. R. Mott and V. A. Clarke, *Lighting Journal*, **3** (1915), 224.

may delay for a few minutes the production of the full intensity of the violet and ultraviolet rays with the enclosed arc. With the high-amperage flame arc, the light rises instantly to practically full intensity and then remains steady with remarkable reliability.

(3) With the enclosed arc, the amperage is limited in amount because too large an arc stream would crack, melt and blacken the globe. With the flame arc, no globe is necessary, and consequently very high amperage can be used. One of the writers (W. R. M.) has burnt 10 mm. flame carbons of special manufacture at 75 to 100 amperes with good results. This is an important advantage because the photographic power, as measured by the effect of the light of a white flame arc increases rapidly with current, as will later be discussed.

(4) With the 110 volt enclosed arc, using  $\frac{1}{2}$ -in. electrodes, the solid angle cut out by the electrodes is greater than with the open flame arc (see Fig. 1). The flame arc operates usually with smaller diameter at carbon ends because of spindling and with an arc stream two or three times longer than the pure carbon arc and hence this gives the flame arc more constant results.

(5) Finally, in the matter of efficiency, the open single white flame arc at 25 amperes, on a 110 volt circuit, is two or three times more powerful in photo-chemical effect than the enclosed arc taking the same power. The twin flame arc lamp is still more efficient.

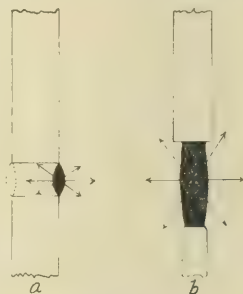


FIG. 1

(a) Enclosed carbon arc showing shadow effect due to short arc, thick electrodes and bowing of arc.  
(b) Open flame arc showing absence of shadow effect due to long arc, thin lower electrode and straight arc.

#### CHEMICAL ACTION WITH GAS-FILLED INCANDESCENT

The gas-filled incandescent lamp has been discussed in so many places that additional comment seems inadvisable here. A few tests were noted earlier in this paper.<sup>1</sup>

#### CHEMICAL ACTION OF A 110 VOLT QUARTZ MERCURY ARC

For equal line energy, the effect on solio paper of the white flame arc was five to six times better than the efficiency of a 110 volt mercury quartz lamp operating at 4 amperes and 60 arc volts. Dye-fading tests gave somewhat similar results. In the effect on dyes, the mercury quartz lamp required 72 hrs. at 8 in. to produce the same effect requiring only 2 to 4 hrs. at 10 in. with an Aristo lamp at 28 amp. on 115 volts direct current with white flame carbons.

#### CHLORINATION EXPERIMENTS COMPARING THE FLAME ARC AND 220 VOLT HERAEUS MERCURY QUARTZ LAMP

The following is a comparison of a flame arc (at

<sup>1</sup> See "Photographic Use of Gas-Filled Lamp," *General Electric Review*, **19** (1916), 187; L. A. Jones, M. B. Hodgson and Kenneth Huse, "Relative Photographic and Visual Efficiencies of Illuminants," *Trans. Ill. Eng. Soc.*, **10** (1915), 963; also note by W. R. M., *Lighting Journal*, **4** (1916), 15.

about 25 amperes and 45 arc volts on direct current) with a Heraeus mercury quartz lamp on 220 volts (at  $3\frac{1}{2}$  to 4 amperes direct current).

The Heraeus quartz lamp, using "Aron's" amalgam (60 per cent Hg, 20 per cent Pb, 20 per cent Bi, 0.5 per cent Zn and 0.5 per cent Cd), and operating under the favorable action of 220 volts, gave far better efficiencies than the 110 v. quartz lamp. Our comparative experiments in chlorination, using the white flame arc and the 220 v. quartz lamp, gave the results shown in Table 7.

TABLE 7—COMPARISON OF LIGHTS FOR CHLORINATION

LIQUID	FLASK	WHITE FLAME ARC		QUARTZ LAMP		Ratio
		Distance	Seconds	Distance	Seconds	
Benzol	Quartz	6 in.	2.0	6 in.	18.0	1 : 9
	Uviol glass	6 in.	1.9	6 in.	25.0	1 : 13
	Glass	6 in.	1.8	6 in.	30.0	1 : 17
Isoamyl Chloride	Quartz	6 in.	1.5	3 in.	3.2	.....
	Uviol glass	6 in.	1.8	3 in.	5.0	.....
	Glass	6 in.	2.0	3 in.	5.5	.....
Isopentane	Quartz	3 in.	0.7	3 in.	1.5	1 : 2
	Uviol glass	3 in.	0.3	3 in.	0.6	1 : 2
	Glass	3 in.	0.4	3 in.	1.5	1 : 4

Chlorine gas was passed into the liquid to be reacted upon until a good yellow color was obtained. The liquid was then divided into two equal parts, the one part being placed in a cool, dark receptacle while the other part was being exposed to one of the lights. Immediately after the reaction was completed, the flask was emptied and rinsed and the second half of the reaction liquid exposed to the other light in the same flask. By this method the same concentrations of free chlorine were used in the same flask for each light, but not for each successive experiment. *The results are comparable in horizontal lines only.* Time was taken by a stop-watch at the moment when the color of free chlorine entirely disappeared.

Experience had shown that a high concentration of free chlorine in a liquid with which it will react, requires comparatively little light to start the reaction and that the lower the content of free chlorine, the greater is the actinic power necessary to bring about the speedy reaction of the halogen. It has also been shown that the higher the temperature the less light is required for maintaining the reaction. In order, therefore, to test better the qualities of the two lights, the concentrations of free chlorine were always kept low, there being only sufficient halogen present to give a good yellow color to the liquid. The initial temperatures were also kept low ( $20^{\circ}$  C.) and in every case the comparison was found to favor greatly the flaming arc.

A further comparison, for the purpose of showing the relative effect of the ultraviolet light from the two sources, was accomplished in the following manner: Three flasks, almost identical in shape and capacity, were obtained in quartz, uviol glass and laboratory glass, passing, respectively, rays as short as 1850 Å, 2800 Å and 4000 Å. The same solution of free chlorine in benzol or isoamyl chloride was divided into three equal parts which were exposed simultaneously to the same light in the three flasks. The results, as tabulated in Table 8, show that the white flame arc emits a small amount of ultraviolet light, but that the amount is so small that very little efficiency is lost when working in glass apparatus. It is also shown

that a large share of the actinic power of the quartz lamp lies in the ultraviolet rays which are not necessary or even desirable for chlorination purposes.

TABLE 8—EFFECT OF DIFFERENT MATERIALS OF CONTAINERS

BENZOL				AMYL CHLORIDE			
Light	Flask	Distance	Sec.	Light	Flask	Distance	Sec.
Arc	Quartz	8 in.	3.2	Arc	Quartz	8 in.	1.2
Arc	Uviol	8 in.	3.8	Arc	Uviol	8 in.	1.6
Arc	Glass	8 in.	3.9	Arc	Glass	8 in.	1.7
Quartz	Quartz	3 in.	7.4	Quartz	Quartz	3 in.	5.0
Quartz	Uviol	3 in.	10.0	Quartz	Uviol	3 in.	6.2
Quartz	Glass	3 in.	11.6	Quartz	Glass	3 in.	7.0

#### CHEMICAL ACTION WITH SNOW-WHITE FLAME CARBONS AS INFLUENCED BY AMPERAGE AND ARC VOLTAGE

The relation of efficiency to amperage and arc voltage will now be discussed. These tests were made in a Macbeth photo-engraving lamp on D. C. The lower carbon was a snow-white flame carbon (10 mm. in diameter) without wire. The upper carbon was an ordinary cored enclosed arc carbon. The carbons were usually set 5 to 6 inches beyond the holders. In order to adjust the current and arc voltage, shunt resistances (in parallel with lamp solenoid and lamp resistance) were used with suitable adjusting weights on the carbon holders. The arc voltages were controlled to the values given at the carbon holders. This was found to be within one or two volts of the true arc voltage at moderate amperages up to 25 amp., but at 40 amperes there were about 5 volts lost in contacts and carbon resistance. The line voltage was kept at 110 volts direct current. Average results of inverse time to affect solio paper to the same degree are given below.

TABLE 9—CURRENT AND VOLTAGE IN EFFECT ON PHOTOGRAPHIC POWER

Observed Arc Voltage at Carbon Holders	10 Amp.	20 Amp.	30 Amp.	40 Amp. (a)
40 Volts.....	9	45	73	86
50 Volts.....	14	57	117	130
60 Volts.....	17	73	146	182
70 Volts.....	20	89	164	245
80 Volts.....	.....	.....	.....	285

(a) Arc voltage for 40 amp. includes about 5 volts drop in carbons and contacts.

The photographic power was called equal to 100 when 25 amperes of current flowed with 60 volts at the arc, as this was near the standard rating of the lamp.

From Table 9, the photographic power is found to be roughly proportional to  $(V-23)$  where V refers to the true arc voltage. The flame arc starts at about 20 volts. The voltage relation will be more fully discussed later, so turning to the very important current relation, we find the increase in efficiency with change in current from 10 amperes to 20 amperes is about fourfold. However, in again doubling by going from 20 amp. to 40 amp., the increase is far less even when allowing for the 5 volt arc correction. Using the average corrected results, the increase in efficiency is as the 1.8th power of the current. Combining the current and voltage relations, we obtain the following approximate relationship:

$$\text{Photographic Power} = KC^{1.8}(V-23)$$

Within the limits of these experiments the average value of K is equal to 0.0085 with an average deviation of  $\pm 0.0009$ . These results apply only to the direct current white flame arc. The efficiency on alternating circuits increases still more rapidly with current increase than on direct current.



The amount of light to the eye also increases more rapidly than the current both with the pure carbon arc and the flame arc.<sup>1</sup>

The effect of arc voltage was tested in further detail by using a 25 ampere arc on 330 line volts D. C. The lamp used was a 220 volt Macbeth lamp with trim as for the 110 volt lamp. Using the 90 volt arc as standard of reference (near usual arc voltage of this lamp) the following results with solio paper were obtained:

TABLE 10—RELATION OF ARC VOLTAGE TO PHOTOGRAPHIC EFFECT ON SOLIO PAPER

Arc Volts.....	20	30	40	50	60	70	80	90	100	110	120	130	140	150
Phot. Power.....	5	35	55	65	70	80	90	100	105	105	110	115	115	120

The following four conclusions can be deduced from Table 10, showing the effect of change of arc voltage:

(1) The photographic power increases as the arc voltage increases and this starts from a point of zero arc length near 20 volts.

(2) The rate of increase in photographic power with an arc voltage beyond 20 to 30 volts decreases rapidly as the arc voltage increases, due to loss of flame material from the arc by diffusion, screening action of the condensed flame material, and cooling action of entering air. The following figures show this decrease in the rate of change:

Arc Volts.....	20-50 V.	50-100 V.	100-150 V.
Rate of Change.....	2.5 per volt	0.7 per volt	0.3 per volt

(3) The arc voltage of maximum efficiency for energy in the arc is 40 to 50 volts under these conditions. This is favorable to the twin arc lamp as well as the better utilization of line energy with this type of lamp.

(4) The equation of the complete curve would be fairly complex and would probably involve a logarithmic function.<sup>2</sup>

#### CONVERSION OF AN ENCLOSED ARC LAMP TO BURN FLAME CARBONS

Instead of using such excellent lamps as the Macbeth, Bogue, Wohl, etc., photo-engraving lamps, there can easily be used some of the high-amperage enclosed arc lamps such as the Aristo 28-ampere lamp used in photographic studios and the Adams-Bagnall 15-ampere blue-printing lamp. These can be readily converted to burn flame carbons by removing the globe and making the lower flame carbon positive (a  $1\frac{1}{2}$ -in. flame carbon is often used, although in some cases a 10 mm. flame carbon is preferred). For the upper negative carbon, there is often used on direct current a regular enclosed arc carbon of proper gauge. Enclosed arc lamps are ordinarily operated with the upper as positive. (However, some use with excellent results, two flame carbons on direct current and then the upper is usually left positive.) On alternating current, flame upper and flame lower are used.

An experimental arrangement with greater control

<sup>1</sup> See Rey, *Ed. Elec.*, **32** (1902), 111; Child's book, "Electric Arcs," p. 132; Gage's book, "Optic Projection," p. 556; Rasch's book, "The Electric Arc Phenomena," p. 161. On flame arc see Czudnochowski, "Das Elektrische Bogenlicht," p. 541.

<sup>2</sup> For practical reference the following empirical equations are fairly close:  $V = \text{Arc Volts (ampereage 25 amperes)}$ . For arc voltages 0 to 60, Photographic Power =  $5.1V - 78 - 0.044V^2$ . For arc voltage 60 to 150, Photographic Power =  $1.47V - 0.0045V^2$ .

can be obtained with an ordinary 5 to 7 ampere enclosed arc lamp by shunting a part of the current around the usual lamp resistance and solenoid. This is apparently the simplest of the several possible electrical arrangements and was used in our chlorination work. The shunt resistance can be made adjustable, if so desired, by using a resistance box filled with carbon plates and arranged with a screw to operate at various pressures. A resistance made of nichrome wire is excellent for a cheap sound fixed resistance. The resistance should be capable of carrying 15 to 20 amperes at 55 volts without deterioration. In the experiments on chlorination, the shunt resistance was a large bank of incandescent lamps placed in a different room from the one where the light experiments were being conducted. The cheapness, convenience and adjustability of this arrangement are apparent, especially for temporary or experimental work.

The shunt arrangement is shown diagrammatically in Fig. II, for a *direct current* lamp. In permanent installations it is well to put on stronger carbon holders than are generally used in enclosed arc lamps. In

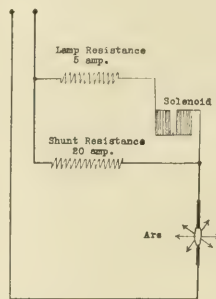


FIG. II

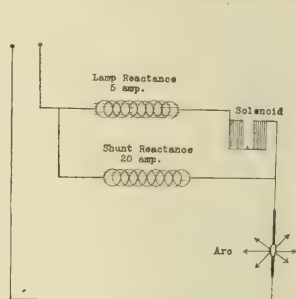


FIG. III

Electrical arrangement for connecting enclosed arc lamp on Direct Current (Fig. II) or on Alternating Current (Fig. III) to burn flame carbons at high amperage.

some cases the manufacturers of the enclosed arc lamp have furnished special holders to use when burning flame carbons in these converted lamps. If desired, the magnetic blow on the arc can be corrected by a small sheet iron shield around the holder which is carrying the current to the arc. However, this is not ordinarily done. In Fig. III there is given a parallel arrangement for an *alternating current* arc lamp using a reactance coil in place of a resistance because of the added efficiency and the desire to keep the lamp solenoid current in phase with the shunt current. In some cases, the lamp resistance (or induction coil) and the solenoid are not on the same side of the arc. In this case, the lamp wiring can be rearranged to fulfill this condition. If this is not done then a separate shunt would be required for each, *i. e.*, lamp resistance and lamp solenoid.

#### BRIEF SUMMARY OF THE ACTION OF LIGHT ON HALOGEN COMPOUNDS IN GENERAL

The light sensitiveness of halogens and their compounds may be briefly summarized as follows: Fluorine, in its compounds, is wonderfully stable to light. Silver fluoride is not light-sensitive like the other halo-

gen salts of silver.<sup>1</sup> Sulfur fluoride does not yield to ultraviolet light (or visible light) although the sulfur oxides and hydride are sensitive to ultraviolet light.<sup>2</sup> As Sheppard points out, the great stability of calcium fluoride is associated with a remarkable transparency to ultraviolet light. Chlorine responds to light chiefly in the blue, violet and ultraviolet. The absorption spectrum extends further into the ultraviolet than that of bromine.<sup>3</sup> In this connection it is of special interest to note that the photo-sensitiveness of silver chloride is apparently more marked in the ultraviolet than silver bromide.<sup>4</sup>

Bromine, in the free form, responds to light less in the ultraviolet than chlorine. On the other hand, hydrobromic acid is more easily decomposed by ultraviolet light than is hydrochloric acid. Iodine extends its spectrum still further towards the long wave lengths and hydriodic acid is decomposed by ordinary blue and violet light.

#### CONCLUSIONS

I—The flame arc at high amperage is in proportion to power taken, the most efficient known light source for photo-chemical reactions.

II—A single flame lamp can easily be made ten to twenty times more powerful, as to chemical effect, than any other single lamp except possibly the high-amperage enclosed arc which at 25 amperes on 110 line volts is about one-third as powerful as the flame arc at the same amperage.

III—The chemical action on solio paper by the light of the white flame arc through glass is nearly three times as powerful as that of the other colored flame carbons under like conditions.

IV—The chemical action on paraphenylenediamine (ultraviolet sensitive) by the light of the white flame arc light through glass is also three times as powerful as that of the other colored flame carbons.

V—The white flame arc is the better suited for use with glass vessels which are cheaper than the quartz vessels.

VI—The direct current white flame arc has a photographic effect on solio paper that can be expressed approximately by the following empirical equation within the limits of moderate arc voltages (40 to 80).

$$\text{Photographic Power} = KC^{1.8}(V-23)$$

$$C = \text{Current} \quad V = \text{Arc Voltage}$$

$K$  = a constant with a value of 0.0085 and an average deviation of  $\pm 0.0009$ . The standard of reference for this equation was photographic power on solio paper, which was called equal to 100 units at 25 amperes and 65 arc volts with a 110 volt direct current flame lamp which was used for making the tests.

VII—At high arc voltages the light and chemical power continue to increase as the arc voltage is raised; however, this is at a decreasing rate.

VIII—A means of using an enclosed arc lamp with flame carbons is here described. This consists in using a shunt around the lamp resistance and solenoid

on D. C. or a reactance coil in shunt around the lamp reactance coil and solenoid on A. C.

IX—Finally, there are opened up by the white flame arc, many new possibilities for controlling and changing chemical reaction. Light is a unique, uncontaminating, catalytic reagent for chemical reactions. We hope sufficient data are here presented to encourage others to take up these applications. As Sheppard says at the end of his book on photo-chemistry, "We are only at the beginning of the conscious utilization of the powers of light, as distinct from the unconscious enjoyment of them."

RESEARCH LABORATORIES  
NATIONAL CARBON COMPANY, CLEVELAND  
GOODYEAR TIRE & RUBBER CO., AKRON

#### THE MONOXIDE MONO RECORDER

By F. D. HARGER

Received September 12, 1916

In a large number of industries where a definite knowledge of the percentages of carbon monoxide present in flue gases is of the utmost importance to the manufacturing processes, such as chemical plants, cement, lime and brick plants, producer plants, etc., great need has been felt for an instrument which will automatically and continuously absorb and indicate as well as record the percentage of this gas.

Such an instrument is shown in Fig. I. It is a combination CO<sub>2</sub> and CO recorder and has lately been so improved that by the throwing over of a switch

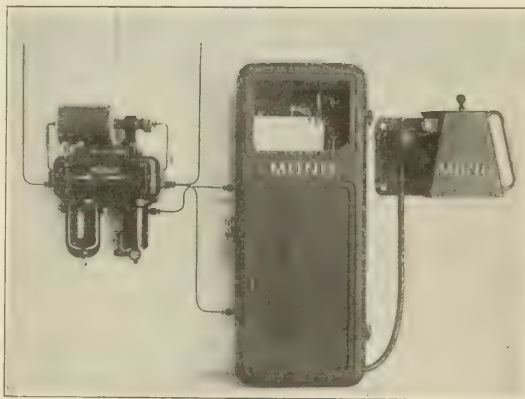


FIG. I

and a separate oxygen auxiliary also a continuous analysis of oxygen can be readily obtained. The intricate value of such an instrument, therefore, will be instantly appreciated.

The principle of the apparatus is based on that of the ordinary CO<sub>2</sub> recorder which is known well enough to need no description here.

Fig. I shows the Mono CO<sub>2</sub> recorder in the center with the filling device at the right-hand side and the monoxide auxiliary to the left. This latter is connected with the CO<sub>2</sub> recorder by means of a copper pipe of small diameter.

Fig. II is a general view of the monoxide auxiliary

<sup>1</sup> See Sheppard, "Photochemistry," p. 315.

<sup>2</sup> See Berthelot and Gaudechon, *Compt. rend.*, **156** (1913), 1243-1245.

<sup>3</sup> See Peskov, *Loc. cit.*

<sup>4</sup> See Eder's "Handbuch der Photographie," p. 292.



apparatus. *A* is the so called dioxide filter, *B* the moisture regulator, which serves to eliminate the condensation that may have taken place in the pipelines and furthermore to keep the gas entering the

into carbon dioxide, which then passes through the moisture regulator into the CO<sub>2</sub> recording apparatus where it becomes measured and the result is recorded in the ordinary way. The record thus gives CO + CH<sub>4</sub> in percentages.

Fig. III shows the design of the CO<sub>2</sub> recording instrument.

Position 2 cuts out the auxiliary altogether excepting the moisture regulator. The electric oven then does not need to be in operation and, therefore, the left cock should be on S. The gas passes directly to the moisture regulator and from there to the CO<sub>2</sub> recording apparatus where the per cent of carbon dioxide is measured and directly recorded on the chart, which has a very wide range, so that fractions of one per cent are plainly visible.

Fig. IV shows a reproduction of a chart taken from one of the instruments installed on board the *S. S. Christianiafford*. The size shown is a little over a fifth of its actual size. (As a matter of interest it may be said here that these instruments in this case are suspended in universal joints, making the same adaptable for marine use.)

The chart shows very distinctly the carbon dioxide and carbon monoxide readings. Those showing about 11 per cent average are the CO<sub>2</sub> records and those

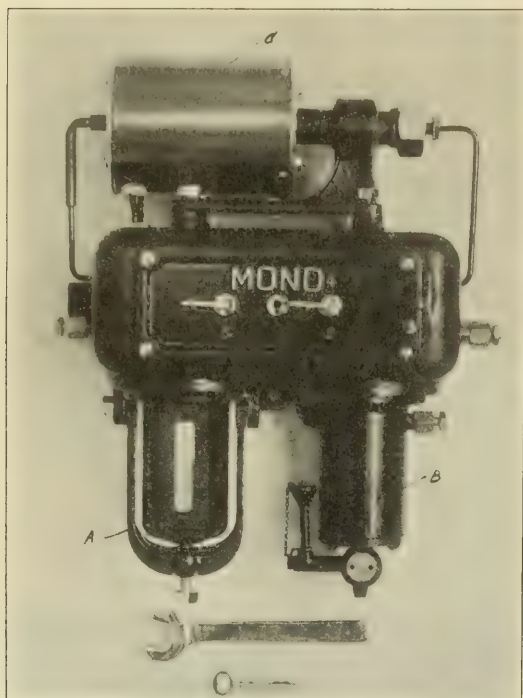


FIG. II

recording instrument always at a constant temperature. *C* is the electric oven for the oxidation of carbon monoxide and hydrocarbons. The cast iron body of the apparatus serves to cover and to protect the connections between the oven, the CO<sub>2</sub> filter and the moisture regulator. Moreover it is provided with two cocks, one on the right and one on the left-hand side. These can be locked in the desired positions by lock and key of a very ingenious design. The left cock controls the current to the electric oven and can be turned in two positions, T. for "on" and S. for "off." The cock to the right regulates the passage, which the gas, drawn in by the recorder, must take according to what analysis is desired. This cock can be turned four ways: 1, 2, 3 and 4.

Position 1 is used for the analysis of the unburnt gases; *viz.*, carbon monoxide and carbon hydrates. Inasmuch as the electric oven should be working at such time, the cock to the left must be in Position T. The drawn-in gases then pass through the carbon dioxide filter, which is filled with an absorbent, capable of completely absorbing all carbon dioxide contained in the gas. The remainder, *i. e.*, carbon monoxide and carbon hydrates, passes into the electric oven where the heat in combination with another reagent causes the oxidation of the carbon monoxide and hydrocarbons

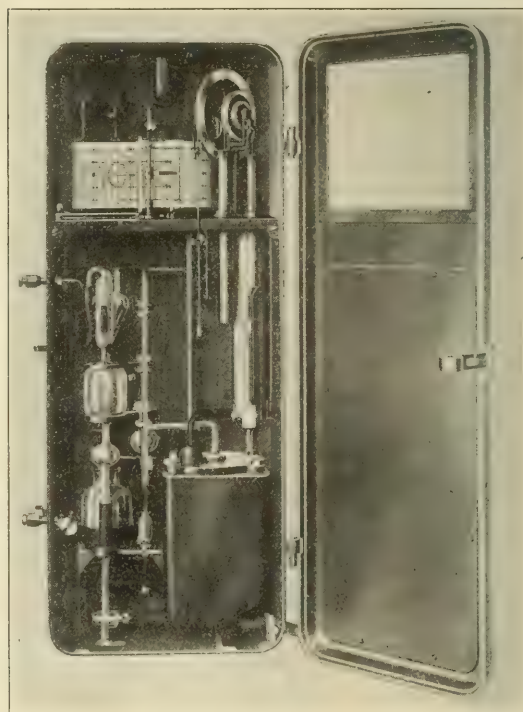


FIG. III

not exceeding the 1 per cent line are the CO records taken from the last pass of marine boilers.

Fig. V shows the recorder installed on ship board.

Position 3 is used for checking the complete ab-

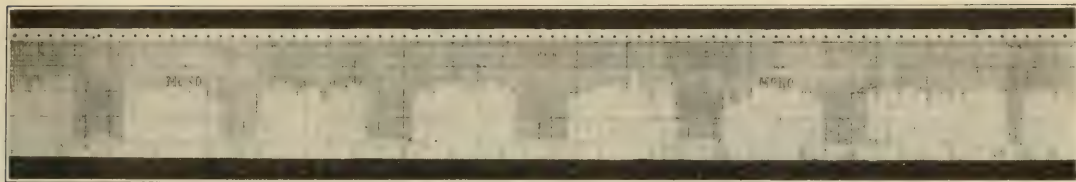


FIG. IV

sorption of all carbon dioxide in the  $\text{CO}_2$  filter. This possibility of easy checking is of the utmost importance because should this filter not absorb all  $\text{CO}_2$  originally contained in the gas, the subsequent oxidation and measuring would be of no value as the result would not truly indicate the amount of  $\text{CO}$  therein. When the cock to the right is in this position the gas is first allowed to pass through the filter where it is freed from all  $\text{CO}_2$ . From there it passes directly into the moisture regulator where it is brought to the proper temperature and then it passes into the  $\text{CO}_2$  recorder to be measured for  $\text{CO}_2$ . If the filter has performed its

plate so that the saturation of the absorbent may be observed without disturbing the apparatus. The absorbent is originally colorless but becomes red as it absorbs  $\text{CO}_2$ , which color gradually spreads over the whole filter and remains as long as the absorbent retains its absorbing quality. As this latter diminishes, the original appearance of the absorbent is resumed. Thus the filter shows when it needs replenishing. The absorbent will last from one to two weeks according to the number of analyses desired and is re-charged with no more labor than is involved in the winding of a clock.

Position 4 is used for the checking of the pipe-lines for leaks.

With this apparatus the analysis is made entirely automatically and at a rate of up to 50 per hr. The correctness of the analyses is readily checked by the simple turning of a cock as above described. Besides, the same instrument can be used for carbon dioxide as carbon monoxide and if provided with a second auxiliary also for oxygen and should, therefore, find a great field in the various industries and power plants.

The instrument as shown in Fig. III is adaptable for recording sulfur dioxide gas, only in this case the parts of the machine that are coming in contact with the gases within the machine, are made of special metal which will withstand their corrosive action. Either  $\text{KOH}$  or an iodine solution is used as absorbent.

21 PARK ROW, NEW YORK CITY

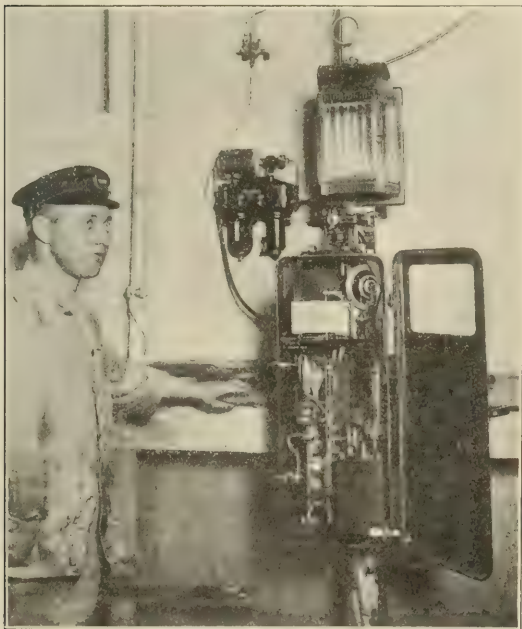


FIG. V

function properly, there should be no  $\text{CO}_2$  left and the recorder should score zero, which will be found to be the case when the apparatus is in proper adjustment. By means of this operation one can satisfy oneself that the gas, which passes to the electric oven when the cock at the right is in Position 1, is free from  $\text{CO}_2$  and when after passing it through the oven it shows a certain amount of  $\text{CO}_2$ , this must have been caused by the burning of the  $\text{CO}$  and  $\text{CH}_4$  to  $\text{CO}_2$  and can be relied upon as correct. The absorbent in the oven will last indefinitely.

The carbon dioxide filter is provided with a glass

## A NEW APPLICATION OF THE BUNSEN VALVE

By ALAN LEIGHTON

Received September 18, 1916

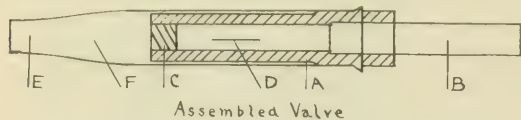
Everyone who has worked with suction pumps in the laboratory knows that occasionally the water pressure goes off, the pump backs up, and the filtrate in the filter flask becomes contaminated. This can be prevented of course by the use of a Woulfe bottle between the pump and the suction flask, but even this safety flask is not always a safeguard, for it may become filled and overflow. This is particularly true if one is trying to distill under a vacuum. It would seem that some simple valve could be constructed that would prevent this danger.

There are several such valves mentioned in the literature but they all have their limitations.<sup>1</sup> Since

<sup>1</sup> A. Kunn, *Chem. Ztg.*, **34**, 1136; *Chem. Abs.*, **5**, No. 3, 397; *Anon.*, *Chem. Ztg.*, **34**, 50; *Chem. Abs.*, **3**, 2763; A. Berg, *Bull. soc. chim.*, **12**, 621-3; *Chem. Abs.*, **6**, No. 17, 2759; R. Behrend, *Chem. Ztg.*, **35**, 807; *Chem. Abs.*, **5**, No. 21, 3527; C. Gerhardt, *Z. anal. Chem.*, **48**, 460; *Chem. Abs.*, **3**, No. 23, 2763; H. Stalzenberg, *Chem. Ztg.*, **32**, 832; H. B. Hutchinson, *Chem. News*, **109**, 99.



these valves all seemed complicated, the so-called Bunsen valve suggested itself as being very simple, and adaptable to the purpose. Therefore a piece of heavy walled, pure gum tubing was taken and drawn over the end of a glass tube, the end of the tubing plugged, and the usual slit made in the side. Another piece of glass tubing was taken of the proper internal diameter to admit the rubber tube and at the same time so small that it would bind where the



first tube was thrust into it. This made the rear end of the valve serve as a rubber stopper and did away with the use of such a stopper.

The operations can best be explained by the use of the accompanying diagram. Tube *B* is about  $\frac{3}{8}$  in. in external diameter and  $2\frac{1}{4}$  in. long. The rubber tube *A*, of about the same length, is  $\frac{1}{2}$  in. tubing with an internal diameter of  $\frac{1}{4}$  in. Tube *B* is forced into the rubber tube for about  $\frac{3}{4}$  in. The opposite end of the tube is plugged with a glass rod, *C*, and a  $\frac{1}{2}$  in. slit cut into the side of the tube at *D*. The outside tube *E* is made from a glass tubing about  $\frac{5}{8}$  in. internal diameter, and is about 4 in. long after one end has been drawn out to fit the ordinary pressure tubing used in the laboratory. If the end *E* is connected to the suction pump and the tube *B* to the flask, when the suction is turned on, air can pass out through the slit, which immediately closes if the pressure is lessened and effectually prevents any backing up of water from the pump. It has been found in practice that if the suction goes off and the vacuum decreases in the filter flask, the valve is released gradually but not soon enough to any more than fill the back end of the valve with water.

This application of the Bunsen valve has the advantage that it is very simple and is made of apparatus that is on hand in every laboratory. It is also effectual and can be easily constructed.

The only possible fault with the apparatus is that the tubes sometimes collapse, but this danger is overcome by the use of the heavy-walled rubber tubing. In case the heavy tubing were not obtainable, possibly a modification of the Bunsen valve published by Albert Kreider<sup>1</sup> could be incorporated into the apparatus. It consists of an ordinary stout glass tube sealed at one end and drawn out in the middle with an opening in the constriction. A piece of rubber tubing containing a smooth slit is placed over this. The collapse of the rubber which is so common on the Bunsen valve is thus rendered impossible. The valve works much better when it is lubricated with glycerol.

RESEARCH LABORATORY  
THE GOODYEAR TIRE & RUBBER COMPANY  
AKRON, OHIO

## A NEW TUBE FOR SODA LIME—A NEW ABSORBENT FOR CARBON DIOXIDE IN STEEL ANALYSIS

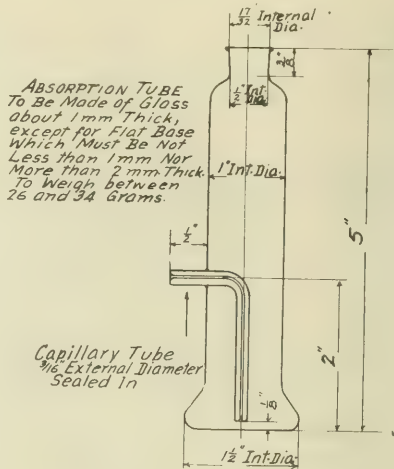
By G. I. KELLEY

Received June 1, 1916

**THE NEW TUBE**—The tube illustrated was designed by H. L. Prevert in this laboratory and has given excellent satisfaction in use here during 3 years. It is for the purpose of calling wider attention to the advantages of this device that this article has been written.

In filling the tube a small amount of absorbent cotton is placed at the bottom of the tube under the end of the capillary tube. This is covered with calcium chloride (20 mesh) to a depth of  $\frac{3}{4}$  in. A thin layer of cotton separates this from soda lime which is next added until the bulb is nearly full. The top of the soda lime is also covered with a small amount of cotton. The tube is closed with a rubber stopper carrying a short length of capillary tubing bent at right angles.

Tubes are always weighed filled with oxygen, change of weight by diffusion having been found to be negligible where the tubes are in constant use. With new



tubes, or with tubes which have been allowed to stand more than 30 min., oxygen is used to displace air before weighing. The outlet of the tube is connected with a small bottle containing clear barium hydroxide solution. This serves as a bubble counter to give an indication of the progress of the combustion and to detect complete saturation of the soda lime in the tube.

**THE NEW ABSORBENT**—When the tube described above was first used the soda lime then available in the market was of such quality that one tubeful would absorb 2.5 g. of carbon dioxide. Much of the soda lime now offered absorbs only 0.759 g. By preparing our own soda lime we were able to make a product which would absorb 2.5 g. to 4 g. of carbon dioxide. In the course of our experiments, however, we tried combinations of sodium hydroxide and asbestos with very much better results.

The new absorbent, which we call "soda asbestos," is made as follows: Dissolve 1 kg. of sodium hydroxide in a liter of water. To each 500 cc. of this solution add

<sup>1</sup> *Am. J. Sci.*, [3] 50 (1895), 132-134; *J. Chem. Soc., Ab.* LXX, 2 (1896), 161.

1 kg. of pulverized NaOH. When this has been well stirred in, add shredded asbestos gradually, continuing the stirring until the mixture no longer appears capable of wetting more asbestos. The whole mass is then heated in an air bath at 150 to 180° for 4 hrs. During the early part of the heating, additional quantities of asbestos are added from time to time until it presents the same appearance as before heating. After cooling, it is ground in a coffee mill until most of it passes a 10-mesh sieve. A tube filled with this absorbent takes up 8 to 10 g. of carbon dioxide, corresponding to 160 to 240 carbon determinations, using the full factor weight on a steel containing 0.5 per cent carbon.

RESEARCH LABORATORY, MIDVALE STEEL COMPANY  
PHILADELPHIA

### LABORATORY TABLE TOPS AGAIN

By HILTON IRA JONES

Received August 17, 1916

Much has been written about various sorts of laboratory table tops—wood, alberene and tile advocates have all had their say. In the past twenty years I have worked and conducted classes on every sort of top—glass, tile, cement, slate, alberene stone and wood. When I came to Dakota Wesleyan I found a new one. Five years ago Dr. Sterling Temple, now of the University of Minnesota, installed the tables here. The tops are ordinary soft pine flooring on which is laid two sheets of tar paper, and this is covered with large sheets of asbestos slate, two to a table. It is one-eighth inch in thickness. The asbestos slate is screwed on, the holes being counter-sunk and filled above the screw head with asbestos cement. The tables every year have been treated with a gasoline solution of paraffin concentrated enough so that it would set to a jelly consistency when cold. This solution is brushed on hot. We have found this method of paraffining much better and quicker than the old ironing in process. This paraffin treatment has given the tops a polished appearance but is really unnecessary and adds nothing to their immediate serviceability or life.

This asbestos top is so much better than any other top I have ever seen that I am sure it would be extensively used if its advantages were more widely understood. It has low first cost, long life, and any one can put it on. I feel certain our table tops will be in good shape twenty years hence. They are fully as good now as when first installed. The asbestos top with the tar paper beneath it has elasticity, and I find there is even less glassware broken on it than on a wooden top. Alberene stone is especially objectionable for beginners for this reason. The asbestos slate top is entirely unaffected by acid or alkali even though

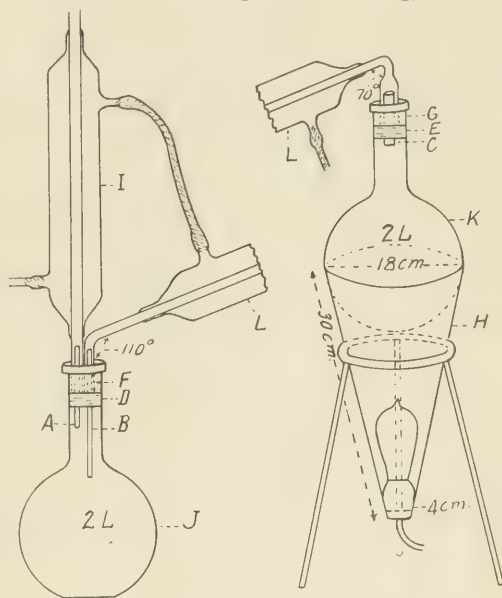
boiling hot. Moreover, it is so poor a conductor of heat that even thick glass containing hot liquids may be set upon it without breaking. This does away with the use of suberite mats such as are required on stone, tile or glass tops. The asbestos slate top has everything to commend it, and after four years of use I have yet to discover a single fault.

DAKOTA WESLEYAN UNIVERSITY  
MITCHELL, SOUTH DAKOTA

### A SIMPLE MERCURY SEALED ETHER STILL

By O. C. SMITH AND D. G. MORGAN  
Received June 27, 1916

The heater *H* was constructed from a sheet of galvanized iron and an electric light socket fitted into the bottom. The corks which are inserted into the necks of the flasks at *D* and *E* should be close-grained and fit tightly so as to hold the mercury at *F* and *G*. It is not difficult to make a mercury-tight fit if care is used in selecting the corks and they are coated with a little vaseline before inserting. Before using, the flasks



should be washed with ether to remove the excess vaseline. The glass tubes *A*, *B*, *C* are about 5, 5, 10 mm., respectively, in diameter. The reflux condenser *I* prevents the escape of ether.

To remove the ether from the receiving flask *J* lift up the condenser *I* and insert a small siphon through *A*.

OKLAHOMA AGRICULTURAL EXPERIMENT STATION  
STILLWATER

## ADDRESSES

### A CENSUS OF THE ARTIFICIAL DYESTUFFS USED IN THE UNITED STATES<sup>1</sup>

By THOMAS H. NORTON

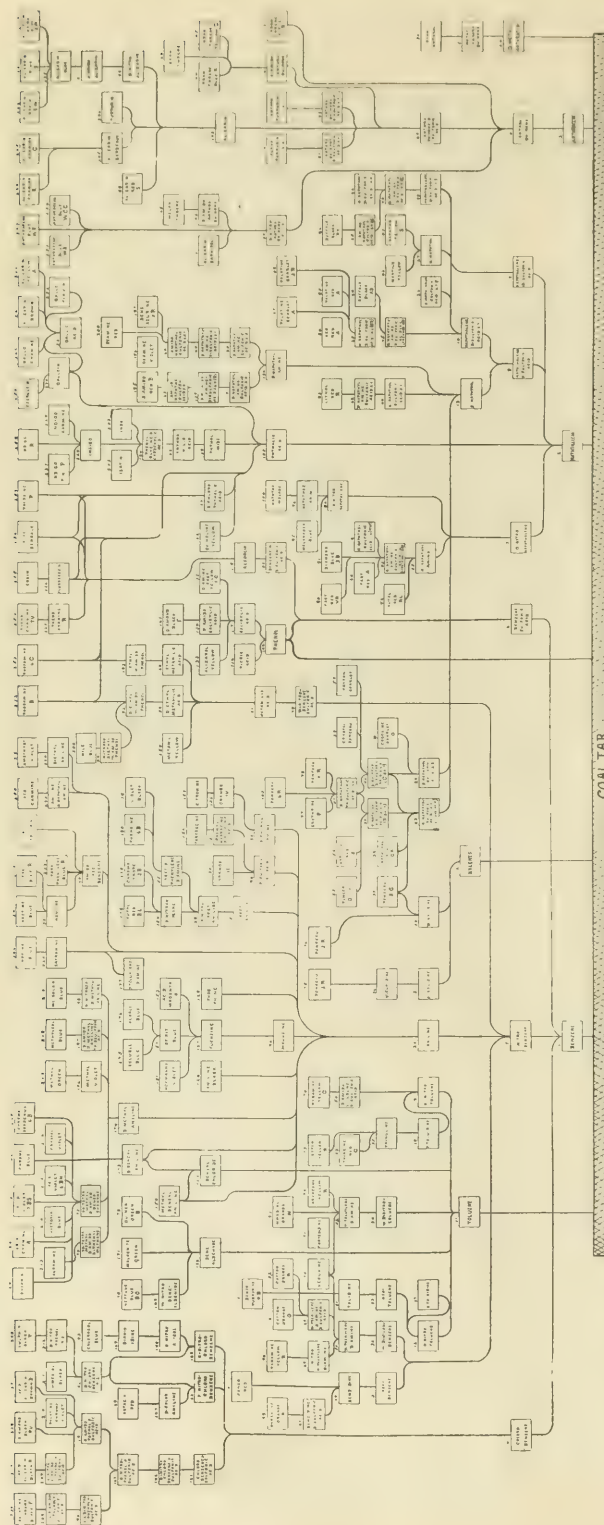
The necessity for a complete enumeration of the artificial coloring matters, regularly consumed by the various manufac-

<sup>1</sup> Address delivered before the American Chemical Society, at the New York Meeting, during the Symposium on "American Dyestuff Manufacture."

turing industries of this country soon became evident when these branches were threatened in 1914 by a dyestuff famine, as a result of the great European war.

Those who took into careful consideration the possibility of creating an independent American coal tar dyestuff industry were obliged to study closely a number of factors bearing upon this exceedingly complicated question. Among these were such items as the supply of crude materials, the chemists and





DERIVATION OF LEADING COAL-TAR COLORS, ADAPTED FROM THE "COAL-TAR TREE" OF H. VON BRUNCK, DIRECTOR OF THE "BADISCHE ANILIN- UND SODA-FABRIK." BY THOMAS H. NORTON

chemical engineers available, the probable attitude of the European interests, hitherto furnishing our synthetic dyes, upon the return of normal international conditions, the requisite fiscal and other legislation essential to safeguard American enterprise and capital against unfair competition on the part of such foreign rivals, etc.

First and foremost, however, came the factor of *quantity*. What is the total annual consumption of artificial colors in the United States? How many different dyes are in current use? What is the average annual consumption of each of these dyes?

The necessity of exact information on these three points is self-evident to some. For most, a brief explanation may be helpful.

In a general way we know how the great dyestuff industries of Germany and Switzerland are organized. We understand the relations of capital, of technical staff, etc., to output. From an economic standpoint it is necessary to know the total extent of the American market for this class of products, in order to estimate approximately the amount of capital required for a comprehensive industry, the number of trained chemists and engineers needed, and the quantities of coal-tar crudes to be provided. These form the main links in the chain connecting the gas works and the coke plant yielding coal tar and the gases laden with benzene and its homologues, with the multitude of mills and shops in which synthetic colors are employed to produce chromatic effects upon wares of the most varied nature—paper, textiles, leather, wood, ink, varnish, fur, feathers, foods, beverages, etc.

While such leading data are of prime importance from a general economic standpoint, of still greater value are the details concerning the specific products of the synthetic color industry.

#### NECESSITY OF A CENSUS OF DYES

There are nearly 1,000 coal-tar dyestuffs of recognized standing in the tinctorial world; *i. e.*, their chemical composition, or at least the methods of preparation, are publicly known. About twice as many are regularly manufactured, and enter into international trade, regarding the preparation or the composition of which little or nothing has been published. Many colors of both categories are encountered commercially in the form of several marks or brands. These represent slight modifications of the primary dye, sometimes in regard to shade, often in regard to convenience of application. The form in which a dye is prepared for use on cotton may not be the best form for the needs of the silk dyer. The requirements of the feather dyer may be quite different from those of the manufacturer of ink.

It is essential that the organizers of a national color industry know, with a certain approximation to accuracy, how much annually is consumed of each primary dye, and how much of each minor modification is employed. Without such data a manufacturer cannot calculate the size and number of the units to be constructed for the production of any given dye, and he is at an equal loss as to the equipment necessary to manufacture it in the different modifications of current use.

Again, the industry is one of great complexity, involving a high degree of coördination and of careful planning to avoid material loss in the way of by-products. In the various steps intervening between

a coal-tar "crude" and a finished dyestuff, each chemical reaction in the sequence is apt to produce certain percentages of closely allied compounds, isomeric substances as a rule. These latter may possess the same general chemical composition as the product more directly sought. The arrangement of the atoms in the molecule is, however, quite different. As a result, physical and chemical properties are totally unlike those characterizing the main substances. Such by-products possess, as a rule, distinct technical and commercial value. One may serve to make an entirely different dyestuff, another may be the raw material for manufacturing a valued medicinal; a third may be employed in the production of a photographic developer, etc.

It is evident, therefore, that the establishment of a synthetic color industry means an elaborate study of a multitude of inter-related operations, allied furthermore with numerous products in a group of closely connected industries, based likewise upon the use of coal-tar crudes. To some extent the changing whims of fashion enter into play. Back of every plan and calculation stands, however, the dominant factor of quantity.

It is now generally recognized that any intelligent effort to build up a comprehensive, self-contained, American coal-tar chemical industry must rest upon the solid foundations of accurate statistical data concerning the American market for artificial colors. In no other way can the creators of such an industry avoid duplication, overlapping, waste, and blundering, tentative struggles to adjust productive mechanism to a vague, indefinite demand. Without such fundamental data the future industry will be heavily handicapped by permanent overhead charges, accumulated as the result of being forced to feel its way in the dark, chemically, mechanically, and commercially.

If the coming American dyestuff industry is to hold its own successfully against foreign competition, it must be free from any unnecessary shackle. It must start into existence during these years of crimson-splashed struggle for Europe—of golden opportunity for this Republic—at the point where a brusque order to halt has been given the giant factories on the Rhine, the Main, and the Spree. It must utilize to the full all the gathered stores of experience accumulated during the six decades since Perkin's epochal discovery, and become a world factor in the seventh period of the history of synthetic color, at whose portal we now stand.

To no one is this country more indebted than to Dr. Bernhard C. Hesse, of New York, for a clear, forcible presentation of the complexity of the synthetic dyestuff industry and of the pressing necessity of accurate data on the domestic consumption of artificial colors. Attention should be directed to his briefer studies on the subject in the JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY, and to his more exhaustive paper read before the National Association of Cotton Manufacturers, in April, 1915, and published in the *Textile Manufacturers' Journal*, May 1, 1915, p. 60.

#### ACTION OF THE BUREAU OF FOREIGN AND DOMESTIC COMMERCE

Early in 1915 the embargo came into force, shutting off German dyes from this country. Long before, the relatively small supply of colors from England, France, Belgium and Holland had practically ceased and the somewhat more important source in Switzerland was threatened with paralysis.

The Bureau of Foreign and Domestic Commerce in Washington was following with the keenest interest, and even with anxiety, the initial steps taken bravely and resolutely by a small band of far-sighted American men, some manufacturers, some capitalists—all patriots—convinced that finally the opportunity had arrived to build up a genuinely national coal-tar chemical industry.

In the earnest desire to second their efforts and facilitate their plans, as well as to insure the most favorable and economical

conditions for the rapid evolution of the new industry on a permanent basis, it was promptly recognized, in harmony with the reasoning detailed above, that nothing could be of such direct assistance as a "census" of the dyestuffs consumed normally in this country. Plans were carefully laid to carry out the work as expeditiously, accurately, and fully as the very limited appropriations at the command of the Bureau for such general purposes would permit.

#### HOW THE CENSUS WAS TAKEN

First of all it was necessary to decide upon the *modus operandi*. It was suggested by some, who had early recognized the desirability of such a "census," that the only available method for securing the needed data was to appeal to all consumers of artificial colors for their coöperation. It was thought that a ready response would be given to circular requests for detailed information regarding the annual consumption of coal-tar dyes by each user of the same. It was proposed, in order to overcome the customary repugnance of manufacturers to communicate facts of this nature, that the replies should be sent to some central financial institution, which would guarantee secrecy in collating the numerical information thus gathered.

A careful analysis of the problem showed that any such method of collecting data was impracticable. It would be impossible to secure a complete list of all users of dyestuffs in scores of trades and manufacturing branches. Assuming that figures could be obtained from all users of colors, their compilation would be a herculean task. Suppose that 5 tons of Congo Red are consumed annually in this country. This amount might be divided up among several thousand consumers, in lots ranging from 5 to 100 pounds.

With a somewhat elementary knowledge of human psychology, it was furthermore certain that no replies could be expected from the great majority of the recipients of circular requests. Indifference, suspicion, or pure laziness are serious factors to overcome.

#### BRITISH ATTEMPT TO TAKE A CENSUS OF COLORS

The correctness of this conclusion has recently been abundantly verified by trans-Atlantic experience. British textile and allied interests have been forced to deal with a far more serious "dyestuff famine" than has been the case in the United States. There was a similar determination to build up a genuinely national color industry. The necessity of a dyestuff "census" was likewise recognized as of paramount importance. An influential committee, representing makers and consumers of dyes, took the matter in hand. Appreciating the futility of dealing directly with the multitude of individual users of colors, the committee decided to collect its statistics through the various powerful organizations of trades employing large quantities of dyestuffs and then double the results, thus roughly approximating at the entire national consumption of the various colors. After months of labor the committee was forced, in November, 1915, to report a practical fiasco. Replies were secured from but 19 associations or large individual consumers. The figures obtained covered but 3,145 short tons, perhaps 12 per cent of the national consumption.

#### FEATURES AND VALUE OF THE CENSUS

The method adopted by the Bureau of Foreign and Domestic Commerce was much more simple, direct and accurate. As in the case of Great Britain, nearly nine-tenths of the normal American consumption is derived from European sources. It was decided to use the data based upon the imports of artificial colors into this country during the 12 months ending June 30, 1914—a month before the outbreak of the present war. The remaining tenth is covered by the returns of the Bureau of the Census for the domestic coal-tar dyestuff industry based upon the production of the calendar year 1914. No serious



## SUMMARY OF THE MOST IMPORTANT COLORS IMPORTED BY U. S. DURING FISCAL YEAR 1913-14

The abbreviation V. M. denotes "various marks." The serial numbers employed correspond to those found in Schütz's "Farbstofftabellen" (edition of 1911). Numbers preceded by letters refer to colors regarding the manufacture and chemical composition of which little or nothing is known. Azo dyes in this category are indicated by A. Sulfur colors by S. and other dyestuffs of unknown composition by U.

## Class I (10,000 to 100,000 lbs.)

Serial No.	COMMERCIAL NAME	Lbs.	Invoice Value	Serial No.	COMMERCIAL NAME	Lbs.	Invoice Value	Serial No.	COMMERCIAL NAME	Lbs.	Invoice Value
<b>Nitroso and Nitro Colors</b>											
4	Naphthol Green	19,146	\$ 2,902	275c	Chrome Fast Black (V. M.)	35,099	\$ 10,532	A176	Benzo Fast Heliotrope (V. M.)	13,018	\$ 5,541
9	Direct Yellow	71,399	11,295	277	Anthracene Black	17,793	2,647	A181	Benzo Green (V. M.)	16,506	2,850
9a	Naphthamine Yellow (V. M.)	42,180	6,748	279	Benzo Fast Scarlet	36,674	9,010	A203	Benzo Red 10 B, 12 B	19,420	4,715
9b	Direct Yellow (V. M.)	79,055	16,784	283	Bismarck Brown	27,576	5,352	A210	Benzo Rhoduline Red	11,873	1,813
9c	Direct Yellow B	29,123	2,766	288	Palatine Chrome Black	18,985	1,607	A215	Brilliant Fast Blue (V. M.)	11,553	3,399
10	Stilbene Yellow	50,457	7,164	296	Cotton Yellow	21,437	6,161	A251	Cashmere Black	12,269	1,881
10a	Stilbene Yellow R. N.	34,588	6,305	303	Renol Brilliant Yellow	12,786	3,290	A227	Diazo Brilliant Scarlet (V. M.)	38,909	14,210
11	Chloramine Orange	24,688	5,914	307	Congo	12,040	1,687	A242	Diazo Fast Black (V. M.)	29,330	7,476
13a	Diphenyl Orange GG	13,646	3,938	308	Diazo Black	62,854	8,257	A259	Diazo Black (V. M.)	12,043	2,019
14	Diphenyl Chrysoline	9,898	3,071	312	Congo Corinth	39,748	6,030	A266	Helio Bordeaux BL	14,703	793
18	Diphenyl Fast Yellow	9,656	2,983	313	Congo Rubine	46,113	6,329	A277	Orange RO	24,288	2,246
<b>Pyrazole Colors</b>											
19	Fast Light Yellow	33,514	10,272	319	Diamine Scarlet	28,887	1,938	A285	Phenylamine Black	14,066	1,619
20	Flavazine Yellow	19,000	4,927	326	Oxy Diamine Violet	11,514	1,552	A286	Pluto Black (V. M.)	30,010	6,034
20a	Flavazine (V. M.)	62,375	10,700	327	Diamine Violet N	13,107	2,840	A292	Pluto Black (V. M.)	14,580	2,542
22	Xylene Yellow	23,074	9,750	333d	Develop Black	17,495	4,333	A303	Alphanol Black (V. M.)	30,189	3,124
<b>Azo Colors</b>											
33	Chrysoidine	63,303	8,585	334	Diphenyl Blue Black	26,240	4,415	A336	Azo Wool Violet (V. M.)	12,944	3,298
37	Croceine Orange	11,366	1,535	335	Naphthamine Black	11,636	2,568	A346	Diamine Catechine (V. M.)	66,876	14,942
38	Orange G	48,456	7,159	337	Benzo Blue	19,035	7,789	A351	Diamine Fast Blue (V. M.)	28,880	7,227
45	Brilliant Lake Red R.	31,674	2,337	338	Naphthamine Blue	11,707	2,455	A355	Diamine Fast Orange (V. M.)	17,387	4,819
46	Azul Red	49,847	5,379	343	Diamine Fast Red	47,724	17,131	A361	Diamine Fast Orange (V. M.)	14,091	4,315
58	Mordant Yellow	26,570	4,112	344	Diamine Brown	63,716	12,457	A362	Diamine Neron BB	36,982	6,204
58a	Alizarin Yellow (V. M.)	59,000	7,676	345	Oxamine Red	13,471	4,015	A367	Diamine Orange (V. M.)	17,068	2,851
58	Orange 13, 14	10,974	2,634	392	Tolylene Orange	55,562	13,236	A368	Diamine Sky Blue (V. M.)	41,115	7,574
61	Victoria Yellow	47,126	10,998	405	Benzopurpurine 10 B	47,708	11,181	A384	Oxy Diamine Brown (V. M.)	23,498	3,810
63	Azo Acid Yellow	8,258	8,354	410	Benzazurine (V. M.)	78,699	21,018	A385	Oxy Diamine Carbon (V. M.)	34,388	7,864
64	Janfuchsine	68,055	9,375	416	Brilliant Azurine 5 G	18,395	3,206	A388	Para Diamine Black (V. M.)	18,634	2,690
66a	Amido Naphthol Red	36,000	25,970	418	Diamine Brilliant Blue	11,592	2,496	A403	Salicine Blue B	16,224	8,449
70	Brilliant Orange O	21,480	8,835	419	Chicago Blue R. W.	15,176	3,364	A404	Amido Naphthol Black 4 B, R. K.	10,750	1,219
73	Helio Fast Red	13,413	2,141	421	Oxamine Blue B	14,091	2,436	A414	Azo Acid Black (V. M.)	19,500	3,042
73a	Lithol Fast Scarlet	36,295	9,287	421a	Oxamine Blue (V. M.)	21,800	3,749	A418	Azo Acid Black (V. M.)	19,500	3,042
80a	Wool Scarlet	29,888	6,293	426	Benzenamine Pure Blue	12,881	5,663	A430	Fast Mordant Blue B, R	17,000	4,612
82a	Ponceau (V. M.)	20,972	1,931	428a	Direct Blue (V. M.)	21,322	5,366	A437	Naphthalene Blue B, DL	28,000	5,102
88a	Acid Anthracene Brown (V. M.)	30,555	7,932	449	Trisolun Brown	16,781	5,255	A439	Victoria Scarlet R	22,400	2,379
96a	Chrome Fast Yellow	15,165	3,056	456a	Benzo Fast Blue (V. M.)	26,559	8,439	A444	Direct Green (V. M.)	31,194	5,091
102	Diamond Flavine G	23,080	4,226	462	Direct Deep Black	32,830	5,092	A451	Heligoland Black F. F. N.	25,132	4,151
112	Bordeaux B	10,383	1,474	462c	Cotton Black (V. M.)	91,485	22,206	A469	Oxychrome Brown (V. M.)	10,490	2,235
112a	Claret Red	14,338	1,291	462d	Union Black (V. M.)	61,218	9,044	A472	Oxychrome Yellow (V. M.)	10,085	1,985
118	Geranine	18,917	6,090	469	Chloramine Black	20,095	5,278	A478	Triazol Blue (V. M.)	10,148	1,580
126a	Union Blue (V. M.)	15,353	2,116	474	Oxamine Green B	19,505	3,951	A485	Triazol Brown (V. M.)	17,067	2,854
132	Lake Red P	40,345	2,019	474a	Diamine Green (V. M.)	23,832	5,134	A489	Triazol Dark Blue (V. M.)	19,489	2,647
137	Acid Yellow	35,982	6,313	476a	Benzamine Brown 3 G	16,988	2,470	A515	Brilliant Scarlet 2 R, 4 R	12,565	1,425
139	Orange IV	11,238	1,966	477a	Naphthamine Brown (V. M.)	48,734	9,452	A524	Anthracyl Chrome Blue 2 B, D	24,979	6,385
140	Carumeine	39,269	6,257	478	Columbia Green	24,749	4,723	A527	Croceine Scarlet MO	12,210	2,235
141	Azo Yellow	59,894	13,755	478a	Direct Green (V. M.)	19,313	4,291	A531	Acid Blue Black	15,501	3,023
141a	Azo Flavine (V. M.)	20,114	3,151	485a	Benzo Brown (V. M.)	41,905	7,125	A532	Acid Chrome Blue	12,952	4,365
141b	Indian Yellow (V. M.)	10,537	2,392	490a	Cotton Brown (V. M.)	23,975	5,207	A533	Acid Fast Green 8 B	14,050	7,068
146	Azo Fuchsine	17,819	2,585	<b>Unclassified Azo Colors</b>							
146a	Azo Fuchsine 6 B	13,206	1,867	A 6	Chrome Fast Black (V. M.)	76,451	10,172	A541	Diazogene Black (V. M.)	30,042	6,813
151a	Orange R O	90,174	7,395	A 12	Columbia Brown (V. M.)	20,793	3,073	A550	Direct Black ABC, C	15,245	2,804
152	Permanent Red 4 B	44,850	14,513	A 16	Columbia Fast Blue (V. M.)	84,661	18,879	A552	Direct Chrome Brown	12,178	2,665
152a	Permanent Red (V. M.)	56,545	7,403	A 28	Naphthogene Blue (V. M.)	33,847	6,824	A556	Drazaline Blue (V. M.)	10,831	4,425
154	Palatine Chrome Brown	18,264	4,674	A 32	Nerol (V. M.)	65,441	9,751	A566	Drazaline Brown (V. M.)	21,756	4,979
150a	Vigoureux Fast Black T	16,000	3,522	A 44	Columbia Blue B	21,784	8,876	A593	Drazaline Sky Blue FF	10,940	5,204
160	Fast Brown N	67,531	6,200	A 69	Corvan Black (V. M.)	10,033	1,870	A600	Excelsior Black	59,956	16,690
161	Fast Red A	46,359	5,463	A 71	Cotton Black (V. M.)	24,505	4,843	A603	Hydrazol Black	10,981	1,629
163a	Carminoine (V. M.)	17,107	2,427	A 81	Lithol Fast Orange R	36,641	4,381	A605	Black CB, DB	51,694	7,499
163b	Chrome Blue (V. M.)	53,404	19,874	A 85	Oxamine Black (V. M.)	50,032	10,472	A612	Chicago Red III	13,195	2,420
164a	Diamond Blue R	20,117	3,800	A 98	Oxamine Brown (V. M.)	93,454	22,569	A617	Diphenyl Blue (V. M.)	12,677	3,842
168	Amaranth	73,973	9,420	A 102	Oxamine Copper Blue RR	10,222	1,941	A622	Diphenyl Deep Black (V. M.)	21,098	4,216
168b	Wool Red (V. M.)	11,497	2,283	A 104	Oxamine Dark Blue (V. M.)	23,810	4,246	A629	Diphenyl Deep Black (V. M.)	18,021	4,667
169	Cochineal Red	29,984	3,669	A 108	Oxamine Dark Brown G. R.	10,599	1,312	A664	Chlorantine Brown (V. M.)	18,267	4,034
173a	Lithol Red (V. M.)	67,515	5,029	A 122	Palatine Chrome Blue BB	42,244	4,679	A674	Chrome Fast Brown (V. M.)	12,204	3,550
177	Mordant Yellow	85,003	11,280	A 124	Palatine Chrome	19,665	6,452	A682	Chrome Fast Green (V. M.)	12,943	6,670
177a	Anthracene Yellow	16,050	3,011	A 131	Scarlet (V. M.)	80,778	7,281	A687	Cupranil Brown (V. M.)	24,851	4,859
177b	Salicine Yellow	23,068	3,536	A 142	Wool Scarlet (V. M.)	12,780	1,417	A692	Direct Fast Black B	11,290	2,790
180	Erichrome Blue Black BC	43,880	8,485	A 144	Acid Black E, M	18,660	2,031	A711	Azo Rhodine 2 B	10,108	2,624
181	Salicine Black U	65,658	10,606	A 147	Acid Chrome Black	39,508	8,052	A719	Direct Sky Blue FF	58,838	12,827
184	Eriochrome Black A	96,570	13,530	A 150	Acid Silk Black R	12,928	2,234	A729	Azomire Milling Black N	22,500	5,124
185	Anthracene Chrome	51,577	7,869	A 157	Benzo Chrome Black Blue B	51,315	9,804				
188	Sulfone Acid Blue R	45,038	11,372	A 166	Benzo Dark Green B, GG	13,038	2,123				
189	Sulfone Acid Blue B	35,112	8,813								
198	Thiazine Yellow	29,879	8,410								
211	Resorcin Brown	13,189	2,549								
212a	Acid Brown (V. M.)	14,705	3,238								
217	Agalma Black 10 B	40,763	7,518								
217a	Agalma Black (V. M.)	13,465	2,359								
217c	Naphthol Blue Black (V. M.)	62,864	8,864								
217e	Acid Black (V. M.)	47,489	7,547								
217g	Wool Black (V. M.)	23,371	4,866								
217h	Acid Wool Black	13,518	4,202								
220a	Amido Acid Black	32,624	3,614								
236	Wool Red	13,245	1,942								
247	Scarlet	36,598	4,228								
257b	Tolyl Blue	16,750	2,967								
265	Sulfon Cyanine Black	69,590	7,663								
269	Acid Black	35,662	5,765								
272	Brilliant Black	39,454	5,588								
272b	Wool Black (V. M.)	15,756	3,596								
275a	Chrome Black (V. M.)	72,521	13,616								

SUMMARY OF THE MOST IMPORTANT COLORS IMPORTED BY U. S. DURING FISCAL YEAR 1913-14—(continued)											
Serial No.	COMMERCIAL NAME	Lbs.	Invoice Value	Serial No.	COMMERCIAL NAME	Lbs.	Invoice Value	Serial No.	COMMERCIAL NAME	Lbs.	Invoice Value
Triphenylmethane Colors											
497a	Victoria Green	41,595	\$10,305	739	Immedial Maroon B.	15,496					
499	Brilliant Green (V.M.)	73,904	16,345	746	Katigene Green (V. M.)	63,929	9,950				
502	Guinea Green	14,066	3,362	750	Kryogene Brown A, G	10,313	972				
502a	Acid Green (V.M.)	35,305	9,779	Unclassified Sulfur Colors							
503	Neptune Green (V. M.)	33,653	13,664	S 3	Sulfur Blue (V.M.)	73,434	15,489	U 20	Guinea Bordeaux (V. M.)	23,252	\$3,233
505	Light Green (Yellowish) (V. M.)	24,946	5,960	S 12	Sulfur Brown (V.M.)	79,691	9,505	U 27	Indo Violet B.	23,060	4,647
505a	Acid Green (V.M.)	46,461	20,176	S 18	Sulfur Catechu G, R.	48,973	5,071	U 24	Metachrome Blue B, G.	14,301	3,996
506	Erioglaucine (V.M.)	66,526	28,971	S 26	Sulfur Indigo (V.M.)	10,488	2,085	U 27	Metachrome Blue B, G.	14,301	3,996
512	Magenta	87,102	25,659	S 37	Katigene Black Brown (V. M.)	11,006	1,336	U 31	Metachrome Brown	17,301	7,271
516	Crystal Violet	13,078	4,362	S 45	Katigene Brown 2 R, V.	22,811	2,452	U 61	Scarlet 53446.	13,344	1,246
516a	Violet (V.M.)	18,219	5,289	S 49	Katigene Direct Blue, B, RF.	11,299	2,305	U 78	Chrome Fast Blue 4 B.	23,585	5,198
517	Benzyl Violet	22,387	6,018	S 51	Katigene Indigo (V. M.)	42,157	5,924	U 86	Columbia Fast Black (V.M.)	82,400	15,756
518	Ethyl Purple	51,933	23,101	S 55	Katigene Khaki G.	14,242	1,691	U100	Basic Kraft Brown Y 2.	11,235	2,039
521	Aniline Blue	50,563	18,586	S 58	Katigene Red Brown R, 3 R.	68,864	9,386	U109	Brilliant Scarlet (V. M.)	23,382	2,588
524	Acid Magenta	19,098	4,030	S 62	Katigene Yellow G, GG, GR.	55,227	9,318	U121	Corvoline BT	10,789	3,241
528a	Acid Violet	13,078	4,362	S 65	Katigene Yellow Brown (V.M.)	36,826	5,617	U138	Fast Acid Marine Blue HBB.	25,567	6,212
527a	Acid Violet (V.M.)	16,106	5,360	S 75	Immedial Direct Blue (V.M.)	73,892	11,145	U145	Japan Black (V.M.)	13,974	2,766
528	Fast Acid Violet 10 B	12,919	3,229	S 76	Immedial Indogene (V.M.)	90,077	13,141	U151	Jet Black APX, RR.	19,442	4,779
530	Acid Violet	50,055	12,806	S 78	Immedial New Blue G.	37,492	10,016	U155	Kraft Brown L, Y 2.	43,807	10,218
530a	Acid Violet (V.M.)	65,395	20,954	S 84	Sulfur Brown	12,735	1,926	U158	Leather Black BO, CR	16,433	4,843
530b	Formyl Violet (V.M.)	19,819	4,185	S 86	Thion Brown (V.M.)	18,579	2,824	U163	Oil Black 6 B, 6 G, HC.	28,603	4,258
530c	Acid Violet 4 B, 6 B.	18,854	5,114	S 97	Thiogene Blue (V.M.)	14,344	2,261	U183	Quercitron Substitute WBL, Y.	16,812	2,422
531	Eriocyanine	25,091	11,987	S100	Thiogene Brown (V. M.)	97,551	10,601	U192	Thiazine Brown R.	12,105	2,809
534a	Acid Violet (V.M.)	19,960	6,310	S109	Thiogene Deep Blue.	13,106	3,049	U206	Acid Chrome Blue 3 G, 2 R, 5 R.	25,633	6,553
537a	Navy Blue (V.M.)	31,499	6,275	S155	Pyrogene Brown (V. M.)	63,450	6,689	U217	Blue 27071.	14,775	994
538a	Cotton Blue (V.M.)	45,019	9,809	S168	Sulfur Bronze	15,152	1,392	U238	Claret Lake BL.	15,290	949
539	Soluble Blue	86,233	31,093	S177	Cross Dye Drab N.	15,788	1,324	U246	Half Wool Blue 3 R.	20,610	3,790
543c	Acid Blue	14,467	4,916	760	Indanthrene Gold Orange G.	20,092	10,088	U271	Wool Fast Blue BL, CL.	19,238	6,331
545	Patent Blue A.	40,848	10,229	761	Indanthrene Gold Orange	50,496	2,052	U279	Brilliant Lanafuchsine (V.M.)	11,289	1,757
545a	Neptune Blue (V.M.)	10,765	2,205	763	Indanthrene Dark Blue BO.	11,096	2,516	U283	Brilliant Scarlet (V. M.)	41,082	4,317
545c	Brilliant Acid Blue (V. M.)	10,120	3,525	767	Indanthrene Violet RR.	68,419	21,516	U290	Leather Black (V.M.)	11,784	3,063
546	Cyanol	40,015	15,757	768a	Indanthrene Black B, BB.	50,034	12,876	U293	Nerazine G, GA.	44,676	8,484
551	Eriochrome Azurol BC.	21,070	14,480	774b	Alizarin Black (V.M.)	61,187	19,239	U304	Acid Red (V.M.)	30,099	6,238
Diphenyl-Naphthyl-Methane Colors											
564	Naphthalene Green.	22,144	5,904	779	Alizarin Orange (V. M.)	14,239	3,184	U321	Carpet Red B, BT, R	15,445	1,649
566	Wool Green S.	33,863	13,526	780	Alizarin Red.	53,154	24,784	U329	Cotton Brown (V.M.)	15,079	4,959
566b	Cyanol Green (V.M.)	10,988	2,193	780a	Alizarin Red (V.M.)	16,375	6,453	U332	Cotton Marine Blue 4676.	79,035	10,902
Xanthone Colors											
571	Rhodamine 6 G.	37,460	18,495	785a	Alizarin (V.M.)	49,021	5,379	U333	Cotton Orange (V.M.)	21,665	5,116
573	Rhodamine B.	58,339	23,777	800	Anthracene Blue (V. M.)	22,444	7,174	U335	Direct Black (V.M.)	42,277	8,438
576	Rhodamine 3 G.	16,940	6,558	803	Anthracene Blue WB, WG.	54,712	9,228	U336	Direct Blue (V.M.)	57,224	14,318
580a	Fast Acid Violet (V. M.)	19,811	13,975	804	Alizarin Blue S, 942	12,409	6,158	U337	Direct Brown (V.M.)	21,828	4,799
587	Eosine	35,511	13,183	804a	Alizarin Sky Blue B.	19,471	24,555	U361	Naphthamine Fast Black, SE, SDE, VE	34,203	10,671
587a	Eosine (V.M.)	21,017	7,891	805	Alizarin Green S.	15,885	2,497	U378	Paper Scarlet (V.M.)	24,372	3,101
587b	Bromo-Fluorescein	38,000	18,397	807a	Patent Alizarin Black (V. M.)	61,500	10,049	U385	Scarlet (V.M.)	29,634	3,363
590a	Acid Eosine	17,499	7,388	808	Alizarin Green S.	11,096	2,337	U391	Wool Blue (V.M.)	23,020	6,854
599	Galleine	15,404	8,817	810a	Helindone Yellow CG	20,744	6,954	U393	Wool Brown (V.M.)	40,736	6,333
Acridine Colors											
606c	Patent Phosphine	28,627	17,881	820	Algol Brilliant Violet R.	12,784	3,623	U394	Wool Cerise SR.	16,038	2,359
606g	Leather Flavine	24,153	8,235	827	Indanthrene Claret B.	28,728	9,923	U397	Wool Green	20,255	5,488
607	Rheonine	19,704	5,261	832	Indanthrene Violet RN.	11,667	5,181	U399	Wool Violet R, SL.	12,584	3,429
608	Euchrysin	15,403	5,343	833	Algol Olive R.	13,334	2,850	U423	Alizarin Pure Blue DPH.	31,000	7,349
609b	Diamond Phosphine	30,336	5,897	841	Indanthrene Blue G, GF.	10,163	4,284	U440	Hansa Yellow G, 5 G, R.	11,014	4,559
609c	Crociavine	40,313	13,438	849	Indanthrene Yellow G, GF.	12,683	4,353	U460	Paratol Chrome Yellow L.	17,336	1,238
Quinoline and Thiohenzyl Colors											
612	Quinoline Yellow (spirit-soluble)	79,553	28,170	851a	Alizarin Direct Blue (V. M.)	10,201	11,878	U465	Paratol Scarlet 3 B.	41,000	8,271
613	Quinoline Yellow (water-soluble)	15,324	7,072	851b	Alizarin Rubinol R.	10,917	11,826	U470	Rosazine B, B, 5, 6 G	17,509	8,536
616	Primuline	56,212	8,478	859	Cyananthrol R.	18,792	27,555	U510	Cresol Black (V.M.)	37,322	4,246
617	Columbia Yellow (V. M.)	86,090	10,165	862	Alizarin Blue Black B, 3 B.	54,706	61,370	U526	Chrysoline A.	15,756	6,575
617a	Diamine Fast Yellow (V.M.)	88,688	12,972	877	Indigo Extract	19,329	6,577	U553	Black BH, HB.	21,239	4,789
618	Thioflavine T.	31,714	17,683	881	Ciba Blue 2 B.	16,880	7,423	U570	Developed Black B, N, R, W.	36,475	9,501
Oxazine and Thiazine Colors											
627	Gallocyanine	78,253	27,227	886	Brilliant Indigo GD.	12,057	1,747	U610	Erie Violet BC, RLC	21,345	6,117
649	Cotton Blue (V.M.)	32,509	9,675	888	Indigo MLB, T.	12,730	1,598	U682	Sepia Black FW.	10,527	2,367
660	Methylene Green (V. M.)	30,812	13,196	901	Ciba Violet R.	19,830	6,975	U687	Solifene Deep Black (V.M.)	61,949	9,509
661	Thionine Blue (V.M.)	18,618	7,873	904	Helindone Brown G.	12,936	6,710	U695	Blue (V.M.)	13,657	3,627
663	New Methylene Blue (V.M.)	30,392	12,127	907	Ciba Scarlet G.	22,265	11,479	U701	Calcutta Blue 2.	26,669	4,669
667	Indochromine (V.M.)	19,060	12,430	910	Helindone Pink (V. M.)	39,393	47,117	U708	Meridian Black AF.	15,157	3,316
Azine Colors											
672	Azo Carmine	17,500	5,453	913	Helindone Orange R.	11,489	5,841	U711	Omega Chrome Cyanine R.	21,001	3,019
679	Safranine (V.M.)	59,921	21,273	918	Helindone Red 3 B.	27,874	10,942	U716	Alpha Black JC, 6 BN.	12,100	2,949
681	New Fast Gray (V. M.)	29,507	10,436	920	Helindone Violet B, 2 B, R.	28,607	15,945	U731	Cachou (V.M.)	56,991	3,430
697	Induline, Soluble in Spirit (V.M.)	25,342	5,016	923	Ursol.	53,720	15,779	U744	Alizadine Black M.	18,979	1,986
699	Induline, Soluble in Water (V.M.)	21,775	5,514	Indigo and Its Derivatives							
705a	Indocyanine B, 2 RF	23,138	5,205								
Sulfur Colors											
708	Sulfaniline Brown O, R.	11,327	1,158	877	Indigo Extract	19,329	6,577	U770	XL Blue (V.M.)	10,047	2,126
710	Immedial Yellow D (V.M.)	13,395	2,266	879	Indigo MLB	53,610	11,604	Class II (100,000 to 200,000 lbs.)			
725	Immedial Brown (V. M.)	23,887	2,558								
726	Pyrogene Yellow M, O	10,034	2,582	881	Ciba Blue 2 B.	16,880	7,423	34	Chrysoidine R.	105,946	16,852
734	Pyrogene Yellow M, O	18,515	5,102	886	Brilliant Indigo GD.	12,057	1,747	48	Alizarin Yellow.	144,761	11,118
735	Pyrogene Indigo (V. M.)	22,661	6,652	888	Indigo MLB, T.	12,730	1,598	145	Orange II.	127,550	10,116
Sulfur Colors											
708	Sulfaniline Brown O, R.	11,327	1,158	901	Ciba Violet R.	19,830	6,975	163	Azo Rubine.	160,252	23,409
710	Immedial Yellow D (V.M.)	13,395	2,266	904	Helindone Brown G.	12,936	6,710	181b	Salicine Black (V.M.)	177,203	26,945
725	Immedial Brown (V. M.)	23,887	2,558	907	Ciba Scarlet G.	22,265	11,479	183	Eriochrome Black T.	129,550	23,447
726	Pyrogene Yellow M, O	10,034	2,582	910	Helindone Pink (V. M.)	39,393	47,117	217d	Naphthylamine Black (V.M.)	122,581	12,240
734	Pyrogene Yellow M, O	18,515	5,102	913	Helindone Orange R.	11,489	5,841	217f	Amido Black (V.M.)	105,005	10,062
735	Pyrogene Indigo (V. M.)	22,661	6,652	918	Helindone Red 3 B.	27,874	10,942	220	Palatine Black.	148,203	15,169
Sulfur Colors											
708	Sulfaniline Brown O, R.	11,327	1,158	920	Helindone Violet B, 2 B, R.	28,607	15,945	220b	Wool Black (V.M.)	110,244	16,868
710	Immedial Yellow D (V.M.)	13,395	2,266	923	Ursol.	53,720	15,779	227	Brilliant Croceine.	123,058	20,333
725	Immedial Brown (V. M.)	23,887	2,558	Indigo and Its Derivatives							
726	Pyrogene Yellow M, O	10,034	2,582								
734	Pyrogene Yellow M, O	18,515	5,102	877	Indigo Extract	19,329	6,577	257	Sulfon Cyanine	128,944	21,118
735	Pyrogene Indigo (V. M.)	22,661	6,652	879	Indigo MLB	53,610	11,604	266	Naphthylamine Black	152,141	21,903



## SUMMARY OF THE MOST IMPORTANT COLORS IMPORTED BY U. S. DURING FISCAL YEAR 1913-14—(concluded)

Serial No.	COMMERCIAL NAME	Lbs.	Invoice Value	Serial No.	COMMERCIAL NAME	Lbs.	Invoice Value	Serial No.	COMMERCIAL NAME	Lbs.	Invoice Value
269a	Naphthol Black (V. M.)	131,890	\$19,436	774	Alizarin Black S. SR.	136,161	\$ 9,936	778	Alizarin (Synthetic)	202,392	\$ 20,465
284	Bismarek Brown 2 R.	170,882	31,241	782	Alizarin Brown (V.M.)	110,211	30,907	806a	Alizarin Black (V.M.)	229,500	33,273
304	Chrysophenine	148,406	40,466	789	Anthracene Blue WR.	107,778	13,622	Class IV (300,000 to 400,000 lbs.)			
333b	Diamine Black (V.M.)	171,211	19,634	808	Alizarin Black S.	198,491	19,902	274	Lake Red C.	306,607	9,495
424	Chicago Blue 6 B.	116,560	32,417	808a	Alizarin Green (V.M.)	124,095	58,491	275	Diaminogen	305,944	56,201
436a	Dianol Black	112,095	12,635	838	Indanthrene Blue RS	187,379	56,532	275	Diamond Black	551,582	55,020
442a	Direct Black (V.M.)	145,738	11,831	U 64	Amine Black (V.M.)	146,163	14,390	363	Benzoazurpurine 4 B.	341,724	45,238
455a	Columbia Black (V. M.)	143,956	26,125	U390	Wool Black (V.M.)	118,791	20,453	A396	Cotton Black (V.M.)	300,473	41,567
462f	Carbide Black (V.M.)	190,304	31,607	U799	Black (V. M.)	138,805	14,781	A432	Lake Red (V.M.)	249,380	11,682
A169	Benzo Fast Black L.	100,268	22,846	Class III (200,000 to 300,000 lbs.)				700	Nigrosine, Sol. in Water	394,718	58,903
A382	Oxy Diamine Black (V.M.)	146,629	24,836	7	Naphthol Yellow	250,409	24,702	803a	Alizarin Blue (V.M.)	302,319	69,712
A387	Oxy Diaminogen (V. M.)	139,118	26,832	23	Tartrazine	265,781	53,137	Class V (400,000 to 500,000 lbs.)			
495	Malachite Green	178,831	43,363	134	Metanil Yellow	284,606	46,614	333	Oxamine Black	417,423	57,464
543	Patent Blue	114,631	49,945	157	Diamond Black	285,047	37,055	493	Auramine	449,276	107,887
558	Victoria Blue R.	109,627	33,117	174a	Scarlet	209,281	20,472	842	Indanthrene Blue	478,980	169,780
565a	Wool Blue (V.M.)	173,904	18,406	303a	Paper Yellow (V.M.)	264,443	45,320	Class VI (over 500,000 lbs.)			
606	Phosphor Blue	101,858	30,442	436	Columbia Black	290,902	41,563	462a	Direct Deep Black E.	862,601	110,096
659	Methylene Blue (V. M.)	185,738	72,619	463	Cotton Black E.	188,550	30,472	A 40	Zambesi Black (V.M.)	629,359	107,669
698	Nigrosine, Soluble in Spirit (V.M.)	186,540	23,435	515	Methyl Violet	255,063	63,183	720	Sulfur Blacks (V.M.)	5,615,458	588,900
				536	Alkali Blue	286,531	117,365	874	Indigo, Synthetic	8,507,359	1,090,733
				748	Hydron Blue (G. R.)	292,729	33,555				

interference in the output of American colors occurred until after the beginning of 1915.

With the cordial coöperation of the Secretary of the Treasury, all the invoices for the year in question were sent by the collectors of customs at the various ports of entry to a central point, where the essential data were transcribed. These include weight, value and price. Some 37,500 different transcripts, each covering these three items, were necessary.

These entries are found under 5,674 heads, each representing a distinct commercial designation. It must not be inferred, however, that this number of different colors comes into consideration. Many standard dyes are manufactured by several firms in the same country as well as in various countries. Frequently, some or all of the competing manufacturers use entirely different trade names for identical wares.

Thus, the red color, known chemically as sodium  $\alpha$ -naphthalene azo- $\alpha$ -naphthol-disulfonate, is manufactured under the name of Palatine Red by the Badische Co. The Bayer Co. sells it under the name of Naphthorubine. Primuline is encountered commercially as Polychromine, Thiochromogen, Aupoline and Sulfine. Malachite Green, a favorite color, is found under 38 different designations, few representing even slight variations in the exact chemical composition.

The reduction of this extensive vocabulary to the limits of the list given in the census has required highly specialized editing. It is hoped that the arrangement and the full use of synonyms are such as to render the published results of the greatest utility, not only to all engaged in the manufacture of artificial dyestuffs, and especially in planning for the establishment of a comprehensive American color industry, but also to all dealers in the wares and to all consumers of dyeing materials.

All three of these categories have hitherto been indebted to the painstaking labors of several prominent German color chemists, notably of Gustav Schultz and Paul Julius, for complete and detailed classifications of the coal-tar dyes in current use. The carefully elaborated "Farbstofftabellen," devised by the two authors, reached a fifth edition in 1914. These "tables," divided into groups according to chemical relationship, give for every artificial dye of known composition or preparation the commercial designation, the scientific name, the chemical formula, the most advantageous process for technical production, physical and chemical properties, methods of application, tests and full references to patents and literature. They have for years been the *vade mecum* of all connected with the manufacture of colors, their commerce, and their manifold uses.

It has remained for a bureau of our Government to supplement the work of the German duo, by adding the all-important factor of quantity. The complete exposition of the exact amounts of the many synthetic dyes required to meet the almost numberless needs of a population of over 100,000,000, portrays

approximately the relative demands of all other nations with highly organized textile and allied interests. The young American dyestuff industry, now in a position to expand rapidly and to embrace in its scope the great majority of the colors in current use, will naturally find in it a sure guide for coordinating the diverse phases of manufacture, establishing the capacity of units, and shaping all plans for harmonious expansion.

More than this, it will be of almost equal value to those seeking to create the national coal-tar industries of Great Britain, France, Russia and Italy. Even the newly organized industry in Japan may profit from its summaries, although in a less pronounced degree, on account of the widely divergent taste for colors between the Orient and the Occident.

Should China plan to manufacture her own coal-tar dyes, but little help could be secured from this compilation in formulating schemes for installing plants. Synthetic indigo constitutes two-thirds of the Chinese consumption of artificial colors. It enters to the extent of 14 per cent into the Japanese imports of dyestuffs, and forms but 10 per cent of the American consumption.

One of the first results of the compilation of this census was to show how exceedingly vague an idea of the extent to which synthetic dyes are consumed in the United States prevailed in commercial and manufacturing circles. Those most closely in touch with the branch have estimated hitherto that the annual American consumption of coal-tar colors did not exceed 20,000 tons. As a matter of fact, it is nearly one-half again this amount—more exactly, 29,000 short tons.

## SUMMARY OF THE MOST IMPORTANT COLORS IMPORTED

It has seemed desirable, in the interest of American chemists who are now studying closely the problems connected with the creation of a national dyestuff industry, to prepare a summary of the more important synthetic colors currently imported into this country and compiled systematically, in the complete census of dyes consumed in the United States, now in press.

The list prepared (pages 1042, 3 and 4) includes practically all colors, the annual importation of which, during the fiscal year 1913-14, exceeded in amount 10,000 lbs. These colors, for the sake of classification, are divided into six groups, according to the amount of the importation.

## PRICES OF DYES

The values of the different colors imported from Europe are taken directly from the invoice entries. The prices varied but little during the course of the fiscal year 1913-14. They are on file in the Bureau of Foreign and Domestic Commerce. It did not seem necessary to reproduce them in full in the enumeration of colors. The average price for the year, in the case of any dye, is easily ascertained by a simple act of division.

In most cases the values stated represent the lowest possible estimate of wholesale cost which can be placed upon the wares in question. The bulk of the importations is shipped from the great

manufacturing firms of Germany, Switzerland and England, to their agents in this country. The latter are ordinarily incorporated American companies, bearing essentially the same names as the European houses which they represent, and may be practically under the control of the latter, if not financed by them directly.

Under these circumstances and in view of the exceptional difficulty of ascertaining market values for the highly differentiated gradations of quality in the thousands of brands of artificial colors, there was a strong temptation to place the lowest possible values upon wares subject to an *ad valorem* duty of 30 per cent.

It is doubtful in many cases, therefore, whether the values published in the following lists are fully equal to those against which American manufacturers of colors would contend, should all the factors, falling under the head of "unfair competition," be eliminated in the international trade in synthetic dyes. In these values there is a slight element of variability and uncertainty, based upon the lack of uniformity in invoicing colors.

In some cases—probably the majority—the prices and values are net, not covering charges for containers and packing, freight, and insurance to seaport, consular certification, minor shipping charges at point of departure and at seaport. Wares shipped by the "Badische Co.," the Berlin "Actien-Gesellschaft," the "Cassella Co.," the "Griesheim-Elektron," and the "Chemikalienwerk-Griesheim" are usually invoiced in this manner.

Other firms, such as the "Bayer Co.," the "Sandoz Co.," "Carl Jäger," and "Beyer and Kegel," include in their prices the cost of containers and packing, freight and insurance to seaport, consular certification, and minor shipping charges. In other words, their prices are f. o. b. ocean steamers at Hamburg, Bremen, Rotterdam, Antwerp, etc.

It has not been possible, on account of time limitations, to estimate this small factor in the case of each shipment and make the accompanying correction in value so as to have actual uniformity in the basis of valuation. The element of quantity is the dominant feature in this work, and in view of what is stated above, very elaborate calculations of values would be of doubtful utility.

COST OF PACKING, FREIGHT, INSURANCE, ETC.

It is well, however, to know with some approximation to exactness the extent and nature of the charges incident to the importation of European coal-tar colors into the United States. They are as follows:

*Consular certification*—A fee of \$2.50 for all invoices covering shipments, the value of which exceeds \$100.

*Freight to seaport*—This is quite variable, depending upon the distance to be traversed and whether rail or water transportation is employed. Rates per lb. (net) of color are \$0.00125 from Berlin; \$0.0056 to \$0.0071 from Basel; \$0.0008 to \$0.00216 for points on the Rhine.

*Insurance, in transit to seaport*—Rates vary from \$0.0007 to \$0.0016 for each dollar of invoice value.

*Shipping charges*—The item appears occasionally and ranges from \$1 to \$2 for each \$1,000 of an invoice.

*Ocean freight*—Customary rates from European ports, such as Hamburg and Antwerp to New York, were, prior to the war, \$9.75 per metric ton (gross weight) for most of the coal-tar dyes, and \$7.91 for certain categories, such as sulfur black and other sulfur colors.

Several large invoices of colors showed an average rate for ocean freight per net lb. of dyestuff, of \$0.00471, ranging from \$0.004125 to \$0.00539. Through freight from Frankfort to New York on a large and varied assortment of artificial dyes was at the rate of \$0.00755 per net lb. of colors.

On an average, 1 lb. of color (net) is represented by 1.165 lbs. gross weight, the tare per lb. ranging from 0.155 to 0.174 lb. on shipments of some size

*Marine insurance*—Insurance on large shipments of dyes from Frankfort to New York, covering both inland and marine insurance, was equivalent to \$0.000916 per lb. (net) of colors.

This represented \$0.00497 on each dollar of value, or about 0.5 per cent on the value. Shipments by another company, located on the Rhine, averaged 0.3 per cent.

*Packing*—There is some diversity in the average cost of containers. This item ranges from \$0.00459 to \$0.00863 per lb. (net) of color in a number of large invoices. A fair average would be \$0.00651 per net lb.

Some of the more expensive colors are shipped in tin boxes, packed in cases holding 100 lbs. (net). Cases cost \$0.48. The charges for tins are as follows: 1 lb., 4.8c.; 5 lbs., 9.6c.; 10 lbs., 15.5c.; 25 lbs., 32c. Kegs, containing 100 lbs., cost usually \$0.95, but range in value from \$0.63 to \$1.14. Casks hold ordinarily about 500 lbs. The net contents range, however, from 415 to 595 lbs. In four large shipments the average net weights were 442, 469, 480, and 531 lbs. The general average was 480 lbs. The average price of casks is \$1.90. They range, however, in cost from \$1.55 to \$3.24.

On an average the importation of European colors to New York costs \$0.014 per net lb. for packing and transportation (packing \$0.0065, transportation \$0.0075), and \$7 per \$1,000 of value for insurance and incidental charges (insurance \$5, shipping charges and consular certification \$2).

American consumers of coal-tar colors, who may wish to compare the prices paid by them two or three years ago for European wares with the prices based upon the values furnished in this report, can add to the prices calculated from these values the cost of the above items. In addition there comes the duty of 30 per cent *ad valorem* on all artificial colors, except indigo and its derivatives, and colors made from anthracene (largely alizarin) and carbazole, which were exempt from duty under the late tariff. This duty is levied upon the combined cost of a dye and its containers. Furthermore, the normal cost of handling, storing, and distributing, in the importing houses, is to be added. The difference between the sum total of these various items and the current price for a given color represents the profit made by the importer.

ARTIFICIAL COLORS MANUFACTURED IN THE UNITED STATES

The manufacture of coal-tar colors in the United States has been in existence for some 37 years. Prior to 1915 it had never become a factor of importance in supplying the American market. The reasons for this slowness of development have been presented in detail in the monograph published in 1915 by the Bureau of Foreign and Domestic Commerce, entitled "Dyestuffs for American Textile and Other Industries" (Special Agents Series No. 96).

The American manufacture was confined almost entirely to the "assembling" into finished dyes of coal-tar intermediates imported from Europe, chiefly from Germany. In its entirety it represented less than one-tenth of the activity to be encountered in any one of the larger companies producing synthetic colors in Germany and Switzerland.

STATUS OF THE DOMESTIC PRODUCTION IN 1914

The status of the industry for the calendar year 1914 is shown by the following tabular statement prepared by the Bureau of the Census.

Number of establishments.....	538
Persons engaged in manufacture.....	130
Salaries.....	398
Wage earners (average number).....	1,376
Primary horse power.....	\$3,380,212
Capital.....	\$ 529,070
Services.....	\$ 273,633
Salaries.....	\$ 255,437
Wages.....	\$1,936,982
Materials.....	\$3,596,795
Value of products.....	
Coal-tar colors.....	
Pounds.....	6,619,729
Value.....	\$2,470,096
All other (including medicinal coal-tar products to value of \$174,508).....	\$1,126,699
Value added by manufacture.....	\$1,659,813

The scope and extent of the manufacture carried on prior to the war by the seven American companies engaged in this branch



are summarized under their respective names. No attempt has been made to estimate the annual output of the individual colors made in the American factories, as it fluctuated largely from year to year.

In nearly all cases the character of the manufacture has been vastly affected by the conditions prevailing since 1914. As a rule the variety of colors has been diminished while the output has been vastly augmented.

The number of employees has been notably augmented. In general, it has been quintupled. In one case the force is 50 times greater than in 1914.

#### THE SCHÖELLKOPF ANILINE AND CHEMICAL WORKS (INC.)

This firm, located at Buffalo, N. Y., was founded in 1879, and is the oldest American company in this industry. A number of dyestuffs in current use originated in its laboratories. It has shown a commendable degree of enterprise in maintaining its position for over a third of a century, frequently under conditions of a most discouraging nature. It has also earned the grateful recognition of a multitude of American consumers of dyes by swiftly enlarging the capacity of its works so as to alleviate materially the severity of the dyestuff famine to which our textile and allied interests have been exposed.

The annual output of this firm constituted about one-half of the American production of coal-tar dyes. The following colors were currently manufactured before the war. The serial numbers correspond to those given in Schultz's "Farbstofftabellen."

STILBENE AND PYRAZOLONE DYES		AZO DYES (concluded)	
9	Direct Yellow F	161	Fast Red S conc.
9	Direct Yellow 2 RF	163	Azo Rubine extra
23	Wool Yellow extra conc.	168	Wool Red 40 F
TRIPHENYL-METHANE DYES		169	Brilliant Scarlet 3 R
512	Fuchsine	188	Buffalo Fast Blue R
513	Fuchsine TR	189	Buffalo Fast Blue B
513	Fuchsine NB	211	Resorcin Brown
521	Spirit Blue, red shades	211	Leather Orange
524	Spirit Blue, green shades	217	Buffalo Black NB
524	Acid Magenta	220	Buffalo Black PV extra
536	Alkali Blues, red shades	227	Crocine Scarlet MOO
536	Alkali Blues, green shades	257	Buffalo Cyanine R
537	Paper Blues, red shades	257	Buffalo Cyanine 3 R
537	Paper Blues, green shades	261	Buffalo Black 8 B, 10 B, R
537	Paper Blue 6 G super	266	Buffalo Black AD
		268	Buffalo Black EA
		269	Buffalo Black 4 B
		272	Buffalo Black 2 B
XANTHONE DYES		275	Buffalo Chrome Black BWN
587	Eosine	283	Bismarck Brown Y
AZINES		284	Bismarck Brown 53
679	Safranin Y extra	303	Brilliant Yellow C
680	Safranin 6 B	307	Congo Red 4 B
684	Brilliant Safranin R	311	Erie Orange 2 R
699	Nigrosines from aniline (indulines)	312	Buffalo Direct Garnet R
700	Nigrosines from nitrobenzol	313	Buffalo Direct Crimson B
AZO DYES		320	Bordeaux extra
31	Oil Yellow A	326	Niagara Violet 2 B
32	Oil Yellow 2625	326	Niagara Blue R
33	Chrysoidine Y extra	327	Niagara Violet 3 R
33	Chrysoidine crystals	333	Diazine Black H extra
34	Chrysoidine 3 R	336	Niagara Blue GW, HW, RW
36	Oil Orange 2311	337	Niagara Blue B, 2 B
36a	Oil Yellow 2338	342	Buffalo Direct Yellow CG extra
37	Crocine Orange Y	343	Niagara Fast Red PD
38	Crystal Orange 2 G	344	Erie Direct Brown 3 RB
64	Buffalo Fast Crimson G	362	Buffalo Direct Orange R
66	Buffalo Fast Crimson R	363	Buffalo Direct Red 4 B
68	Oil Yellow 2681	375	Buffalo Direct Violet 4 R
70	Crocine Orange R	386	Buffalo Blue BR
82	Xylidine Scarlet	392	Buffalo Direct Orange Y
83	Cumidine Scarlet	394	Buffalo Direct Yellow CRR extra
94	Buffalo Flaming B	405	Buffalo Direct Cardinal 7 B
95	Buffalo Flaming G	410	Buffalo Direct Blue G extra
105	Sudan Brown S	424	Niagara Blue 4 B
110	Buffalo Rubine	436	Panama Black R extra
112	Azo Bordeaux	436	Panama Black 3 G extra
126	Indoine Blue	441	Niagara Black Blue R
134	Metanil Yellow	462	Erie Direct Black G extra
141	Azo Yellow	463	Erie Direct Black R extra
141	Azo Yellow A 5 W	464	Erie Direct Green ET
143	Resorcin Yellow	464	Erie Direct Green WT
145	Orange A	474	Erie Direct Green MT
147	Buffalo Fast Fuchsine B	477	Erie Direct Brown GR
151	Orange R	477a	Erie Direct Brown GB
161	Fast Red conc.	488	Erie Direct Brown RF, 2 RF

#### THE HELLER AND MERZ CO.

This firm, located at Newark, N. J., stands second in point of seniority and importance. Its annual output of coal-tar colors was estimated at slightly less than one-quarter of the country's production. It has catered very largely to the needs of the paper trade. In addition to organic dyestuffs, it has manufactured large quantities of mineral colors, notably ultramarine. The equipment for the production of coal-tar dyes has been largely augmented during the past year.

The following artificial colors were currently manufactured in 1914 (serial numbers of Schultz's Farbstofftabellen):

AZO DYES	TRIPHENYL-METHANE DYES	XANTHONE DYES
33 Chrysoidine	512 Fuchsine	587 Eosine
145 Orange II	515 Methyl Violet	
283 Bismarck Brown	536 Alkali Blue	AZINES
	537 Soluble Blue	698 Nigrosine, spirit-soluble
	538 Methyl Blue	700 Nigrosine, water-soluble
	539 Acid Blue	

#### THE BAYER CO. (INC.)

This company owns works at Rensselaer, N. Y., where several of the staple colors and medicinal products of the Farbenfabriken vormals Friedr. Bayer & Co., of Leverkusen, Germany, are manufactured on a scale of some importance. The output of coal-tar dyes prior to the war constituted somewhat less than one-fifth of the entire production. The expansion during the past year and a half has not been as pronounced as in the case of the other establishments.

Prior to the war the company manufactured the following colors:

AZO DYES	TRIPHENYL-METHANE DYES	AZINES
33 Chrysoidine	512 Fuchsine	698 Nigrosine, spirit-soluble
283 Bismarck Brown	536 Alkali Blue	699 Induline
	537 Soluble Blue	700 Nigrosine, water-soluble

#### W. BECKER'S ANILINE AND CHEMICAL WORKS (INC.)

This company, founded in 1912, is located at Brooklyn, N. Y. Prior to the war it specialized on alizarin substitute colors. The annual output was modest, estimated at about 180 tons. During the past 18 months the plant has been rapidly enlarged. To-day it is second in importance as a factor in the domestic color industry.

The following colors were manufactured regularly prior to 1915:

AZO DYES	TRIPHENYL-METHANE DYES	AZINES
48 Alizarin Yellow FF	189 Acid Fast Blue SB	599 Chrome Blue R, powder and paste
84 Ponceau 3 R	217 Acid Black 10 B	
145 Orange II	333 Diazo Black BHN	OXAZINE DYES
163 Azo Rubine WB	337 Direct Blue WEB	626 Chrome Blue B, paste and powder
166 Fast Red A	342 Direct Yellow WH	
188 Acid Fast Blue SR	410 Benzazurine WB	
	426 Direct Sky Blue B	

#### THE CENTRAL DYESTUFF CO.

This company, located at Newark, N. J., was founded in 1898. The output was not large, possibly 4 per cent of the country's production. It included, however, several dyes of importance for the textile industries. The plant has been notably enlarged during the past year.

Prior to the war the following colors were currently manufactured:

AZO DYES	TRIPHENYL-METHANE DYES	AZINES
31 Amido-azo-benzene	161 Fast Red	697 Enduline
33 Chrysoidine	163 Azorubine	698 Nigrosine
37 Crocine Orange	168 Amaranth	
68 Amido-azo-toluene	174 Scarlet	
112 Bordeaux B	223 Sudan III	
145 Orange II	232 Sudan IV	
	283 Bismarck Brown	

#### THE CONSOLIDATED COLOR AND CHEMICAL CO.

This company, located also at Newark, N. J., manufactured for some years prior to the war less than 100 tons annually of colors. The following colors for textile works were currently produced.

58 Alizarin Yellow R.	168 Fast Red	144 Naphthol Orange
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In addition, a certain variety of colors for pigments, especially alizarin, para and scarlet lakes, and for use in paper making, were regularly manufactured. During the past year the plant has been greatly enlarged. It is at present an important center of production.

#### HUB DYESTUFF AND CHEMICAL CO.

This company, located at South Boston, Mass., manufactured on a modest scale, for a few years, prior to 1915, 58 Alizarin Yellow R.

#### IMPORTATION OF COAL-TAR CRUDES AND INTERMEDIATES

As stated above, the synthetic colors manufactured in the United States prior to 1915 were made almost exclusively from intermediate coal-tar products imported from Europe. Germany was the chief source. A considerable amount, however, was of British origin.

A single noteworthy exception is found in the case of aniline. The American manufacture of this all-important intermediate was organized in 1910. The annual output had attained about 900 short tons in 1914—the product of a single establishment.

At present aniline is regularly manufactured by over 30 companies and the annual output is in excess of 16,000 short tons.

In connection with the preceding enumeration of the artificial dyes currently produced in the United States prior to the war, it is of considerable importance to know what coal-tar crudes and intermediates were imported for use in their manufacture and, further, the quantity and value of each crude and intermediate. This information is furnished in the following tabular statement based upon the importations for the fiscal year ending June 30, 1914:

## IMPORTS OF COAL-TAR CRUDES, FISCAL YEAR 1913-14

	Pounds	Value
Benzene.....	131,211	\$4,247
Toluene.....	199,088	7,892
Xylene.....	30,681	1,722
$\beta$ -Naphthol.....	3,880,108	70,428
Anthracene and anthracene oil.....		32,175
Phenol (carbolic acid).....	8,393,216	531,535
Phenol, ref.....		109,146
Cresol.....	404,361	16,139
Creosote oil (gallons).....	59,271,677	3,822,919
Total.....		4,596,203

An exceedingly small part of the above-mentioned coal tar crudes was utilized in the manufacture of artificial colors. The creosote oil was employed in the preservation of timber. The phenol served chiefly as a disinfectant and antiseptic. The chief use of naphthalene was in the familiar form of "moth balls."

During the calendar year 1913, according to official German records, the following coal-tar crudes were imported into the United States from Germany: Naphthalene, 7,900 short tons; carbolic acid (pure and crude), 1,320 short tons; cresol, 220 short tons; creosote oil, 17,600 short tons.

## IMPORTS OF COAL-TAR INTERMEDIATES, FISCAL YEAR 1913-14

The values given are net invoice values of European manufacturers and do not include cost of containers, etc.

INTERMEDIATES	Pounds	Value
NITRO COMPOUNDS		
Nitro-benzene.....	1,087,911	\$59,835
Dinitro-benzene.....	164,650	10,399
Nitro-toluene.....	6,670	359
<i>o</i> -Nitro-toluene.....	42,482	2,969
Dinitro-toluene.....	547,701	36,660
Nitro-toluene.....	57,242	13,242
$\alpha$ -Nitro-naphthalene.....	2,247	165
<i>m</i> -Nitriline.....	3,527	1,037
<i>p</i> -Nitriline.....	506,961	67,638
Methyl-nitriline.....	500	135
Nitro-toluidine.....	10,874	3,415
<i>m</i> -Nitro- <i>p</i> -toluidine.....	10,313	4,400
<i>o</i> -Nitro- <i>p</i> -toluidine.....	20,737	6,524
<i>p</i> -Nitro- <i>o</i> -toluidine.....	30,642	9,723
<i>p</i> -Nitro-phenol.....	4,780	774
CARBOXYLIC ACIDS		
Benzoic acid.....	278,896	51,701
Phthalic acid.....	63,574	15,597
Tetrachloro-phthalic acid.....	1,102	659
Ethyl- <i>p</i> -toluene-sulfonic ester.....	21	19
PRIMARY AMINES AND DERIVATIVES		
Aniline oil.....	1,444,772	116,628
Aniline salts.....	3,083,467	222,728
Acetanilide.....	1,060	164
<i>p</i> -Amido-acetanilide.....	5,568	1,365
<i>p</i> -Sulfanilic acid.....	4,477	257
Toluidine.....	108,835	14,161
<i>o</i> -Toluidine.....	309,595	27,361
<i>m</i> -Toluidine.....	174	25
<i>p</i> -Toluidine.....	24,686	4,764
Xyline.....	18,600	2,167
<i>p</i> -Phenetidine.....	33,093	11,925
Naphthylamine.....	25,573	2,705
$\alpha$ -Naphthylamine.....	112,226	10,620
Naphthylamine-sulfonic acid (constitution unknown).....	500	161
$\alpha$ -Naphthylamine sulfonic acid (1, acid; 1,5).....	2,832	497
$\alpha$ -Naphthylamine-sulfonic acid (Cleve's acid; 1,6 or 1,7).....	5,493	711
$\alpha$ -Naphthylamine-sulfonic acid (Freund; 1,3,6).....	5,246	604
$\beta$ -Naphthylamine.....	5,073	997
$\beta$ -Naphthylamine- $\alpha$ -sulfonic acid ( $\alpha$ or Badische acid).....	23,265	7,579
$\beta$ -Naphthylamine- $\beta$ -sulfonic acid ( $\beta$ or Bröner's acid).....	2,316	495
$\beta$ -Naphthylamine-disulfonic acid ( $\alpha$ or R acid; amido-R salt; 2,3,6).....	46,267	4,495
$\beta$ -Naphthylamine-disulfonic acid ( $\gamma$ or G acid; amido-G salt; 2,6,8).....	3,603	230
SECONDARY AMINES AND DERIVATIVES		
Dimethyl-aniline.....	48,642	7,045
Diphenylamine.....	55,556	9,042
Ethyl- $\alpha$ -naphthylamine.....	1,102	138
Ethyl- $\beta$ -naphthylamine.....	375	190
Phenyl- $\alpha$ -naphthylamine-8-sulfonic acid.....	9,139	2,860
<i>p</i> -Tolyl- $\alpha$ -naphthylamine-8-sulfonic acid.....	1,097	568

## DIAMINES AND DERIVATIVES

Phenylene diamine.....	37,907	\$ 7,704
<i>p</i> -Phenylene diamine.....	11,088	3,414
<i>m</i> -Tolylene-diamine.....	131,375	25,582
<i>m</i> -Tolylene-diamine-sulfonic acid (1,2,4,6).....	2,277	835
Benzidine.....	55,245	16,991
Diamidine.....	10,656	4,217

## PHENOLS AND DERIVATIVES

Salicylic acid.....	18,821	4,425
Acetyl-salicylic acid.....	22,841	11,873
Resorcin.....	61,624	18,175
Hydroquinone.....	66,596	2,835
Pyrogallol.....	23,615	20,476
Gallie acid.....	61,635	20,429
Naphthols ( $\alpha$ and $\beta$ ).....	70,469	4,193
$\alpha$ -Naphthol.....	44,089	2,271
$\alpha$ -Naphthol-5-sulfonic acid (L or Cleve's acid; 1,5).....	25,126	5,026
$\alpha$ -Naphthol-3,6,8-trisulfonic acid (1,3,6,8).....	5,443	1,344
$\beta$ -Naphthol.....	1,030,268	74,238
$\beta$ -Naphthol-monosulfonic acid (constitution unknown).....	32,852	5,998
$\beta$ -Naphthol-7-sulfonic acid (H salt; 2,7).....	1,996	382
$\beta$ -Naphthol-6,8-disulfonic acid (C acid; 2,6,8).....	11,624	1,404
1,8-Dioxynaphthalene-4-sulfonic acid.....	2,178	1,056
$\beta$ -Oxy-naphthoic acid.....	2,359	972
$\beta$ -Oxy-naphthoic anilide (Naphthol AS).....	1,997	1,218

## AMIDO-PHENOLS AND DERIVATIVES

<i>o</i> -Amido-phenol.....	625	223
Sodium picramate.....	5,207	1,485
Oxy-nitriline.....	200	32
Diamido-phenol.....	441	391
<i>p</i> -Amido-phenol.....	10,631	1,684
<i>p</i> -Amido-phenol hydrochloride.....	652	189
<i>p</i> -Amido-salicylic acid.....	9,188	2,996
Methyl- <i>p</i> -amido-phenol sulfate.....	10,582	13,658
1,8-Amido-naphthol-3,6-disulfonic acid (H acid; 1,3,6).....	96,296	22,168
2,5-Amido-naphthol-7-sulfonic acid.....	1,153	445

## ALDEHYDES AND QUINONES

Benzaldehyde.....	12,950	2,757
Oil of bitter almonds (benzaldehyde).....	7,525	21,954
Anthraquinone.....	25,193	4,676

## DEVELOPERS, REDUCERS AND INDICATORS

Fast Blue Developer AD (amido-diphenylamine).....	100	39
Oxamine Developer H.....	11,096	2,119
Orange Developer R.....	701	36
Developer Z (phenyl-methyl pyrazolone).....	1,397	377
Phenolphthalein.....	14,076	14,090

Total..... 10,165,896 \$1,082,775

## SUMMARY OF IMPORTS OF COAL-TAR PRODUCTS, 1913-14

The coal-tar crudes and intermediates listed above, with the exception of aniline oil and salts, several acids, such as carbolic acid and salicylic acid, alizarin and colors derived from alizarin, anthracene and carbazole, indigo and its derivatives, and a few other compounds, such as antipyrine, aspirin, saccharin, and phenolphthalein, are included in the following summarized statement of the imports for consumption into the United States of coal-tar products, for the fiscal year ending June 30, 1914, published by the Bureau of Foreign and Domestic Commerce.

Imports designated by an asterisk (\*) are for the period July 1 to October 3, 1913. Those designated by a dagger (†) are for the remainder of the fiscal year.

COAL-TAR PRODUCTS	Rate of duty	Value
Anthracene and anthracene oil.....	Free†	\$32,175.00
Colors or dyes, n. s. p. f.....	30 per cent	7,537,869.55
Do. (for use of the United States).....	Free	54.00
Dead or creosote oil (59,271,677 gallons).....	Free	3,822,919.00
All other, not medicinal and not colors or dyes, known as benzol, toluol, naphthalin, xylol, phenol, cresol, toluidine, xylin, cumidin, binitrotolul, binitrobenzol, benzidin, tolidin, dianisidin, naphthol, naphthylamine, diphenylamin, benzaldehyde, benzylchloride, resorcin, nitrobenzol, and nitrotolul; naphthylaminsulfocids, naphtholsulfocids and amidonaphtholsulfocids and their sodium or potassium salts; amidosalicylic acid, binitrochlorbenzol, diamidostilbendisulfocid, metanilic acid, paranitranilin, and dimethyl-anilin.		
Distillates, n. s. p. f., not medicinal and not colors or dyes, benzol, naphthol, resorcin, toluol, xylol.	Free*	288,799.00
Not medicinal and not colors or dyes, known as toluidine, xylin, cumidin, binitrotolul, nitrobenzol, benzidin, tolidin, dianisidin, naphthylamine, diphenylamin, benzaldehyde, benzylchloride, nitrobenzol, and nitrotolul; naphthylaminsulfocids, naphtholsulfocids, and amidonaphtholsulfocids and their sodium or potassium salts; amidosalicylic acid, binitrochlorbenzol, diamidostilbendisulfocid, metanilic acid, paranitranilin, and dimethyl-anilin.	5 per cent†	138,636.00
	10 per cent*	398,996.00



COAL-TAR PRODUCTS	Rate of duty	Value
Do. (for use of the United States)	Free	40,741.00
Naphthalene, phenol, and cresol	Free	195,713.00
All preparations of, not colors or dyes, and not medicinal, n. s. p. t.	20 per cent*	162,864.13
All other products or preparations of, not colors or dyes, n. s. p. t.	15 per cent†	496,548.00
Do. (for use of the United States)	Free	18,082.00
Total coal-tar products	{ Free Dutiable	{ \$ 4,398,483.00 8,734,913.68

## IMPORTS OF INTERMEDIATES FROM GERMANY

The official records of exports of intermediates from the German Empire to the United States show that the following quantities, in short tons, were shipped during the calendar year 1913:

Aniline oil and salts	2,640
Naphthol and naphthylamine	660
Anthraquinone, nitrobenzene, phthalic acid, resorcin, toluidine, etc	1,067
Benzoic acid, salicylic acid, and their sodium salts	297
Total (short tons)	4,664

## THE MARKS OF COAL-TAR COLORS

The great diversity of marks employed by the different manufacturers of artificial dyes is a source of confusion and bewilderment to many, especially to those in the United States now taking an active interest in the evolution of a domestic coal-tar chemical industry, and but slightly familiar with the commercial features of this most complicated of all the varied branches of technology. As the subject has never been treated to any extent in the literature devoted to this industry, it seems desirable to furnish some information of a general character, as explanatory of the symbols used to discriminate between the different shades of dyestuffs.

Several of the managers and chemists of the leading firms in New York City devoted to the sale in this country of the dyes, tabulated in the census, have kindly responded to inquiries in this connection. The following excerpts from their letters furnish a fairly good portrayal of the few conventional features, and the general lack of uniformity characterizing the use of marks for coal-tar colors:

The customary designation of dyestuffs as practiced by the manufacturers, their representatives, and the free-lances in the dyestuff business does not appear to be governed by any set formula. In the early days of the artificial-dyestuff industry, when dyes were few, the manufacturers designated distinct differences in shade by the letters B, R, and G, signifying blue, red, and yellow (gelb). Our French confrères used the corresponding B, R, J (jaune), and V (vert), which became familiar to dyers and dyestuff users. As dyes multiplied, differences in shade became more numerous and it became necessary to alter or to augment, as the case might be, the distinguishing marks. Consequently the marks 2 B, or 2 R, or 2 G, etc., became common and continue to this day.

No uniformity, however, exists between the corresponding marks of different concerns. For example, Chicago Blue 6 B, the lightest and brightest of the substantive blues, is designated in the schedule of another firm as 7 B, while among the products of still another firm it is indicated as FF.

Such marks serve to distinguish in a great measure the brands of different houses. One skilled in the art of buying and selling dyestuffs can, without great difficulty, distinguish a competitor's types among a variety of designations.

As far back as 1888 I went into this matter of type designations, discussed it with prominent dye agents, and was supplied by them at the time with comprehensive lists of their dyes and the meaning of their distinguishing letters. These demonstrated conclusively that each firm selling dyes was a law unto itself, so far as the commercial designation of its products was concerned.

Many individuals in and out of the textile industry and dabblers in tinctorial chemistry have entertained the idea that there was a key to a prescribed code of type designations which, in the hands of one possessing it, would unlock the numerous combinations of dyes required by individual customers, but this is not so.

We have, for example, a familiar instance of one of the smaller dyestuff firms, which designates its dye mixtures by numbers preceded by letters. These letters indicate the mixture books, Volume A, Volume B, Volume C, etc., and the number is that of the mixture. In order to duplicate the mixture, as in the case of a physician's prescription, one simply goes to the volume indicated by the letter and picks out the corresponding number. For all time the number holds good for one particular customer. No real trade secret is divulged by communicating this bit of information.

The letter X does not necessarily mean "extra," whatever "extra" is. In the codes of some firms probably it does mean "extra," presumably higher strength or greater brilliancy or solubility. In other cases it may designate the region where certain dyes are sold. NY, for example, indicates brands of colors prepared especially for the American market (New York).

The whole subject of dye designations is so complex that it becomes a hopeless problem to untangle. General references to it in literature are scarce, for the reason that there is nothing definite to say upon the subject. It is much like patent medicines; the medical trade has not formulated a code to designate such remedial agents.

Some dyestuffs are differentiated from others by appended letters to indicate their source, or the materials of which they are prepared. For instance, one of the well-known commercial types of Methylene Blue—specifically Methylene Blue SZ—of no particular merit as to shade, possesses

properties peculiar to itself on account of having been prepared free from zinc (zinc-zinc).

From the foregoing it is easily realized that the matter of commercial designations of dyes is very complex. While there are standards, *i. e.*, established types of individual dyes, such as those enumerated in the Schultz tables, from which millions of combinations are possible, every dyestuff firm has thousands and thousands of these combinations upon their books. Each is necessarily designated by some intelligible and comprehensive system in order to guard against errors and mistakes in compounding when called for.

Many well known types of "straight" dyes as produced by the manufacturer are, *per se*, of little value when used alone. Their value is brought out when used in combination with other dyes, and this is the strong point of many valuable mixtures that under no circumstance can be replaced by "straight" dyes. While we prefer to use straight or unmixed colors, we are frequently compelled to make use of mixtures, the value of which for dyeing purposes far outweighs the usefulness of the individual components when used separately. Such mixtures, of necessity, must be designated by different letters or numbers, to prevent confusion. A common instance of this is the very extensive series of combination shades, of great value, produced with the fast reds and azo scarlets, which may or may not be modified in tone by the judicious admixture of acid violets.—L. J. M.

There is no uniform practice and not much of a system in the marks which are used to distinguish the different brands of dyestuffs. This fact may seem rather strange, but it may be readily understood if one realizes that all dyestuff concerns have manufacturing and selling ends of the business—two loosely connected departments. The dyestuff is sent from the manufacturing department to the dyeing house, which is connected with the selling department. Both the dyeing house and the selling department are kept in ignorance regarding the chemical nature of any new product which is brought out. The same has, therefore, to be classified according to its shade and its dyeing properties. The result is that in many cases the dyer identifies a color with a group of others having similar dyeing properties but which, in fact, are chemically entirely different. The leading principle in naming the colors is less one of general classification than to furnish the salesman of a special factory with some hint as to the dyeing properties of any given color.

In most cases it is understood, for instance, that the letter B stands for "bluish." Hence, 2 B, which is equivalent to BB, denotes a still bluer shade. G means "greenish" or "yellowish;" R, "reddish;" V, "violet." Apart from these few cases of uniform practice the marks are open to all kinds of explanation. The mark L, for instance, may mean "soluble," or "fast to light," or even may stand for Ludwigshaven, which means that the color is identical with the well known dyestuff of the Badische Anilin- und Soda-Fabrik Co. at Ludwigshaven. In the same way C may stand for "Casella" (Leopold Casella & Co., Frankfurt); H for "Hoechst" (Farbwerke vorm. Meister, Lucius & Brüning, Höchst a. M.); E for "Elberfeld" (Farbenfabriken vorm. Friedr. Bayer & Co., Leverkusen, formerly at Elberfeld); and B or A for "Berlin" (Actien-Gesellschaft für Anilin-Fabrikation, Berlin). All these refer to types against which the competitive products have been standardized.

The word "extra" indicates either a special shade or a special concentration. It is a rule with us that our "extra" marks are more concentrated than the single brands, which otherwise bear the same name and mark. The letter X is often referred to by other firms in the same way as our "extra," for higher concentrations without, however, giving any definite information regarding the proportionate strength.

Many suggestions have been made in order to do away with this rather confusing habit of classification, but so far without success. The reason is that the selling staff on the one hand, and the millman on the other hand, are not expected to possess much chemical or coloristic knowledge. Such knowledge only would enable them to benefit from a more complicated and scientific system.—A. M.

It is a pretty well-established practice among dye manufacturers to use certain marks and letters in connection with the name of any color. All dyestuffs may be said to vary in shade from red to yellow or from blue to yellow, and this variation from the standard type is designated by the letters B, G, R, etc.

Take, for instance, Methyl Violet, which varies in shade from 3 R to 6 B. The 3 R indicates a reddish shade, nearly approaching Magenta, and 6 B indicates a bluish shade nearly approaching a product like Victoria Blue B. It follows from this that 3 R means a tint redder than 2 R, 3 B means a tint bluer than 2 B, and 6 B denotes a still bluer shade than 3 B.

The letter G is generally the abbreviation for the German word "Gelb," which means yellow. The French word for yellow is "jaune." Consequently, French, Belgian, and sometimes Swiss firms use the letter J where Germans use G. English and Americans employ for the same purpose the letter Y. 2 G means the same thing as if the letter G is repeated twice, and 3 G means the same as if it were repeated three times.

As to the use of the letter X and the word "extra," these two designations are by no means alike. The word "extra" is ordinarily used to indicate a quality superior to the regular type. This is sometimes shortened simply to the letter X. More generally X indicates that the product in question is reduced 10 per cent below the standard type. XX in that case would mean that it is reduced 20 per cent below the standard type.

The mark W indicates that a dye is employed preferably for "wool," and HW refers to the wool fabric industry. The mark S indicates frequently a bisulfite compound, as in the case of Alizarin Blue S, SR, and SW. Sometimes it denotes a sulfonic acid, as when used with Alizarin Red S, SA, and WS, or Fuchsine S, SS, SN, and ST.—E. C. K.

WASHINGTON, D. C.

CONDITIONS AFFECTING THE ESTABLISHMENT OF THE NITRATE INDUSTRY IN THE UNITED STATES<sup>1</sup>

By LAWRENCE ADDICKS

The general problem of the establishment of the nitrate industry in the United States is complicated by the existence of several more or less conflicting and unrelated factors which fact in large measure accounts for the present confusion as to the relative merits of the various available processes for the production of nitric acid. These factors may be stated as difficulties in

<sup>1</sup> Read before the 53rd Meeting of the American Chemical Society, September 25-30, 1916

properly evaluating (1) military necessity, (2) the forced-sale price of Chilean nitrate, (3) certain technical difficulties, (4) the attitude of the Government regarding water power development, and (5) that of the farmer toward changes in fertilizer practice.

The standard method of manufacturing nitric acid by digesting sodium nitrate with sulfuric acid is very satisfactory. The investment in plant is reasonable, the process is simple and the end-product is nitric acid in quite concentrated form. As sulfuric acid and nitre are easily transported, such a plant may be operated anywhere, while nitric acid is at best an undesirable article of freight.

It has been long evident and for a little while generally appreciated that were we to have a war with a first-class power about half our navy would be engaged in protecting our line of communication with Chile instead of protecting our coasts, and, as nitric acid is indispensable in the manufacture of explosives, this has given the government a special interest in the development of a process requiring no imported supplies. This introduces the question of military necessity, which is a need for a prompt supply of concentrated nitric acid in enormous quantities upon a sudden demand and in a time of commercial isolation. In view of the tremendous expenditure of explosives in the European war it is hard to stipulate our maximum need, but considering only defensive warfare and that distance from possible enemies would make the assembling of a nation's entire land fighting force against us very unlikely, the estimated requirements are much more than the probable consumption of nitric acid as such in peace times at present. This means that if the Government undertakes to guarantee its requirements by building and operating a plant it will cripple industry in two directions—first by marketing nitrates at forced-sale prices in time of peace in order to keep the plant in shape and justify the investment, and second by stopping commercial exploitation of one or more of the processes for producing nitrates now in private hands. The alternative is to stock a large quantity of Chilean nitrate, which is easily stored, until the day when commercial rivalry develops the best process. Thus the military argument instead of stimulating work on the production of nitrates has an unpleasant possibility of strangling it.

If we dismiss the military preparedness issue we are at once confronted with another problem—how low can the price of Chilean nitrate be driven by domestic competition? Nitre is generally considered to command a price of a little over 2c. per lb. in this country in normal times and the total available supply in Chile is estimated at thirty years more or less, so that progressive exhaustion would tend to send the price up as the years pass. On the other hand these nitrate fields have enjoyed such a natural monopoly of the market that they have never had to meet real competition. It must be remembered that about one-fourth of the assumed saleprice goes to the Chilean Government as an export duty, that increased trade with South America may drive down freight rates for return cargoes, and that improved mining and leaching methods may lower costs. Finally the life of the district is constantly being extended by including leaner deposits than formerly thought workable, so that it is quite possible that the forced-sale value of Chilean nitre may prove to be surprisingly low.

Then we come to the processes, of which there are a surprising number considering the difficulties of the problem. They may be classified technically as chemical, electrochemical and biochemical; or by source, as utilizing the nitrogen in the atmosphere or that in coal; or finally as producing nitric acid directly by the combustion of atmospheric nitrogen or indirectly by the oxidation of ammonia. Altogether there are some ten distinct processes, most of which have enthusiastic advocates in this country, and I have been solemnly assured by the representatives of three that each has been the method relied upon by Germany these last

two years, which probably simply means that that blockaded country has found it necessary to use every source of nitrogen available to meet the combined demands for explosives and fertilizers.

The most direct process is of course the oxidation of atmospheric nitrogen in the electric furnace upon which so much work has been done in Norway. This is an enormous consumer of power but no greater than the standard process for the reduction of aluminum per ton of product. The hopeful part of this process to me is its low efficiency, but 2 or 3 per cent of the nitrogen in a given volume of air being oxidized at last accounts. On the other hand the efficiency is high when the equilibrium of the reaction under the conditions of operation is considered. We know, however, that greater efficiencies are possible with mixtures richer in oxygen than the atmosphere; this is interesting when coupled with the fact that oxygen obtained as a by-product in the cyanamid process is at present thrown away. Other ways of obtaining conditions affording an increased yield may be discovered and an improved efficiency lowering the power cost would give the arc process a commanding position, the raw materials being free and present everywhere in unlimited quantities.

The cyanamid process appears to be fully developed and the high efficiencies obtained in every step of the process would seem to preclude the possibility of any great lowering of the cost in the future. It has the advantage, however, of making several useful intermediate products and in fact from the nitrate point of view cyanamid may be considered simply as a raw material for the production of nitric acid.

The Haber process for the synthesis of ammonia seems to have surmounted great obstacles abroad. It makes no demands for power beyond a reasonable quantity of coal and the records of the patent office indicate that serious attempts are being made to make the working conditions less extreme.

Passing over the various processes based on nitrides or cyanides and similar compounds, of which cyanamid has been the only notably successful instance so far, we have the biochemical action which is the basis of the "saltpeter plantations" of the East Indies.<sup>1</sup> Wood ashes, animal refuse, stable products and earthy material are piled up and allowed to stand for several years, when it is found that the outer crust contains potassium calcium and magnesium nitrates which can be leached out. This bacterial action is worthy of systematic study.

Finally we have the large and steadily increasing output of ammonium sulfate from the by-product coke ovens in various parts of the country. Unfortunately little or no work seems to have been done on the oxidation of crude ammonia to nitric acid, and it is hard to form any just opinion of the magnitude of the difficulties reported in the poisoning of catalyzers by impurities. Truth to tell when ammonia is available as a market product, but little commercial interest has been shown in the further step to nitric acid owing to its limited market, and only the arc processes enter the field by compulsion.

Practically all of the processes have to meet the problem of concentrating dilute nitric acid and all but the arc processes must contend with the more formidable one of the economical oxidation of ammonia. The electrochemical processes have the power cost problem in addition and altogether we have the elements of a first-class family quarrel in selecting the method best adapted to our local needs. If the Government keeps hands off for two or three years the quarrel will go merrily on and result in the survival of the fittest.

The water power problem has a very serious bearing on this whole matter. In fact it is possible to range the arc process, the cyanamid process and the Haber process in any order we desire as to cost by suitably varying the cost of power. Unless water power is available it seems certain that no electrochemical process can survive and the whole legislative situation regarding

<sup>1</sup> Remsen's "Inorganic Chemistry," p. 488.



the use of water rights in this country has been impossible for ten years. Until this has clarified, the chemical processes, which at present have the advantage, always have to face the possibility of a truce between the conservationists and the liberals which may turn the field abruptly over to the electrolytic methods.

Finally we have the American farmer to deal with. He insists on being supplied with a complete fertilizer, which can be put on in a single application and fed through drills which cuts out any hygroscopic material. This means that nitrogenous products must either be sold to a fertilizer manufacturer or made the basis of a fertilizer manufactory. In order to get around this, various bucolic advisory staffs have been organized by competitive interests and the farmer is being shown one week why ammonia is better than nitrate and the next why nitrate is better than ammonia, and so on. Said farmer has by this time probably reached my own conclusion, that the whole problem is both interesting and complex, if not convincing, but when he finally makes up his mind it may have much to do with the establishment of the nitrate industry in these United States.

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NEW YORK CITY

### WHY OUR CHEMICAL IMPORT STATISTICS SHOULD BE OVERHAULED<sup>1</sup>

By BERNHARD C. HESSE

On three previous occasions<sup>2</sup> I have pointed out in more or less detail the need of a revision of our chemical import statistics, more particularly in reference to the need of a finer subdivision of the itemization of the entries and have indicated how this might be accomplished.

Assurances of enthusiastic and sympathetic coöperation have been received from a number of technical and commercial associations and organizations, as well as from the Department of Commerce and from the United States Geological Survey. Many high executive officers of domestic chemical manufacturing and merchandising enterprises have assured me of their belief and faith in the great potential good residing in such an effort, and editors of our leading trade publications such as the *Oil, Paint and Drug Reporter*, of New York, and the *Paint, Oil and Drug Review*, of Chicago, have in sincere and emphatic editorials seriously commended this endeavor to the thoughtful consideration of their readers and have urged intelligent and prompt coöperation.

It is, therefore, only reasonable to assume that these proposals bear, on their surface at least, evidence of potential constructive good for the country at large. It now remains for us to realize this supposed potential good. To this end the coöperation of all the sections of the American Electrochemical Society and of the American Chemical Society has been solicited and there is plenty of evidence of a whole-hearted desire on the part of all to contribute all they can and to coöperate to the extent of their opportunities and ability.

As a result of considerable correspondence with sectional secretaries and of conversations with a number of local counsellors during the holding of the Second National Exposition of Chemical Industries last month, it has seemed to me that after all I had not succeeded in clearly bringing out the crux of the situation, so that all were clear as to just what was wanted and as to how it might be done, although quite a number of sectional secretaries did fully get the ideas and suggestions conveyed by my publications and have proceeded accordingly.

In view of the situation as a whole, it may be well to say what are *not* the objects of this project, since many seem to have

obtained enlarged notions of its scope, which would be unworkable.

1. We are *not* now concerned with exports in any sense.
2. We are *not* now concerned with prices or quantities in any sense.
3. We are *not* now concerned with locus of import or consumption.
4. We are *not* concerned at any time with the names of users or importers.

What we *are* after is the names, and *the names only*, of those things that in normal times come to us from abroad and are used by or can be made by a branch of our chemical industry.

For example, what material of construction or what chemical raw materials come to us from abroad which our domestic chemical industry in any branch thereof needs?

What materials that can be made by a branch of our domestic chemical industry are imported?

It must be noted that quantities, prices—unit or otherwise—and locus of consumption are wholly irrelevant and immaterial, and any attempt to superimpose those data upon the simple request for names only of materials, etc., will very likely lead to confusion and embarrassment and probably refusal. It is merely a *qualitative* list we are now after.

Now, why should we want such a list and why bother you with the labor of finding that list out? That is a question that I have been frequently asked. The answer to that is that the person does not live who can formulate a sure-enough definition of a product of or for chemical industry that will be intelligible to any one and that would answer our purposes. Obviously our government cannot feasibly list separately each of the thousands upon thousands of different articles that enter our ports, and if it did so list them many of them would not be used. Just think of the sized volume that such a list would require! Since a verbal definition is out of question the only refuge is in illustration. Now, your answer, like others, may very well be: "Tell the government we want all products of and for chemical industry listed item by item. Give them a copy of all chemical catalogues and tell them we want to know all about each item in those catalogues." Now the answer to that kind of an answer is that it is no answer at all. Self-evidently, we as American commercial, industrial or manufacturing chemists cannot possibly be interested in every chemical listed in every chemical catalogue, and moreover, we are interested and deeply so in many things that never are mentioned in any chemical catalogue of any kind. For the same reasons we cannot refer the government to any one of the numerous Buyers' Guides. We cannot give the government a blanket list for the simple reason that there is no such list. England, France, Germany, Sweden, Canada, Switzerland, Italy and the United States, each and all have a different official notion of where products of and for chemical industry begin and end. Our own government's list is not adapted to our best service and I am sure that none of the other governments' lists would be satisfactory. I have compiled such a composite list which has been published in at least four places.<sup>1</sup>

Your next question will probably be: "What will you do with that list after you get it?" To that the answer is that the Central Committee, of which I am chairman, will, if the response is satisfactory, compile all of the submitted material into a composite list and ask the government to give us the quantities and values imported monthly, quarterly or annually as may appear best suited to our needs.

Then you will say: "Be sure and get a good classification; have it logical and scientific; the present classifications are so illogical and so unscientific." The answer to that is that we cannot, in reason, ask the government to alter its mode of

<sup>1</sup> Presented at the Joint Meeting of the New York Sections of the American Chemical Society, American Electrochemical Society and the Society of Chemical Industry, Chemists' Club, October 13, 1916.

<sup>2</sup> THIS JOURNAL, 7 (1915), 58; 8 (1916), 672 and 749.

<sup>1</sup> THIS JOURNAL, 8 (1916), 749; *Met. & Chem. Eng.*, 15 (1916), 143; *Oil, Paint and Drug Reporter*, July 31, 1916, p. 16; *Paint, Oil and Drug Review*, Aug. 16, 1916, p. 11.

collecting and classifying its information; all we have a right to do is to ask for a finer subdivision of the items reported. The reasons, among others, for this are:

The original sources of information are the consular invoices which are filed with the Treasury Department; for the purpose of determining the duty to be levied, the items of each invoice are classified or marked according to the relevant tariff law paragraphs and the duty rate stated.

In making up its returns the Treasury Department is primarily interested in the amount and value of dutiable goods entered under each of the paragraphs and the duty collected, and to a secondary or subordinate extent as to the nature, quantity or values of the various items under each of those paragraphs. Then the Department of Commerce takes these invoices or the collated records of the Treasury Department and selects from them those items that it has reason to believe are specifically of interest to the public. Now, that is where *we* come in. *We* must tell the Department of Commerce with as great practical and practicable detail as we now can what specific items *we*, as industrial chemists, are really interested in. We cannot seriously be interested in every single item imported by any one or all of our chemical supply houses, and for that reason to have the government go to all that trouble would be in large part useless labor. The best we can do is to give the government the best sort of a line that we can on what we are really interested in.

At this point you will no doubt say: "Now, won't your committee get a lot of duplications in names and how am I to know what some other section reports?" The answer is: "Never mind about duplicates; you send in your stuff; duplicates are our troubles and we will handle that."

Still you may say: "Must I get a complete list of all we are interested in?" The answer is: "Not at all; just tell us what things are lacking in the various lists published in *THIS JOURNAL*, for August, 1916, or in *Metallurgical and Chemical Engineering* for August 1, 1916, or *Oil, Paint and Drug Reporter* for July 31, 1916, or *Paint, Oil and Drug Review* for August 16, 1916, in which you are interested and we will do the rest. That is one way of doing it and as near as I can figure it, it is the shortest and easiest way, and further, it is the way I suggested in the article containing those lists. If you prefer to do it some other way—go to it, but get there!

"In other words, if our commerce reports were to list separately all the items given in all those various lists would your section of the country and its interests be taken care of? If not, what do you want added to those lists? All we want is the *name* of every addition you want."

Then you will probably ask: "What good do you expect from all this trouble you are asking us to go to?" The answer is: "Suppose antimony oxalate (which is not now reported in our reports) were shown to be imported in increasing quantity quarter by quarter, some domestic maker might make up his mind to go after that market, and bag it for himself; tally one for the list—for we would be just that much nearer independence and so on *ad lib*. Some day you might be the lucky man to make a ten-strike."

By this time if you are like most of those to whom I talked during "Chemists' Week" in New York, you will begin to show signs of great personal interest and you may ask: "Will I have to dig through those big volumes every month to find out about these thousand-and-one-things?" The answer is: "Not at all, if the A. C. S. is alive and on the job." The government cannot reasonably be expected to get out a separate publication for us chemists; if it did it would have to do so for every other branch and there would be many overlappings. For example, suppose the leather industry to want such a separate list; many of its items are on our list, and so on down the line. The A. C. S. will have to separate out that information every time such a

government report comes out and publish it in the *INDUSTRIAL JOURNAL*. So that not everybody goes to sleep and gets the idea that that information is published merely to take up space, I should like to see a standing head something like the following:

"The information herein given was collected by our government in the expectation that with its help our chemists will most intelligently and effectually work towards the self-containedness of the nation."

This standing head would be a constant reminder to our members that they are expected to make intelligent and constructive use of that information, and also a reminder to our government that it too must keep awake and tell us of any newcomers as soon as they show up.

As I see it, the real lesson of the war to us as a people should be that our national well-being requires a diversified industry as well as an industry turning out large quantities. Up to twenty years ago or thereabouts Germany was largely engaged in diversifying her industry, and for the past twenty years or somewhat longer she has been engaged in "mass-production," so that for many years past Germany has had not only a highly diversified industry, but also one dealing in and producing large tonnages.

We have the large tonnage capacity and point of view, but we do not have the diversified industry point of view, and it is in order that we may acquire this latter in the shortest possible time that this present work has been undertaken.

With this fragmentary and sketchy introduction, I will proceed to the more fundamental aspect of the case.

For upwards of thirty years the attitude of the country as expressed in three Republican and two Democratic tariffs and one Democratic partial tariff-revision, has been that our chemical industry in general and coal-tar dyes, in particular, shall not be protected and that any tariff laid on chemicals and dyes shall be non-protective and for revenue-yielding purposes only. The tariff efforts at protection were and are directed toward other industries.

Immediately upon the outbreak of the present war our press and the public severely scolded us chemists for not making coal-tar dyes; dyes seemed to be the limit of their information as to what chemists do. Many other and more important things which were in the same condition as dyes were overlooked, deliberately or otherwise, in this tirade and this fusillade of criticism. The reason was and is clear. The raw cotton market had been shot to pieces and fabricated cottons then on the market were made from high-priced cotton and buyers demanded sales at the then prevailing very low raw cotton prices; thereupon the manufacturers set up the dyestuff bogey to bolster up their demands for higher prices for fabricated cottons. Going behind the scenes, it is clear that this demand for dyestuff independence is, far more likely than not, artificial, and in the light of the experience of thirty years past, insincere and thoroughly non-dependable. Economic beliefs of the two political parties and the business policies of the nation more than thirty years old cannot be expected to be overturned so suddenly and such sudden alleged change cannot be sincere nor lasting, panic-time conversions and statements to the contrary notwithstanding. The chemists of the country will simply be living in a fool's paradise if they bank on it that the above view of our industry by the public has undergone or will soon undergo any lasting change.

#### THE KITCHIN REVENUE BILL

In his speech of acceptance on September 2, 1916, President Wilson said: "We have driven the tariff lobby from cover and obliged it to substitute solid argument for private influence." While this may be true as a general statement it does not at all apply to the inside history of the making of the dyestuff section of the Kitchen General Revenue bill. Leader Kitchen himself says that it was compromise between the Hill bill rates or no



added rates at all. The Kitchen rates are and were dictated solely by private influences privately exercised and rest upon no "solid argument" nor public proceedings whatever; they are merely the result of "take what the dye-users offer you or you get nothing at all." A few only of the dye-users forced this situation; let no one be deceived, the big influences in the dye and chemical using field are not behind this movement at all. When the right time comes, and signs to that effect are already evident, those influences will have any rates above the Underwood tariff taken off, and taken off quickly at that, for they probably will not be permitted to raise the duties on their own finished products; then our domestic dye and chemical makers will be as badly off as ever, and our chemical industry instead of having been helped forward will have been given a "black eye" by the very politicians who professed to be its friends. The underlying reason for this on-the-surface solicitude for the welfare of our domestic chemical industry by both political parties is votes and is not dictated by any primary or real desire for a domestic chemical industry; our politicians are not yet educated up to that point. It has been variously estimated that 400,000 to 800,000 votes are to be found among the operatives of the dye-using industries; by some political legerdemain both political parties hope to convert this alleged dyestuff solicitude into a solicitude for the welfare of those voters. The chemists of the country are worth hardly 10,000 votes to the politicians.

Further, it must be remembered that among domestic dye and chemical users the feeling is growing: "Well, we were more scared than hurt; we 'got by' this time; it's a long time to the next war; we should worry. Let others take care of themselves; we want cheap dyestuffs and cheap chemicals and we do not care who makes them; dyes and chemicals are our raw materials and raw materials must be free."

On the theory of the "greatest immediate good to the greatest number," and this is perhaps for the present and the immediate future properly expressed by the number of influenceable or affected votes, it is reasonably certain that our country will not lastingly reverse itself in its fiscal and economic policy of the past generation. Products of chemical industry are not themselves and as such very largely sold to the "ultimate consumer," that is, the voter. They are largely used in making things that are made by and do reach the voters and to those who make these things that thus reach the voter the products of chemical industry are raw materials, and the country long has been and still is fairly well united on the proposition that "raw materials must be free," and particularly where the making of those so-called "raw materials" in this country will not directly affect many—particularly voters.

Contrary to all the expectations raised by the recent discussions of the press, the country seems to have set adrift its newborn desire to insure to those industries that it has a domestic supply of such of their raw materials as are in reality highly manufactured products of other industries and has definitely decided to continue in this respect to be dependent upon foreign nations.

Based upon the classification and the figures of the census of 1909 and if we compare the average chemical plant with the average plant in all domestic industries, it appears that the average chemical plant, when so contrasted, costs 330 per cent of that general average, employs 144 per cent as many persons of which the salaried employees are 264 per cent of the general average and the wage earners 134 per cent; the output value is 261 per cent of the general average and its enhancement in value is 248 per cent. Therefore, as a unit, the average domestic chemical plant costs more, produces more, enhances more, employs more salaried persons and more wage earners than the average industrial plant.

A dollar invested in our chemical industries is not so productive as in our industries as a whole; it spends less for wages, salaries

and materials and produces less product value and less enhancement value.

Per \$100 of product, the general average and the average domestic chemical plant, respectively, expend \$16.58 and \$9.09 for wages, \$4.54 and \$5.65 for salaries, or \$21.12 and \$14.74 for services.

Per individual wage earner the annual output of product is \$3,125 for the general average and \$6,035 for the average domestic chemical plant.

Per individual salaried employee, the annual output of product is \$26,157 for the general average and \$25,733 for the average domestic chemical plant.

The average salaries are \$1188 and \$1455, respectively, for our industries as a whole and our domestic chemical industries; the average wages are \$518 and \$549, respectively; in the industries as a whole there are 8 wage earners to each salaried employee and in our chemical industries there are 4 wage earners to each salaried employee.

Relatively, our chemical establishments are 0.79 per cent of all our industrial establishments and the number of persons employed is 1.15 per cent of all persons employed in manufacture.

So that while an average chemical plant, as such, is of greater importance to the community than the average industrial plant, yet the capital so invested is not so productive as in the average industries. It is possible that sooner or later the American public will decide that our national well-being requires greater development along chemical lines since chemical products are raw materials for so many domestic industries, and will be prepared to take what steps may be necessary to accomplish that result, but until that time arrives, we chemists must be prepared to make our own way and on our own merits and independently of any economic help from politicians, for we must remember that whatever one set of politicians may give us another set of politicians can take away; such artificial help may merely be producing more of those undesirable ventures known as "War Babies."

Obviously, therefore, we chemists cannot stop to quarrel with the facts, but we must simply make friends with the situation as it is. These are simply "the rules of the game." The country does not want to help us broadly, as is for the sixth time and conclusively proved by the happenings of the past two years, and yet the country, in a half-hearted way, wants and really should have a chemical industry—complete to be sure—but it will have to be content with what it can get in that direction. It is our duty to give the country the utmost that we can give it. We have done the best possible under the conditions of the past and present. In order to help our country more we must know with considerable particularity what our country buys from abroad. If our country wants us to help more than we have heretofore the country must tell us more than it has in the past. Chemists are not mind-readers, nor clairvoyants. When the country says: "We import \$800,000 worth a year of fifty different chemicals," what good does that do it or do us? Could anything be more tantalizing to chemists? Why not tell us what those fifty things are and how much of each and at what price it reaches this country? Then we might be able to do something additional. Why should we be called upon to guess what these fifty items are and what their respective values and poundages are? The country has that information and why hide it?

If the chemists of the country were fully informed as to the values and amounts of imports into this country of products of and for chemical industry, we could then more intelligently and more surely work towards the self-containedness of the nation, and more completely utilize to the utmost all opportunities around us; if then, added economic help in certain directions were clearly needed, and if by then President Wilson's above statement has actually been realized with respect to our products and the

country really wants our industry, it seems only reasonable to expect that such added help would then be forthcoming, promptly, permanently, willingly and intelligently.

Our first duty, then, is to tell the country *how* we suggest to have this added information imparted; then, if the country does really give us that, it will be our second duty to take hold of the opportunities thus disclosed and make them give up all they can be made to give up; we can then cross the next bridge when we come to it. In the meantime we have our hands full trying to get this request for more information into presentable and convincing form.

In making up this list of *import* items we must bear in mind that it should contain everything that a well rounded-out and self-contained chemical industry needs either in materials or apparatus or makes in the way of products, finished or intermediate, for its own use or for use in other and wholly non-related industries, and this is much more varied than any available list of such products; this is our real task—to make the list complete in every respect.

The function of such a complete list is threefold:

I—It will inform government officials and the public of, and will visualize to both, the variegated and ramified activities and interests of chemical industry.

II—By its illustrative character it will enable our government officials to "spot" a relevant newcomer in our field much more readily than otherwise.

III—It will tell us chemists ourselves a great deal more about our own business, our own opportunities and our obligations to other industries than any collection of text or handbooks ever could.

It is rather a "tall order," but if we will not make up such a list why should we expect others to do our work for us? And who else should do it? It is our job and no one's else.

When considering the taking up of making things in this country that are up to then largely or wholly imported from abroad, we must bear in mind that, in general, increased domestic consumption follows domestic manufacture so that an imported item of \$10,000 per year may in a few years of domestic manufacture reach a consumption of three or four times that figure.

Finally, it must not be lost sight of that when we ask for greater subdivision of the items of imports in our commerce and similar reports we are not at all asking for a revision of the general classification. These reports can convey the same financial and other information as to the sources and amounts of revenue as heretofore; we do not ask to have this function of those reports curtailed nor hampered in the least; all we ask is that they be made to contain and to give *more detailed* information as to our items of purchases of products of and for the chemical industry from abroad.

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## GERMAN PATENT-BIBLIOGRAPHY

By EARL N. JESSOP

In most cases, it is a difficult and tedious task to find the specification data of a German Patent unless one is familiar with the method of procedure.

The German Patent system differs from the United States Patent system, in that the German Patents are not published in the "*Auszuge aus den Patentschriften*" ("Abstracts of Patent-text," corresponding to the U. S. Patent Office Gazette) in chronological order, but are distributed, according to their subjects, among various classes and sub-classes. At present there are approximately 380 classes and sub-classes which include many and varied subjects; such as *Sprengstoffe* (Explosives), *Photographie* (Photography), *Tabak*, *Zigarren*, *Zigaretten* (Tobacco, Cigars, Cigarettes), etc., with appropriate sub-classes. The class especially interesting to chemists is Class 12, *Chemische*

*Apparate und Prozesse* (Chemical Apparatus and Processes). There are numerous sub-classes (denoted by letters) to Class 12; e. g., Class 12d, *Klaren, Scheiden, Filtrieren* (Clarification, Separation, Filtration), Class 12h, *Allgemeine elektrochemische Verfahren und Apparate* (General Electrochemical Processes and Apparatus), etc.

Thus the patents are placed in the particular class to which they belong, regardless of a chronological arrangement of numbers, and present rather a confused appearance; e. g., in 1913, Patent No. 266,863, is followed by Patent No. 267,138.

Corresponding to the Index to the U. S. Patent Office Gazette is the *Verzeichnis erteilten Patente* (Index of Patents granted), which is the proper starting point in the search for a patent.

There are five sections in the *Verzeichnis* (Index), as follows:

1—*Chronologische Uebersicht der Patente* (Chronological List of Patents), a chronological list of the patent numbers, followed by the number and letter, showing in which class the patent has been placed.

2—*Systematische Uebersicht der Patente* (Systematic List of Patents), a chronological list of classes and sub-classes, with the patents as they have been distributed, including the patent number, title of patent, date, and a page reference to the *Auszuge* (Abstracts).

3—*Alphabetisches Namenverzeichnis der Patentinhaber* (Alphabetical Name-Index of Patentees) gives the name of patentee, number of patent, class, and a page reference to the above class from which can be obtained the data desired.

4—*Alphabetisches Sachverzeichnis* (Alphabetical Subject-Index) indexes the patents according to subjects and gives the patent number, class, and a page reference to Section 2 above. This list gives no names.

5—*Verzeichnis der Patente* (Index of Patents):

(a) *Nach Patentklassen geordnet* (Arranged according to classes).

(b) *Nach Patentnummern geordnet* (Arranged according to numbers).

This list gives all patents which are in effect at that date, but gives only the patent numbers. In (b) the patent numbers are given, and after them are the class numbers and letters given in parentheses.

The only index given in the *Auszuge* (Abstracts) is the chronological list of classes and sub-classes, with the patents included in them.

With this preliminary information, the method of procedure, which is comparatively simple, is as follows: There are three possible starting points, viz.:

I—Patent Number. II—Name of Patentee. III—Subject of Patent.

I—If the number of the patent is known, look first in the following table to find in which year of the *Verzeichnis* (Index) the patent was published.

Year	Pat. No.	Year	Pat. No.	Year	Pat. No.
1877-8	1-4390	1890	50781-55460	1902	128483-139092
1879	4391-8800	1891	55461-61010	1903	139093-149056
1880	8801-12766	1892	61011-66910	1904	149057-158245
1881	12767-17105	1893	66911-73340	1905	158246-167845
1882	17106-21236	1894	73341-79620	1906	167846-181275
1883	21237-26084	1895	79621-85340	1907	181276-194525
1884	26085-30543	1896	85341-90750	1908	194526-206135
1885	30544-34561	1897	90751-96190	1909	206136-218130
1886	34562-38569	1898	96191-101760	1910	218131-230230
1887	38570-42431	1899	101761-109190	1911	230231-242870
1888	42432-46374	1900	109191-117974	1912	242871-255950
1889	46375-50780	1901	117975-128482	1913	255951-269470

Then look in either the first or last table in the *Verzeichnis* (Index) for that year—where the patent numbers are arranged alphabetically—and a class number will be found following the patent number. Then look under that class in the *Systematische Uebersicht* (Systematic List) and here will be found the patent number, name of patentee, title of patent, date, and a page reference to the *Auszuge* (Abstracts) for the same year. On this page in the *Auszuge* (Abstracts) will be found a short



abstract of the patent (such as appears in the U. S. Patent Office Gazette).

11 If only the name of the patentee is known, look in *Alphabetisches Namenverzeichnis der Patentinhaber* (Alphabetical Name-Index of Patentees) and there will be found the patent number, class number, and a page reference to *Systematische Uebersicht* (Systematic List). From this point the procedure is the same as in I.

III If only the subject of the patent is known, look in *Alphabetisches Sachverzeichnis* (Alphabetical Subject-Index) and there will be found the patent number, class number, and a page reference to *Systematische Uebersicht* (Systematic List), but no names are given in this section. From this point the method is the same as before.

An example would probably be helpful. Suppose one wishes to find Pat. No. 266,863. First look in above list and there it will be seen that No. 266,863 is in the *Verzeichnis* (Index) for 1913. Upon looking in the first table in the 1913 *Verzeichnis* (Index), Pat. No. 266,863 will be found in Class 12i. Then by looking under Class 12i in the following section of the *Verzeichnis* (Index) there will be found the following:

Pat. No. 266,863. A. Messerschmidt.

"Process for Generation of Hydrogen by Alternate Oxidation and Reduction of Iron, etc." 9 7 11 2534.

(Note that the Germans in writing the date in this manner, always reverse the month and day. Where we write 9/7 for Sept. 7, the Germans use 7/9; where we use 7/9 for July 9, the Germans use 9/7.)

An abstract of the patent will be found on page 2534 of the *Auszuge* (Abstracts) for 1913.

If only the name "Messerschmidt" were known, there would be found by looking in the *Alphabetische Namenverzeichnis der Patentinhaber* (Alphabetical Name-Index of Patentees) under "Messerschmidt," the No. 266,863, Class 12i. Knowing the patent number or class, the above method can be used.

If neither the number of the patent nor the name of the patentee were known, but only the subject, the patent could be located by looking under *Wasserstoff* (Hydrogen) in the *Alphabetische Sachverzeichnis* (Alphabetical Subject-Index), where there would be given the patent number, class, etc., and from this the patent could be traced as explained above.

MELLON INSTITUTE, PITTSBURGH

## SYMPOSIUM ON OCCUPATIONAL DISEASES IN CHEMICAL TRADES

Papers presented at the Annual Meeting of the American Chemical Society, New York City, September 29, 1916

### OCCUPATIONAL DISEASES IN THE CHEMICAL TRADES

By CHARLES BASKERVILLE

Chairman of the American Chemical Society Committee on Occupational Diseases in the Chemical Trades

An International Congress, dealing with the subject of industrial diseases, was held at Brussels in 1910. The first Congress took place in 1906 in Milan, and since then an institution has been established there devoted to the study of diseases of occupation and to matters of industrial hygiene. Previously, museums of safety had been established in Berlin (1904) and Vienna (1909). The American Museum of Safety is established, but in very inadequate quarters in New York City.

The Brussels Congress was attended by over 600 delegates, and approximately 20 per cent of the papers presented were by medical men of Great Britain, where the subject has received attention for a number of years, both by the Factory Department of the Home Office and by the Association of Certifying Factory Surgeons.

A Committee on Occupational Diseases in the Chemical Trades was appointed by the New York Section of the American Chemical Society in February, 1912. Some of the reasons for the existence of the Committee appear in the statement of its objects which were, specifically:

1—To hold itself ready to advise the Legislature of the State of New York in reference to matters appertaining to occupational diseases in the chemical trades.

2—To study various bills presented in the Legislature in an effort to avoid unwise technical legislation.

3—To superintend and inaugurate such investigations as might be decided upon which would look toward improvement of conditions of labor in the chemical trades.

Two members of that Committee served the New York State Factory Investigating Commission and assisted in formulating the present laws having to do with inorganic chemicals, ventilation, and the regulation of the use of wood alcohol.

Subsequently the Parent Society appointed the present Committee, whose personnel has changed but little since its creation. The objects of this Committee have been to extend the intent and purpose of the Sectional Committee in so far as legislation was concerned. It was and still is the hope of the Committee to secure sane and uniform legislation in all the states. This accomplishment, however, requires time and patience, which are essential for bringing about things in a re-

public, where so many states of different interests, different modes of thought, etc., constitute the whole.

Another purpose of the Committee has been to learn of specific conditions in particular chemical trades which might call for improvement. To that end its members in the several parts of America represented have sought information, solicited and offered advice. It has cooperated with Boards of Health and private corporations. Its work, however, has not been systematic or in accordance with any well-defined plan, for the simple reason that no funds have been available to meet the expenses of investigation, adequate clerical force for propaganda, etc. The work requires financial support to be properly organized.

Informally the Committee has learned that some manufacturers are doing much toward the protection of their labor, while others are absolutely inconsiderate. The former are governed by motives altruistic, an appreciation of the efficiency of a healthy workman, and they are frequently supported by laws covering the employment of labor in factories. They are often handicapped, however, by unwillingness on the part of labor to utilize the precautionary facilities placed at hand.

The other group of manufacturers, fortunately relatively few in numbers, are selfishly inhuman in some instances and go their way lawlessly or more often in blind ignorance, for the untoward action of some chemicals is slow and insidious. In fact, one of the important questions in connection with industrial diseases is, "Is it possible to draw a distinction between maladies which are the result of certain occupations and accidents?" This is of great significance in connection with the "Workmen's Compensation Act" of England, and of the same importance in the relations between "Master and Servant" in this country. It is indeed difficult in many cases to ascertain whether a disease is the direct result of the nature of employment; but the justness of the principle of compensation for so-called industrial diseases is generally accepted, and the method of procedure by the aid of a schedule of diseases as adopted by the English law is regarded as a good example to follow. In the United States, certain severe and clearly traceable diseases resulting from occupational causes have had recognition, and active campaigns against such industrial maladies as plumbism and phosphorus poisoning have resulted in specific legislation.

Workmen's Compensation Laws have been enacted in about one-third of the States of the Union and there is hope that a federal bill proposed may yet receive favorable action. The

various State factory laws are, for the most part, however, concerned with minimizing fire-risks and obviating accidents to workmen engaged in purely mechanical operations.

Even though two excellent books on Occupational Diseases written in this country wholly or in part by some of the participants in this symposium have come from the press within the past two years, yet, as reverted to above, the action of some chemicals is insidious and not always known. It is of prime importance, therefore, that the introduction of any novel substance into industrial operations or the introduction of a novel procedure (electrolytic zinc at Anaconda, for example) should be studied to detect possible danger at an early stage so that due precautions may be taken. Usually trouble is recognized only after its results have become more or less pronounced. It gets before a board of health and at once there is friction with the manufacturer, who naturally resents interference.

Investigations on general industrial hazards should be carried on by the State, but only with coöperation of the manufacturers. Of the latter I am well assured. A form of benign paternalism, inevitable and to be desired in a safe republican form of government, would be welcomed by chemical manufacturers, but they resent wild legislation not founded upon technical and scientific investigation. It is, therefore, urged that there be a greater extension of the work on these lines by the Public Health Service in Washington, the Bureau of Mines, and the Department of Labor, as well as the several states. But the work requires coördination. It is the opinion of the Chairman of this Committee that a Museum of Safety should be established in Washington where the several governmental (national, state and municipal) officials and representatives of selected lines of chemical activity might coöperate by conferences and advice. The proposed Museum should perform not only an educational function, but investigate new as well as old conditions, and if need be volunteer advice to legislative bodies.

It is a fond hallucination of many to plan out something for the government to support, when its underwriting seems unlikely in other directions. A Department of Public Health may yet be established and the proposed Museum would naturally come within its scope.

[AUTHORS' NOTE: The American Museum of Safety is established but in very inadequate quarters in New York City.]

COLLEGE OF THE CITY OF NEW YORK

## THE OCCUPATIONAL HAZARD IN THE CHEMICAL INDUSTRY: THE NEED FOR PROPHYLAXIS

By J. W. SCHERSCHESWY, Surgeon, U. S. Public Health Service

We are observing in this country, as a part of the general campaign for the improvement of the public health, an awakening on the part of the industries to the necessity for safeguarding life and limb. That, in the past, we may be charged with indifference to the physical welfare of the worker, arises from the fact that, in the midst of our unparalleled industrial expansion we have somewhat lost sight of the man behind the machine. Production has been our aim; we have been as prodigal of the life and health of our workers as of other less important natural resources.

Yet we are now rapidly coming to a lively sense of the social and economic importance of protecting the health of workers. In former years the chemical industry has been accused with neglecting this paramount duty. The occasion, therefore, of holding this symposium is a sign of the happiest augury for future improvements in this respect.

Indeed, the necessity for adequate protection of the health of chemical workers is a self-evident proposition, for, aside from the ordinary hazards to health, inseparable from industrial life, there are many specific hazards provoked by the nature of the substances dealt with. The great German hygienist Weyl,<sup>1</sup> in writing of the chemical industry, thus characterizes it: "Com-

pared with the chemical industry, there is none other in which the workers may be exposed to such varied and manifold injuries to health."

The chemical industry, together with its allied branches, is so extensive that in the time at my command I can give but little more than a bird's-eye view of the possibilities of damage to health which occupation in this industry may cause. This industry has made gigantic strides in our country. Its colossal development in the past promises to be transcended by its future growth. A summary, dated September 14, 1916, of the Census Bureau concerning the general chemical and allied industries gives the following comparative figures: in 1909 the total value of the products of the chemical and allied industries was \$800,722,356, whereas in 1914, the value of the products was \$1,228,403,984, an increase of \$427,631,628, or 53 per cent. The forthcoming extension of the manufacture of coal-tar products, as well as European conditions, seems to portend an accelerated expansion of this industry in the future.

In the past the chemical industry has been but little studied in this country from the standpoint of industrial hygiene. Chemical works are usually located on the outskirts of communities; the general public has always been convinced of the mysterious and alchemistic character of chemical processes; many processes are so-called trade secrets and, therefore, jealously guarded by manufacturers; many branches of the trade have been surrounded by mystery. Notwithstanding these conditions which tend to discourage investigation, there have been certain investigations in this country, notably by the Illinois Commission on Occupational Diseases, and the New York State Factory Investigation. Abroad, especially in Germany, conditions in the chemical industries have been more thoroughly studied, although, even there, with the necessity for knowledge of industrial conditions required by the operation of health insurance laws, information concerning health conditions in the chemical industry is not so full as in other occupations. While, therefore, our knowledge of the subject is not so definite as is desirable, we may outline at least the main hazards to health to which chemical workers are subjected.

We have, first, the ordinary hazards which may arise in any industrial environment, and second, specific hazards caused by the nature of the substances handled.

### ORDINARY HAZARDS

The ordinary hazards to industrial health are those caused by darkness, dampness, stagnant air, exposure to extremes of cold and heat, long hours, fatigue, and monotony.

**DEFECTIVE ILLUMINATION**—While the chemical industry makes but little demand for close eye work on the part of its workers, the fact should not be lost sight of that dangerous substances are handled, the establishments are full of unexpected stairways, open vats containing caustic or corrosive liquids and dangerous substances are concerned in many packing and loading operations. Consequently adequate illumination is required to assist the worker in escaping accidents or injury to the health. Adequate illumination is moreover an important sanitary aid even in industries which involve but little exposure to eye-strain. A generous flood of light has a stimulating psychological effect; production is increased; dark nooks and corners are illuminated; collections of dirt and rubbish are revealed, which otherwise would lurk unnoticed. Therefore, adequate illumination is an important adjuvant to the sanitation of industrial establishments. Yet in the investigation of the chemical industry made by the New York Factory Commission,<sup>1</sup> lighting was found inadequate in 64 per cent of the establishments visited.

**VENTILATION**—While there is some divergence still as to the harmful factors resident in poor ventilation, all are agreed

<sup>1</sup> "Handbuch der Arbeiterkrankheiten," Jena, 1908, G. Fischer, p. 183

<sup>1</sup> State of New York, 2nd Report of the Factory Investigating Commission, Vol. II (1913), p. 465.



that an abundant supply of fresh air is a necessity for the worker. It makes but little difference if we base our standards of ventilation upon the content of carbon dioxide of interiors, or if we consider the physiological needs of the body in the way of removal of the body heat as it is generated, together with an adequate stimulus to the skin by moving air currents, we cannot secure healthful conditions with respect to any of these factors except by an adequate air supply of the proper temperature and humidity. Reasonable provisions for ventilation are therefore necessary for the maintenance of health in any industry. They become doubly so in the chemical industry, where the numerous poisonous materials, dusts, fumes, and gases, peculiar to the processes involved, require special attention to ventilation. Yet in the report of the New York Factory Commission just referred to, we are told (*loc. cit.*) that provision for mechanical ventilation was found in but 41 out of 259 chemical plants, or about 15.4 per cent. Of course, in many instances, the nature of the processes and the relative size of buildings may make such provisions superfluous; yet there can be no doubt but that the chemical worker is too frequently subjected to the ill effects of poor ventilation.

**EXTREMES OF HEAT AND COLD**—The necessity for tending furnaces of various kinds subjects many chemical workers to the effects of extreme heat, often alternated with cold. While workers, subjected to such conditions, often intolerable to the casual visitor, when asked, "How they stand the heat?" reply that they grow used to it, it must be remembered that tolerance to any injurious condition by no means constitutes a state of physiological adaptation. In young and healthy adults, living otherwise hygienic lives, we are often surprised at the little harm apparently resulting from exposure to intrinsically unhealthful conditions, yet a short period of lowered resistance, some temporary hygienic fault in the manner of living, some slight excess when off duty, is enough to cause the factor of safety to be exceeded, with resulting injury to the health. It is well known that exposure to great heat throws increased work upon the heart and blood vessels, interferes with nutrition, increases fatigue, diminishes endurance, and renders the individual more susceptible to diseases of the respiratory system. While exposure to great heat is inherent to many industrial processes, the amount of exposure is often needlessly great, and the degree of heat unreasonable. Problems of heat mitigation may be said to constitute a branch of industrial hygiene too extensive to be entered on here. Suffice it to say that workers are often subjected to heat when by due forethought the necessity for and the degree of the exposure might be greatly reduced.

**LONG HOURS**—The continuous maintenance of bodily efficiency requires that the worker return to his work completely recuperated from the previous day's fatigue. It is difficult to fulfill this condition when hours of labor have been unduly prolonged. Many instances of long hours of work in the chemical industry exist. This is especially true in continuous processes in which the working week consists of at least 72 hours, and often 84. Thus in the Census bulletin<sup>1</sup> on the general chemical industry for 1909, the prevailing hours of labor for some 20 per cent of the chemical workers were 72 hours or more weekly; 29 per cent worked more than 60 hours weekly; while in the case of only 43 per cent of the workers were the weekly hours less than 60. It is evident, therefore, that the hazard of prolonged working hours is present in the chemical industry to a considerable degree.

**FACTORY SANITATION**—The absence of proper facilities for factory sanitation, such as a pure drinking water supply, distributed in sanitary drinking fountains, sanitary toilets, ample washing facilities, separate lunch rooms, and the like, exert an untoward influence on the health of the factory personnel. We hear much of the indifference or carelessness of workers in

matters of personal hygiene, yet it is the duty of every progressive manufacturer to provide ample facilities for the care of the body. This is especially true in the chemical industry, where so many irritating, corrosive, poisonous, and dusty materials are handled, yet the same report of the New York Factory Commission referred to shows that the general sanitation of chemical plants is sadly neglected. Attention to proper factory sanitation pays, not only so far as the individual worker is concerned, but also to the community at large. It is true that provision for good factory sanitation must be combined with education of the personnel, especially of the unskilled, as to the use of these facilities. Such education, however, not only promotes the intelligent use of these provisions, but also raises the sanitary standards of the community, for the reason that the worker soon learns to apply to his home life what he has learned in the sanitary factory.

#### SPECIFIC HAZARDS

Apart from the ordinary industrial hazards just enumerated, the chemical trades obviously present certain specific hazards arising from the nature of the materials handled. These hazards consist of the effects upon the body of irritating or poisonous dusts, fumes, and gases. Dust and fumes have been characterized by Sir Thomas Oliver, in his plenary address before the 15th International Congress on Hygiene and Demography as the "foes of industrial life." Now the chemical worker may be exposed, according to the branch of industry in which he is engaged, to practically any one of the entire list of industrial poisons published in Bulletin 100, by the Federal Department of Labor. While highly poisonous substances are handled daily with but little danger, in chemical laboratories, it should be remembered, in the chemical trades, that workers, especially unskilled workers, have but little idea, as a rule, of the dangerous character of many of the materials with which they come in contact. This point has been repeatedly emphasized by various investigators. Acute poisonings are fortunately rare; in such cases the relation between cause and effect is usually self-evident. Who but an instructed worker, however, would correlate the gradual onset of weakness, impulsive laughter, uncertainty of movement, inability to go down hill without running, or inability to walk backwards, with chronic manganese poisoning; or who would ascribe the gradual clouding of his vision to long continued exposure to weak fumes of nitronaphthalene.

Without going into exhaustive detail, I will, therefore, attempt at this point to discuss briefly the injurious effects on the body of certain well recognized classes of chemical compounds. Ramboisek<sup>1</sup> states that industrial poisons from their action may be grouped into three general classes:

(1) Poisons which act superficially, *i. e.*, which cause gross anatomical lesions in the tissues with which they come in contact. To this class belong especially irritant and corrosive poisons, such as the caustic alkalis and mineral acids.

(2) Blood poisons, *i. e.*, poisons which are absorbed by the blood, and change it. Such change affects either the coloring matter of the blood with which certain poisons form definite chemical compounds, such as carbon monoxide, or the blood corpuscles themselves can be altered or destroyed, as for instance, by nitrobenzol.

(3) Poisons with definite internal action, a so-called remote or specific effect. To this class belong the poisons which upon absorption act upon definite organs or tissues in a specific manner. Lead is, perhaps, the most common and best known of this type of poison.

While this grouping does very well as a rough means of classification, it is well to remember that some poisons display two or all of these modes of action. Since industrial poisons may be absorbed either as solid substances, as liquids, or as gases,

<sup>1</sup> 13th Census, U. S., 1910. Manufactures, 1909, statistics for the manufacture of chemicals and allied products.

Ramboisek, "Industrial Poisoning" (Legg's Translation), 1913, p. 158.

we may also classify them according to their physical characteristics, *i. e.*, poisonous dusts, poisonous liquids, and poisonous fumes. This difference in physical form influences the method of absorption by the body. Dust poisons are either inhaled or swallowed; liquid poisons, as a rule, may enter the body only through the skin, intact or broken; gaseous poisons, as a general rule, are absorbed only through the respiratory tract. There is also a certain relation between the amount absorbed and the effects. All poisons are without effect if the dose be sufficiently small. There is, therefore, in each case a minimum dose which, if exceeded, will produce symptoms. This minimum dose, however, is relative only, as it is often modified by the characteristics of the individual, such as age, sex, and body weight, or his habits, such as in the use of alcohol. We may also distinguish acute, sub-acute, and chronic poisonings, according to whether the symptoms are produced by the sudden absorption of large quantities, the frequent absorption of moderately large quantities, or the repeated absorption of small quantities.

As the list of industrial poisons, compiled by Fischer and Sommerfeld,<sup>1</sup> and published by the Federal Bureau of Labor mentions some 82 substances, all of which are capable of producing poisoning, it is impossible for me to enter into great detail.

**POISONOUS FUMES AND GASES**—So far as their action on the body is concerned, these gases may belong to any one of the three groups previously mentioned. In general we distinguish two types of gases and fumes, the irritating and the toxic. The irritating quality of gases and fumes arises from their ability to attack the mucous membrane of the respiratory tract. If their concentration is sufficient, immediate death may ensue, with symptoms of suffocation. Less concentrated doses attack the delicate lining membrane of the pulmonary air cells, bringing about a condition of acute pulmonary oedema or swelling. Doses still less concentrated may cause pneumonia, while repeated exposures to small doses give rise to chronic bronchitis. It seems almost superfluous to mention that the chemical industries offer abundant opportunities for the inhalation of such gases of which the most usual are the halogens and their acids. The fatal effects of the inhalation of high concentrations of chlorine gas have been illustrated over and over again in the present war. Hydrofluoric acid gas is more active than the other halogen acids in its attack on mucous membranes, including that of the eye. Sulfur dioxide, nitric and nitrous acids, nitrous fumes generally, and ammonia must also be mentioned.

In regard to nitrous fumes, which unless due precautions are taken, are so frequently encountered by workers in cleaning out sulfuric acid lead chambers and towers, as well as in other industrial processes, such as nitration, their delayed action is worth mentioning. After inhaling a fatal amount of these fumes, the worker may feel but a momentary sense of suffocation, from which he apparently recovers on reaching fresh air, only to be seized several hours later with symptoms of a severe and rapidly fatal oedema of the lungs. Apart from the acute effects of the gases just mentioned, there are the harmful results of chronic and repeated exposures to their diluted fumes. This causes a chronic catarrh of the respiratory tract, of varying severity. The lowered resistance produced by this chronic inflammation may create a favorable soil for the implantation of the pneumonia or of the tubercle bacillus. In addition to this, acid fumes exert a deleterious effect upon the teeth, dissolving the enamel, and causing them rapidly to rot. This effect of acid fumes is well high classical in the literature; no writer on occupational diseases would consider his book complete without an illustration depicting this effect of acid fumes, which is likely to be followed by chronic indigestion. The following table by Leymann shows the minimum concentration of such fumes causing symptoms.<sup>2</sup>

CONCENTRATIONS IN PARTS PER 1000

NAME OF GAS	Rapid and Dangerous Injury	Bearable for 30 to 60 min. without Grave Effects	Trifling Symptoms after Action for some hour
Hydrochloric acid.....	1.5 to 2.0	0.05	0.01
Sulfurous acid.....	0.4 to 5.0	0.05	
Carbonic acid.....	About 30	6 to 8	1 to 2
Ammonia.....	2.5 to 4.5	0.3	0.1
Chlorine and Bromine.....	0.04 to 0.06	0.004	0.001
Iodine.....		0.003	0.005 to 0.001
Hydrogen sulfide.....	0.5 to 0.7	0.2 to 0.3	0.1 to 0.15
Carbon disulfide.....	0.01	0.002	0.001
Carbon monoxide.....	2 to 3	0.5 to 1.0	0.2

So much then for irritating fumes and gases. Passing now to fumes more distinguished by their poisonous than by their irritating action, the following, according to Rambousek,<sup>1</sup> are especially worthy of mention: metallic vapors, arsenical vapors, gaseous blood poisons, which have special action on the haemoglobin of the blood, carbon disulfide, fumes of coal tar and coal-tar products, which have action both on the blood and on the nervous system, certain organic compounds; *e. g.*, the higher alcohols of the fatty series, wood alcohol, the pyridine bases, acrolein, amyl nitrite, nitroglycerine, camphor, and turpentine. In addition to irritative action, these have special action on the nervous system.

Among metallic vapors, the most poisonous are those of mercury and lead. Among arsenic compounds, arseniuretted hydrogen is the most dangerous, as the inhalation of 1 mg. may produce fatal results. I need hardly remind you that the possibility for the generation of arseniuretted hydrogen is present whenever hydrogen is generated by the action of acids upon metals containing arsenic as an impurity. In recent years a not infrequent industrial accident has been the generation of this gas by the accidental access of water to ferrosilicon. Phosphorus fumes are distinguished by their ability to cause disease (necrosis) of the jaw bone. Fortunately the match industry, which in the past has been the greatest offender in this respect, has been relieved of this odium in this country by Federal legislation against the use of white phosphorus in matches. Among gaseous blood poisons must be mentioned carbon monoxide, hydrocyanic acid gas, and sulfuretted hydrogen. Carbon monoxide, because of its great affinity for the haemoglobin of the blood (some 200 times greater than that of oxygen), rapidly displaces oxygen from the blood, thus preventing its transport to the tissues. Death thus ensues from oxygen starvation. The action of hydrocyanic acid gas is similar. Sulfuretted hydrogen exerts a reducing action on the blood. Coal tar not only is irritating, but is capable of poisonous action, by reason of the volatile aromatic compounds it contains. The most important of these are benzol, xylol, toluol, phenol, and naphthalene. Among coal-tar derivatives the following are especially poisonous: benzol, nitro and nitroso derivatives, and amido derivatives. Of the nitro compounds, nitrobenzol and trinitrophenol may be especially mentioned. Of the amido derivatives, aniline is by far the most important. In Germany, aniline, in spite of stringent regulations, probably causes more industrial poisoning than any other chemical compound, with the possible exception of lead. Many of these coal-tar products are doubly dangerous because they may be absorbed not only by inhalation but also through the unbroken skin. This latter property arises from the ability of many of them to dissolve fat, to the presence of which the skin owes not a little of its non-absorbent qualities. Among the volatile compounds of the hydrocarbon series, wood alcohol, which has a selective action on the optic nerve, thus causing blindness, is probably the most important industrial poison.

**POISONOUS DUSTS**—By far the most important of these is lead. While we must regard the manufacture of lead products as an allied branch of the chemical industry, the subject of lead poisoning is so extensive and important, and lead products enter

<sup>1</sup> Bull. 100, May, 1912, Bureau of Labor, Department of Commerce and Labor, Prof. Th. Sommerfeld and Dr. R. Fischer.

<sup>2</sup> Thompson, "Occupational Diseases," p. 304, New York, 1914.

<sup>1</sup> Rambousek "Lehrbuch der Gewerbehygiene," Hartleben, Wien and Leipzig, 1906, p. 33.



so extensively into other industries that it should be the subject of separate treatment. Other harmful dusts are those of the chromates, which attack the skin and mucous membranes, producing painful and intractable ulcers (chrome holes), dusts which by their hygroscopic nature can produce irritation of the skin and mucous membranes, such as quicklime, calcined dolomite, and the like; arsenical dusts, such as Scheeles green, Schweinfurt green, and Brunswick green; antimony dusts, such as the golden sulfide and the trioxide of antimony.

While the foregoing is necessarily but the briefest survey of the varied hazards of the chemical industry, I think enough has been said to show the manifold nature of the hazards to which chemical workers are exposed, and the necessity for careful surveillance if unnecessary diseases and deaths are to be avoided. The necessity for such surveillance is further emphasized when we consider that but a small proportion of the personnel of chemical establishments consists of skilled workers, the great majority being unskilled workers of foreign birth, who, besides having the most rudimentary ideas of personal hygiene, are ignorant of the nature of the substances which they handle.

#### ILLNESS IN CHEMICAL INDUSTRIES

Before concluding, some reference, however, should be made to the frequency of illness in the chemical industry. Unfortunately we have practically no data in the United States as to this morbidity. Like others, therefore, I am forced to make use of foreign statistics. So far as the chemical industries are concerned, the best known of these statistics are those published by Grandhomme and by Leymann. Grandhomme's figures refer especially to workers engaged in the manufacture of coal-tar products; those of Leymann, to workers in a number of branches of the chemical industry. The establishments which furnished these figures operate under the German system of health insurance, and were carefully supervised with a view to reducing the incidence of disease. Grandhomme's figures show that the average number of sick days for each worker annually was 6.73. According to Leymann, it was 10.2. Weyl thinks it justifiable to average these figures, and estimates that in Germany the average annual loss through sickness for each worker in the chemical industry would be in the neighborhood of 8.5 days. According to Weyl,<sup>1</sup> this would give among 185,820 chemical workers insured in Germany in 1905, an annual time loss of 1,572,037 days. As the number of cases of illness was 0.88 to each worker, figured on this basis, Weyl calculates that there were 163,822 cases of illness, or out of 100 workers, only 12 on the average worked through the year without sickness. In addition to illness, there were 10,000 accidents in 1905 in the German chemical industry, of which 122 were fatal. The fatality rate among accidents was, therefore, 1.22 per cent. This tends to show a rather high fatality rate for accidents in the German chemical industry, considering the attention that accident prevention has received in that country, for in the State of Pennsylvania,<sup>2</sup> during the month of February, 1916, there were 24,475 accidents reported, of which 222 were fatal, a percentage of 0.91. Certainly the incidence of disease and accident is not less among chemical workers in this country than in Germany, indeed we would expect it to be somewhat greater, in view of the lack of racial homogeneity of the workers and the retarded development of protective measures.

In considering the incidence of disease in the personnel of the chemical plant, the fact should be borne in mind that such personnel does not present statistical unity. The personnel consists of two groups: one portion, the true chemical workers coming in contact with the manufactured products, while a second portion, consisting of representative and various trades,

such as carpenters, bricklayers, machinists, etc., and a still larger force of ordinary laborers, are very much less exposed to the specific hazards of the industry. This difference in exposure is well illustrated in Leymann's statistics. Thus the average annual loss from illness was 11.8 days for chemical workers, while for the others it was but 8.6 days, a difference of 3.2 days in favor of the latter. Among the various branches of the chemical industry, covered by Leymann's statistics, that of the manufacture of chrome products, with 17.2 sick days annually, yielded the greatest amount of illness, while the manufacture of potassium permanganate and organic chlorine compounds showed the least, 8.8 days.

Again, considering the type of illness, a striking difference between these two groups of workers is manifest. Thus while 45 per cent of the illnesses among chemical workers were internal diseases, only 27 per cent of such diseases prevailed among the other workers. On the other hand, external diseases were distributed with some approach to equality among the two groups, the figures for chemical workers being 43 per cent, and for the other workers 37 per cent. In considering these statistics, we find a special predilection for certain groups of diseases, in the following branches of the industry, while they are much less numerous in the remainder. Thus, diseases of the respiratory system, according to Leymann, are especially frequent in the manufacture of acids, sulfates, chromates, caustic alkalies, bleaches, and trinitrophenol; diseases of the intestinal tract, while common in all chemical trades, predominate in the manufacture of acids, crude soda, the chromates, aniline, sodium sulfide, and in the regeneration of sulfur; burns are especially frequent in acid making, especially nitric acid, also in the manufacture of caustic soda, the chromates, and trinitrophenol; we find skin diseases particularly affecting workers in coal-tar products.

It is evident from the foregoing that our duty to chemical workers lies plainly before us. Studies of health conditions in this industry should be made in this country, with a view to minimizing its inherent occupational hazards. It is time for us to awaken to the great social and economic losses due to the neglect of the health conditions in our industries. There are hopeful signs that this apathy and indifference is being removed. Thus a large chemical company has requested the Federal Public Health Service to undertake a survey of its establishments so that recommendations may be made for the removal or mitigation of occupational hazards. It is earnestly to be hoped that other companies will follow this example, by studying the conditions under which their workers are employed, and by removing unnecessary risks to health, gaining thereby not only increased efficiency and economy of production, but doing their share towards alleviating the needless burden of illness and suffering.

PITTSBURGH

#### INDUSTRIAL POISONING FROM ANILINE AND ALLIED PRODUCTS

By GEORGE P. ADAMSON

General Chemical Company and Member of American Chemical Society Committee on Occupational Diseases

Aniline poisoning in the United States was, until the present foreign disturbance, given but slight consideration. It was supposed to cause a rash and a blue discoloration, usually accompanied with a slight headache, and few precautions were taken to protect the men working aniline or nitrobenzol.

The introduction of the manufacture of nitrobenzol and aniline in this country brought very quickly to the attention of manufacturers and physicians the necessity of precautions. Very few, if any, physicians had ever seen, or ever heard of aniline poisoning and were not prepared to recognize or treat cases when serious enough to be called to their attention. Eng-

<sup>1</sup> Weyl, "Handbuch der Arbeiterkrankheiten," Jena, 1908, p. 184.

<sup>2</sup> Pennsylvania Department of Labor and Industry, *Monthly Bulletin*, May 1916, No. 5, p. 4.

land and Germany have reports on many cases, and it was necessary for the manufacturer in this country to ascertain the best method of treatment.

We have noted for at least ten years that men working in the fumes of aniline would complain of dull headache and giddiness and show the familiar bluing of gums, lips and ears, as well as the rash on the arms, particularly when the skin came into contact with aniline oil. When workmen are continuously in the fumes of aniline, the first symptom noted is the bluing, then, in most instances, boils, with considerable inflammation, the sores becoming easily infected. We have also noted that all cuts or sores, if exposed to fumes or oil, were quickly infected, causing pain and swollen limbs.

Our observations lead us to believe that working in the fumes of aniline does not lead to any serious cases, nor is the poisoning cumulative, having never in our experience noted any serious effects from breathing fumes of the oil beyond the bluing of the lips and ears. The only serious cases were from absorption, caused by splashing the oil on the body without immediately removing same by washing.

Cleanliness is an absolute necessity, and bathing before leaving the plant should be positively required; also washing of hands and face before eating. A dose of Rochelle salts is given every day. A kit containing wash brush, soap, tooth brush, gloves, wooden soled shoes, goggles and respirators is supplied to every man. In case of aniline splashing on the skin the man is washed with dilute acetic acid. It is very difficult to remove aniline oil from the skin by washing with water, as the oil is almost insoluble. Dilute acid (preferably acetic acid) combines with aniline to form a soluble salt, and should, therefore, be used, washing both the skin and clothing. Then the man is washed with water under a shower, his clothing washed and dried; he is usually given a dose of Rochelle salts and compelled to drink a liberal quantity of milk, which should be supplied daily. A locker room with sufficient lockers, showers and towels should be supplied. A lungmotor, oxygen, first aid crew and hospital are a necessity.

We were surprised to note that many instances of slight poisoning developed in men who were not actually employed in the department. Mechanics who were called to make slight repairs in and about the buildings, etc., were slightly poisoned. We found in every instance that the men who developed the symptoms wore old shoes, the soles being worn so as to allow sufficient absorption through the feet to produce the symptoms. Since using the wooden soled shoes this difficulty has been overcome, new shoes being given when the shoes are unserviceable or accidentally soaked with oil.

Before employing men in the departments where aniline is used, we compel the applicant to submit to a physical examination given by the works physician, a complete examination particularly of heart, lungs, kidneys and bladder. If rejected on this examination the man is not employed. A blood test is made on all men.

The first serious case was an Austrian who, in his haste to quit work, placed his shoes under a tank in which aniline was used. During the day some aniline was splashed in his shoes, and after he had put them on and was working in them for a few hours he complained of weakness in his legs, becoming very dizzy shortly after. Becoming unconscious, and his body turning blue, the physician was called and, looking at the man, asked for the Priest, never having seen a case of the kind before. The man was removed to the hospital and in a few days had entirely recovered.

The next case was of a man who was cleaning a still. Removing his rubber gloves and absorbing it through his hands he became very rigid, and was unconscious for hours. He was at work again in six days.

The third case was of an American who was removing tar from an oil still. His shirt sleeves became saturated with aniline at the elbows, and his trousers at the knees. He removed his rubber gloves and substituted canvas ones. After wearing the canvas gloves for a period of about two hours, they were completely saturated. He was at home for two weeks. This man was 56 years old.

Another case of this poisoning was of an American, 27 years old. He was found asleep on the top of the still. The ashes upon which he was lying were saturated with aniline, due to a leaky pipe connection. He was partly overcome when awakened and was at home for one week.

The fifth case was of an American 27 years old. There being a defective cock on the condenser, the plug broke while turning and the aniline splashed in the face and mouth of the victim. He swallowed about two teaspoonfuls of the aniline and was at home for 5 days.

The sixth case was of an Austrian 29 years old. He was tearing out old stills, and his shoes being poor and the mule-skin gloves that he was wearing becoming saturated, he was overcome and was at home for one week.

The seventh case, a Slav, 28 years old, was identical with the sixth.

The eighth case was of a Slav 28 years old, who was removing tar, etc., from a still. The tar contained aniline and his clothes became saturated. He was at home 9 days.

The ninth case was that of an American, 31 years old, who was removing a defective plug from the cock. The aniline held in the gas chamber above a cock was released when the plug was removed, and splashed over his hands and arms. He neglected to wash immediately and was at home for 8 days.

When the vapors of nitrophenols, amidophenols and beta naphthol come into contact with the skin, they produce a very irritating rash. The parts present a swollen and very red appearance, which, if not treated, become very sore. The best treatment that we have found is to wash the affected part carefully first with soap and hot water and then with 5 per cent hydrogen peroxide; remove the peroxide by washing, carefully drying and rubbing with glycerine. An ointment consisting of lead acetate and vaseline is also very effective. Greasing of the hands, face and exposed parts is a good preventative.

We have noticed that the blonde type of men are more susceptible than the darker types.

#### REPORTS OF BLOOD EXAMINATIONS

I—BY FRANCIS S. CHAMBERS, M.D., EASTON, PA.

Twenty men were examined and full blood counts made; 7 of these men were examined in 1915 and again in 1916. The other 13 continued to work in aniline but a short time after the first examinations were made, and unfortunately we cannot draw any definite conclusions from our examinations of them. We also examined specimens from 12 men under the spectroscope to see if any traces of methemoglobin could be detected by this means.

SPECTROSCOPIC EXAMINATIONS were all made at about 5 P.M. after the men had been working in aniline for some hours; a few showed slight blueness of the lips, but no other symptoms. In no instance did we detect any traces of methemoglobin.

REGULAR FULL BLOOD COUNTS were made in all instances, consisting of hemoglobin estimation with Dare's instrument, counts of the red cells (erythrocytes) and also the white cells (leucocytes). Smears were prepared in the usual way and examined with Wright's stain. We noticed that the most frequent change was a slight anemia, characterized by a reduction in the hemoglobin and a fall of the red-cell count. Thus in the men who were examined in 1915 and again in 1916, four showed such changes. The first examinations on these four men were made shortly after they began to work in aniline.



HEMOGLOBIN Per cent			FULL BLOOD COUNTS				LEUCOCYTES (White Cells)			
			ERYTHROCYTES Red Cells		Loss	1915	1916		Loss	1915
No.	1915	1916	1915	1916						
1	94	88	92	5,800,000	5,040,000	137	9000	6,200		
2	95	87	8	8,500,000	5,900,000	30	9100	10,000		
3	90	80	11	8,900,000	4,408,000	7	8000	7,700		
4	80	70	11	8,300,000	4,600,000	11	9400	8,000		
5	87	88		4,440,000	4,240,000		7700	8,200		
6	70	82		4,880,000	4,182,000		6600	5,800		
7	78	90		6,000,000	5,968,000		6100	6,200		

No. 2. Increase of polymorphonuclears and reduction of small mononuclears may be due to some foreign causes.

No. 4. The red cells also show some variation in size, about 5 to 8 microns. No nucleated reds present.

No. 5. Some variation in the size of the red cells, about 6 to 8 microns.

No. 6 was an old employee when first examined and this is the probable cause of the increased number of small mononuclears, in 1915. His hemoglobin shows an increase on second examination and with the reduction of the number of small mononuclears, his blood has somewhat improved.

His first examination was made before the shorter hour shifts were adopted.

No. 7 had been working in aniline for some time before the first blood count was made and this is the probable reason that the differential count shows no changes. His hemoglobin shows an increase.

DIFFERENTIAL COUNT OF LEUCOCYTES

No.	Polymorpho- nuclears		Small Mono- nuclears		Large Mono- nuclears		Transitional Forms		Eosino- philes		Baso- philes	
	1915	1916	1915	1916	1915	1916	1915	1916	1915	1916	1915	1916
1	5940	3286	2880	2666	90	62	0	124	90	62	0	...
2	5642	7700	3003	2100	91	0	91	100	273	100	0	...
3	4560	4104	2560	2592	480	216	0	144	400	72	0	72
4	7308	4320	2162	3440	282	80	376	80	188	80	0	...
5	4464	3936	2016	3116	360	738	144	164	316	246	0	...
6	3432	3364	2904	1740	366	348	66	116	132	242	0	...
7	3294	3186	2135	2604	183	124	183	None	308	186	0	...
Percentages												
1	66	53	32	43	1	1	0	2	1	1	0	...
2	62	77	33	21	1	0	1	1	3	1	...	...
3	57	57	32	36	6	3	0	2	5	1	0	1
4	68	54	23	43	3	1	4	1	2	1	0	...
5	62	48	28	38	5	19	2	3	3	3	0	...
6	52	58	44	30	1	6	1	2	2	2	0	...
7	54	53	35	42	3	2	3	0	5	3	...	...

Of the 13 men who were examined once, 4 were men who had been working in aniline for some time before the examinations were made, the other 9 were new applicants for positions in the aniline department. Of these 4 men, 3 show rather poor amount of hemoglobin; the percentages are lower than in the other thirteen men. Number eight had some pulmonary disease and his low percentage of hemoglobin was not entirely, if at all, due to aniline.

Three men did not show a reduction in hemoglobin after working over a year in aniline. Two show an increase. These men had been working in aniline for some time prior to the first examinations and subsequently shorter hours of work were adopted, which may account for their improvement.

The leucocytes (white cells) showed no abnormal variations. In the differential count of the white cells, a reduction in the polymorphonuclears and an increase in the small mononuclears, both relative and absolute, were observed in two (Nos. 4 and 5). In the others, the variations were not great, although many of the men showed a relative high small mononuclear count.

CONCLUSIONS—The chief change of importance is in the percentage of hemoglobin and the number of red cells, long continued exposure to aniline causing a reduction in both elements. While it is desirable to have some idea of the condition of the blood of these men, it is not always practicable to have repeated full blood counts made, owing to the time, expense and fear which it arouses in the men. Frequently the men seek other occupations for this reason.

However, it is desirable to have an estimation of the hemoglobin made on all men seeking employment in the aniline department and if same is found to be below 85 per cent, the applicant had better be rejected. For this purpose, the Fleischel instrument of Dare's hemoglobinometer can be employed by any intelligent person with a little practice.

Subsequent examinations should be made at intervals of three or four months or in special instances, where an employee looks badly, more frequently. If the hemoglobin falls below 75 per cent, he should be kept under observation, and if it should fall below 70 per cent, he should be advised to seek other employment.

In all doubtful cases, a full blood count should be made. Obviously, blood examinations do not offer any protection against acute poisoning, but they do enable a better selection of men suitable for this work.

BY W. P. O. THOMASON, M.D., EASTON, PA.

The data available from our medical department seems to bear out the following.

MODE OF ENTRANCE OF ANILINE INTO BODY—Absorption through the skin by direct contact or by saturation of the clothing through the digestive organs; through the respiratory organs as volatile particles.

#### SYMPTOMS OF POISONING.

ACUTE (a) *Mild Cases*—Pallor of skin and mucous membranes, with slight cyanosis, a feeling of weariness and weakness; head symptoms—vertigo, reeling, unsteady gait; deficient elasticity of movement; slow, labored speech; irritability (aniline "pip"); condition of slight inebriation, with loquacity, gaiety, and defective power of orientation; loss of appetite, constipation, and tense, rapid pulse.

(b) *Severe Cases*—Dark blue to swarthy cyanosis; formation of methemoglobin; bounding pulse; "air-hunger," with great frequency of respiration; lowering of sensibility; obliteration of reflexes; sometimes vomiting, strangury and bloody urine.

(c) *Most Serious Cases*—Sudden prostration; cold, pale skin, blue lips, nose and ears; diminution and even extinction of sensibility; moist, cold skin; small pulse; death in a comatose condition, sometimes after antecedent convulsions.

SUB-ACUTE AND CHRONIC—Anemia; slowing of the pulse; disorders of digestion, such as eruptions, loathing of food, vomiting, diarrhea and eczematous and pustular eruptions on various parts of the body, especially on scrotum; nervous symptoms, as general debility, headache, ringing in the ears, vertigo, unrestful sleep, disturbances of sensibility, often of motility; spasmodic muscular pain. This form of poisoning is rare. Anemia and retarded pulse are early symptoms. The blood is of brownish hue but microscopically unchanged; occasionally the urine contains blood.

#### TREATMENT

At the first symptoms of poisoning, immediate removal from workroom to cool shady spot; change of clothing, cool effusions, administration of oxygen in connection with artificial respiration; latterly the pulmotor has met this emergency with great success; in severe cases, blood-letting with subsequent infusion of physiological salt solution; copious ingestion of milk; in weak action of heart, stimulants (black coffee, camphor, ether, but no alcohol). Caution against the use of alcohol during and immediately after labor; abstinence is advisable. Treatment, however, is entirely symptomatic and expectant. Immediate removal of all marked cases to hospital or other well-equipped domicile is recommended.

In view of these facts and our own experience, it appears that our best means of reducing the danger to operatives attending the manufacture of aniline would be in prevention. And, inasmuch as at present there is no certain evidence to prove just which avenue of entrance into the body is most concerned, it is well to regard all as possible sources of danger.

To do this each separate accident or occurrence resulting in poisoning should be studied and means devised to prevent recurrence, if possible. This would include:

- (1) Apparatus designed to keep contents constantly confined.
- (2) Better or more easily manipulated cocks, pipes, joints, etc.
- (3) Long or variously shaped handles on wrenches, allowing operator to stand out of possible range of escaping aniline.
- (4) Adequate and accessible containers of water and antidotes for immediate washing of contaminated bodies or clothing.
- (5) No eating or drinking on premises without previous washing of hands, etc.

(6) Where apparatus is known to be saturated with aniline and requires cleansing or renewal (repairs), foremen should be instructed to work men in short shifts, possibly only a few minutes at a time, according to the degree of danger.

(7) Workmen should be taught to observe symptoms on themselves or others and immediately resort to remedial measures.

(8) Where feasible, men should be worked in pairs or within easy seeing distance of each other.

(9) If necessary to work in confined spaces, a fan or vacuum system to draw fumes to a higher or lower level might be used to advantage.

III—BY J. C. LYONS, M.D., BENZOL PRODUCTS CO., MARCUS HOOK, PA.

As a preface I would say that the only two compounds that have given us any trouble are aniline oil and binitrobenzol and the products made therefrom. The labor employed in these processes is largely Polish and Russian. We have had in all during the past year, which includes all the time of operation of the plant, nine cases of aniline oil poisoning and three cases of binitrobenzol poisoning, the treatment of which has been as follows:

**PROPHYLACTIC** Under this is embodied examination of each man when employed and a subsequent monthly inspection, examination being a thorough one of heart and lungs with an estimation of both systolic and diastolic blood pressure and an examination for any physical defects. Any applicant for work or who develops during the period of his employment any defect or disease of the heart or lungs is not allowed to come in contact with any of the processes of manufacture. The men are told of the danger signals. Each foreman of the department has charge of the welfare of the men and notices are posted instructing the men as to the proper procedure to follow. Clogs are issued to each employee and respirators and rubber gloves are worn. That the process is largely automatic and the plant is so well planned and constructed with the view of exposing the men the minimum amount of time to dangerous fumes probably explains why so few really serious cases have been seen here. There is also a Service Building equipped with shower baths and lockers and a temporary structure used as a First Aid and examination room. Plans are under consideration for a well-equipped First Aid room, examination room and research laboratory.

**TREATMENT OF A MILD ACUTE CASE** On the development of an acute case of aniline poisoning, the usual symptoms being headache and vertigo with cyanosis, the man is at once taken to the Service Building, his clothing removed and a bath is given, followed by sponging with dilute solution of acetic acid and dressed in the clothing he wears to his work. He is then given a mild cathartic, put at rest in the fresh air and watched by the First Aid man. On the development of any untoward symptoms the physician is notified and takes charge of the case. This treatment is always efficacious, the employee returning to work in 24 hours, but he is not exposed again to aniline for several days.

**TREATMENT OF A SEVERE CASE** This is the same as for a mild case with the addition of oxygen inhalations and a more vigorous eliminative treatment after the employee has in a measure recovered. Stimulation is used if required, the best agent being a hypodermic injection of camphorated oil, repeated as required. We have had only two severe cases of aniline poisoning, which I will cite: (1) A pipe fitter who got a quantity of aniline on his clothing and neglected to report to his foreman, was taken about 6 hours after with violent symptoms. The treatment as outlined above was instituted and the man was back at his work in less than a week. (2) A workman was attempting to stop a leak in the top of one of the storage tanks and a large quantity of aniline was spilled on the floor. He, wishing to conceal the mishap, had attempted to clean it up without reporting to his

foreman. The fumes overcame him and he dropped and lay in it for between one and two hours before being discovered, it being at night when few are employed. He could be roused when discovered but was so cyanosed as to be almost black. His pulse was rapid and feeble and respirations shallow and very irregular. This man required continuous use of oxygen for 24 hours with vigorous stimulation and treatment for the anemia following this experience. He returned to work in 2 weeks and is, as far as can be determined, none the worse. In my estimation this case had every license to terminate fatally as you can scarcely conceive of a more extensive exposure, his clothing being actually saturated with the aniline. The plant is equipped with both lungmotor and pulmotor but has never had occasion for their use.

In regard to the three cases of binitrobenzol poisoning, while the symptoms and treatment are substantially the same as of aniline poisoning, the recovery is much slower and is followed by a more pronounced anemia.

It is our purpose to do research work in the near future to determine if there are any blood or kidney changes in men who have been working in aniline for several years and to make a report of these results at some future time.

IV—BY W. G. HUDSON, M.D., E. I. DU PONT DE NEMOURS & CO., WILMINGTON, DELAWARE

The poisonous effects of nitrobenzol, aniline and the allied compounds vary slightly, but there are many points of similarity so that for practical purposes their diagnosis and treatment may be considered as one.

Their mode of entrance is (1) by inhalation, (2) by absorption, and (3) by way of the stomach. Of these, the first two are the more important. Poisoning by inhalation is quite common and is caused by the accumulation of vapors in poorly ventilated rooms, especially during damp, close weather when the vapors hang close to the ground.

Absorption through the skin generally results through the accidental spilling of these compounds on the clothes of the workmen. Unless these clothes are quickly removed and the body thoroughly washed, symptoms of poisoning are almost sure to result, often several hours after the time of the accident.

Often the first intimation that a man is being poisoned will be the appearance of blueness of his face, especially the mucous membranes of his lips and oftentimes even of the finger nails. This blueness, or cyanosis, is generally more alarming in appearance than is actually the case, and unless a man's history is known a wrong diagnosis may be easily made; some cases have even been diagnosed as acute cardiac failure. There is usually a severe headache, syncope, a feeling of suffocation and in some cases nausea and vomiting. The pulse is rapid and weak and the blood pressure is usually lowered. The rate of respiration is increased, and in some cases may even become dyspneic. There may be considerable mental confusion. Difficulty in swallowing and in speaking have been noticed. In very severe cases coma may develop. Examination of the urine shows it to be decreased in quantity, highly colored, and it may have the odor of nitrobenzol or aniline. Microscopic examination may show red blood cells and casts.

Much can be done to prevent these accidents by providing proper ventilation and installing shower baths so that if a workman becomes covered with any of this material he can at once change his clothes and take a bath, using any of the sand soaps that are on the market. In the treatment of the acute attack it is, of course, essential to remove the patient to the open air. His clothes should be removed and he should be given the sand soap treatment. We have found that sponging the entire body with dilute acetic acid, such as ordinary vinegar, is very efficacious.

The effect of these poisons is essentially on the blood, causing a destruction of the red blood corpuscles and the formation of



methemoglobin, which is made evident by the cyanosis of the face and lips and in the accompanying dyspnea. The treatment is mainly stimulation of the cardiac and respiratory centers. Hypodermic injections of camphorated oil, strychnine and caffeine are very useful. Enemata of hot coffee are sometimes used. In very severe cases it may be necessary to resort to the use of oxygen, but in the majority of cases fresh air, together with such stimulants as may be indicated, is all that is necessary. Magnesium sulfate may be given to promote catharsis and the ingestion of water will aid diuresis. Most cases recover promptly and are able to return to work in a few days.

These are the symptoms of the acute cases, but there are many which do not reach this stage but at the same time show the effects of chronic poisoning. These cases will be found to be anemic, and complain of general weakness. They may have occasional slight attacks of blueness, or cyanosis, from which they quickly recover without treatment. Gastric disturbances are quite common and jaundice may occur. Various sensations in the hands and feet ranging from tingling to actual pain are often complained of. These cases usually recover when transferred to other work.

The above are the most important points in the diagnosis and treatment of these poisons as we have found out from our own experience.

EASTON, PENNSYLVANIA

## BUREAU OF MINES' STUDIES OF OCCUPATIONAL DISEASES

By DR. W. A. LYNOTT of the U. S. Bureau of Mines

Early in the history of the Bureau of Mines, the subject of occupational diseases among miners and metallurgical workers came under consideration. The late director, Dr. Joseph A. Holmes, entered into a cooperation, continued by the present director, Mr. Van H. Manning, with the Public Health Service, to investigate the prevalence of certain specific diseases among those engaged in the mining industry. These studies were first undertaken among the miners to discover the prevalence of the hookworm disease and pulmonary troubles, more especially silicosis; and, later were broadened to ascertain the extent of poisoning among blast furnace workers by carbon monoxide gas.

The foregoing efforts, and a preliminary research regarding the possibility of miners being affected by nystagmus, as is the case among some coal miners in Europe, were conducted by special investigators, generally assisted by sanitary and mining engineers connected with the Bureau of Mines. While these special studies were being forwarded, general investigations have been made regarding the sanitation and prevalence of general diseases in mining camps and villages, and the effect of temperature and humidity on the health of miners has been noted by the surgeon connected with the mine rescue and first aid work, and by a sanitary engineer on the Bureau's staff.

Dr. A. J. Lanza, of the Public Health Service, and Edwin Higgins, Mining Engineer of the Bureau of Mines, made an exhaustive study of pulmonary diseases and its relation to rock dust in the mines among the miners in the Joplin (Missouri) District in 1915.

It is known that inhalation of sharp particles of siliceous dust injures the mucous membranes of the lungs, bronchial tubes, etc., and in this way the lungs are in a receptive mood to pathologic conditions, especially to the germ of tuberculosis. This has been proven by investigations of morbidity among workmen in dusty trades and by study of the prevalence of lung diseases in the mines of South Africa and other foreign countries.

The report, as submitted by Dr. Lanza and Mr. Higgins, deals with sanitary conditions, more especially the prevalence of siliceous rock dust in the lead and zinc mines of the Joplin district and the bearing of these conditions on pulmonary diseases of the miners.

## RECORDS OF FATALITIES FROM TUBERCULOSIS IN JOPLIN DISTRICT

The records of the State Board of Health for the calendar year 1912 show 180 deaths from pulmonary tuberculosis in Jasper County, Mo., which represents a death rate of 200.8 per 100,000 population.

It seems to be the general opinion in Jasper County that lung diseases became more prevalent after the beginning of active mining in the sheet ground in the early eighties, and that the flint dust from drilling and other mine operations is largely responsible for this condition. The investigators concluded that when working conditions in any locality are such as to expose the workers to a hard, flinty, insoluble rock dust and when among those workers there is a high death-rate from pulmonary tuberculosis, that there is a definite connection between the dust and the disease and that the dust is largely responsible for the disease; not entirely responsible for all pulmonary disease but a prime factor in its causation.

In this Joplin district a physical examination of 93 miners was made by Dr. Lanza: 64 showed plain and definite evidence of pulmonary disease, 3 were suffering from non-pulmonary disease and 26 were seemingly well. Of the 64 sick men, 22 had stopped work on account of their health, the remaining 42 still being at work underground. Moreover, of these 64 men, 39 had the classical symptoms of pulmonary tuberculosis. The physical signs of the other 25 were not such as to justify a diagnosis of tuberculosis on one examination—all of these 25 had noticeable dyspnea, cough, etc.; 11 of the 25 showed evidence of lung injury, whereas 14, in spite of marked subjected symptoms, presented no definite sign of tuberculosis on physical examination, their condition resembling rather sclerosis or miner's consumption.

## TUBERCULOSIS AMONG COAL MINERS

Tuberculosis among coal miners is uncommon. The writer had occasion to visit a district in 1913 and 1914 where there were about 7000 miners. While a physical examination was not suggested the doctors in the various camps unhesitatingly said that rarely if ever a case of tuberculosis was found among the miners. All told not over 15 cases were admitted by the doctors. It was true that some members of the miners' families were affected but the miners themselves seemed to have a certain immunity.

Many mine surgeons were under the impression that the coal or coal dust, in a measure, was responsible for this immunity.

So far as mine injuries are concerned, where open wounds are found and where coal dust, dirt, etc., have entered the wound, if removed under aseptic conditions, infection seldom follows, unless germs were carried to the wound by fellow workers in an attempt to remove foreign particles.

## ASTHMATIC CONDITIONS AMONG MINERS

In the olden days many of the miners had miners' asthma, and it was thought to be due to coal dust inhalation. In recent years, however, asthma among miners is very rare and this improvement is due in a measure to better ventilation in the mines.

## EFFECT ON THE MEN COMING IN CONTACT WITH RADIUM DURING THE PROCESS OF CRYSTALLIZATION

Dr. R. B. Moore, physical chemist for the Bureau of Mines, has made an exhaustive study of uranium, radium and vanadium. In Bureau of Mines *Bulletin* 104, he reports that there has been no injurious effect of any kind attending this work. Practically all of the young men he examined have taken their turn at the work each day for two or three months and one of them worked for five months in the crystallizing room. No ill effects have resulted in any case although the air in the room was, of course, quite radioactive due to the emanations driven off from the solutions. Rubber gloves have been used to some extent in connection with crystallizing the richer fractions, but such gloves have not always been used. Under these conditions the alpha

rays are all shut out and only a very moderate proportion of the beta rays reach the operator.

#### BRASS SHAKES

Dr. H. W. Gillett, alloy chemist, of the Bureau of Mines, made an exhaustive study of "brass shakes," and I quote freely from his article on this subject found in U. S. Bureau of Mines *Bulletin* 73. This disease is also known as "brass founders' ague" or "smelter chills." It is somewhat similar to malaria ague. There is no specific remedy. The symptoms are dry throat, feeling of lassitude, a hacking cough, a dull headache, a feeling of oppression in the chest, difficulty of thoracic breathing, and sometimes a feeling of nausea. In a few hours, but usually not until the subject leaves the furnace in the evening so that perspiration ceases, a slightly chilly feeling occurs which increases to a distinct rigor, the subject shaking violently. During the chill the actual temperature may rise to as high as 103° F. The chill is accompanied by muscular pains. After a few hours the chills cease rather suddenly and a profuse perspiration sets in. The attack is then over and the patient sleeps profoundly, rising in the morning with only a slight feeling of weakness. Zinc is eliminated in the urine and feces and its presence is suspected in the perspiration also. Swelling of the spleen, and albumin in the urine are also sometimes reported.

The theories as to the exact agent that causes the diseases are varied, the blame being variously laid to zinc oxide, metallic zinc, arsenic, cadmium, copper, a mixture of copper and zinc or carbon monoxide. Of these the most probable cause is zinc oxide, the main constituent of the fumes. It is unlikely that metallic zinc reaches the lungs unoxidized. No definite proof has been adduced to show that the minute traces of arsenic that may be present as an impurity are the cause. Cadmium being far more volatile than zinc practically all the cadmium in the spelter is lost.

Some persons, especially those not indulging in alcoholic liquors, are naturally immune from the shakes; most others, if constantly breathing small amounts of zinc fumes, develop practical immunity and have the shakes only when they get an overdose of fumes as when ventilation is poor or after a day of rest, when the system becomes freer from zinc. Monday night is the time when most cases of "shakes" occur, both for the above reason and because the Saturday night and Sunday indulgence in alcohol puts the system in such condition that the subject is more susceptible.

The "shakes" are inconvenient and unpleasant but seldom or never fatal, very few cases coming under the hands of a doctor.

The disease involves temporary discomfort and some doctors claim that it lowers the bodily resistance so that other ailments, particularly pulmonary diseases, are more readily contracted and that the average life of brass smelters and casters is thereby shortened.

**PREVENTION**—To prevent "shakes," the zinc fumes must not be allowed to enter the nose or mouth. The use of respirators is seldom employed as the men prefer an occasional attack rather than the continual discomfort of wearing the respirator.

As enough fumes to develop immunity are not present in foundries where yellow brass or manganese bronze is seldom poured and as the small amount produced would not warrant installing forced ventilation the inconvenience from "brass shakes" may be as great and the cases as many as in rolling mills where alloys high in zinc are constantly poured, but where there is proper ventilation and where immunity is developed. Hence in the plants where alloys high in zinc are poured only occasionally the wearing of respirators during such pouring should be made compulsory. As the toxicity of the zinc fume probably exists whether the fume be inhaled or swallowed, eating food or chewing tobacco in the presence of zinc fume or without previous washing of the hands and face should be prohibited. No trouble from "shakes" is reported from any plants dealing only with bronze,

red brass or other alloys low in zinc, save for one isolated case showing symptoms similar to those of "shakes" where cupronickel, free from zinc, was melted in a battery of furnaces sometimes used for yellow brass, but no alloy containing zinc was being melted at the time the attack was contracted.

The fumes given off during the melting and pouring of brass, lead, tin, antimony, zinc or bismuth are poisonous and should be avoided as much as possible.

Excessive inhalations of the fumes of these materials may be the cause of mild forms of metallic poisoning indicated by temporary illness, such as the feeling of exhaustion, nausea, marked pallor and chills. For treatment give hot non-alcoholic drinks and induce perspiration. Proper ventilation, maintenance of proper temperature, etc., should be adopted in all cases.

#### THE EFFECT OF TEMPERATURE ON THE HEALTH OF MINERS

In Northern Minnesota a number of readings were taken which represented 25 per cent of the total places. In one place dry bulb registered 72° F., wet bulb 69° F., with a relative humidity of 86 per cent. In an isolated stub end the average for mine on air course was 48° F. dry bulb, and 46° F. wet bulb. Another reading showed wet bulb 46° F. and dry bulb 45° F. with a relative humidity of 87 per cent.

In a stub end ventilated by mechanical fan, dry bulb registered 73° F., wet bulb 69° F., giving an average humidity of 82 per cent which is a desirable working mine. In some of the iron mines of Minnesota warm places were observed, especially in isolated spots, but this was due primarily to falling timber, and decayed timber. These figures in a measure represent nearly all the iron mines in Northern Minnesota.

European coal mines are deep and, therefore, hot; American coal mines are shallow and it is very rarely that the temperature rises much over 70° F.

In a certain section of Minnesota, statistics were compiled, to show the natural causes of death among miners. In this particular section there are 2840 miners employed. From January 1, 1914, to November 16, 1915, 33 men died as a result of illness—divided as follows: typhoid fever, 3; kidney trouble, 2; cancer, 2; acute alcoholism, 4; heart trouble, 4; blood poisoning, 1; pneumonia, 7; gangrene, 1; intestinal obstruction, 1; duodenal ulcer, 1; exposure to cold, 1; tetanus, 1; brain abscess, 1; consumption, 3; and hemorrhage of brain, 1.

It will be seen that pneumonia was responsible for the most deaths among the Minnesota miners, seven men out of 2480 having succumbed to this disease. This may or may not be alarming and could not be considered a criterion as the prevalent diseases which readily respond to treatment have not been recorded. However, it may show that miners were subjected to this disease by reason of their walks from upcast shafts and while perspiring walking to dry houses which are in some places a considerable distance from the mine exits.

#### MINERS' NYSTAGMUS

Dr. Frederick T. Hoffman made an exhaustive study of miners' nystagmus for the Bureau of Mines and his report may be found in U. S. Bureau of Mines *Bulletin* 93.

He claims that miners' nystagmus is the result of a peculiar form of eye-strain which often results in the impairment of vision and consequent diminution of the wage-earning capacity of the workman. According to Greer an authority on industrial diseases and accidents, miners' nystagmus occurs in 5 per cent of all miners, but it is quite probable that the reference is to European coal mines rather than to men employed in all branches of the mineral industry.

According to the same authority miners' nystagmus is associated with a twitching of the eyelids and with considerable diminution of the range of movement of the eyes, and is particularly liable to occur in patients whose vision is subnormal owing to errors of refraction, especially astigmatism. It causes much wear-



ness to those suffering from it and prevents them from following their usual occupation, as, owing to the movements of the eyes, everything at which they look appears to be in a state of perpetual motion and in consequence their visual acuity is more or less reduced. When the movements cease the vision becomes as good as it was previously. Nystagmus as an occupational symptom is not alone confined to miners but may develop in those who are compelled to give close visual attention to constantly moving objects.

Nystagmus is found chiefly in miners who work at the coal face in a more or less constrained position of the body and the eyes. A man lies almost on his side with his legs crooked up and strikes the coal with a horizontal swing of his pick at the bottom of the coal seam. A miner engaged at this work will direct his gaze to different places as it becomes necessary for him to strike, for the eyes will follow the pick point, but the tendency will be for the gaze to be directed upward (using the ocular elevation) more or less obliquely. He will be sometimes on one side and sometimes on the other. His head will be thrown back and flexed more or less on the shoulder beneath.

Snell says that nystagmus occurs among miners working with all kinds of lighting, and that he has met with it among those working with safety lamps, candles, large open lamps as well as when artificial light was really good. He says, however, that there are reasons for believing that the strain is greater in poor light and that nystagmus is met with in greater frequency under such conditions.

**SYMPTOMS**—Oscillation of the eyeball, objects dancing before the eyes, headache, giddiness, both eyes affected, tremors of the head and eyelids and of the muscles of the face or neck are often associated.

Prognosis is usually good even for old standing cases if the directions are to change of the work are followed.

In some cases, according to Snell, it will suffice if the patient ceases from coal-getting without altogether stopping work in the mine, but generally it is advisable, especially if the nystagmus be of a high degree and of some standing, to recommend cessation altogether from work underground. After relief has been effected, return to the mine is practicable, provided the head can be kept straight and the upward turn of the eyes avoided. Resumption of the old kind of work is followed sooner or later by a recurrence of the symptoms. Medical treatment is of service.

#### HOOKWORM

As regards the prevalence of hookworm in this country, preliminary investigations have shown comparatively little in northern coal mines, although it is undoubtedly prevalent in southern coal mines.

J. H. White of the Bureau of Mines has recently completed an exhaustive study of the hookworm in deep California mines and he found that the spread of the disease is due to the warmth of the mines and to climbing up and down ladders, it being very easy for the infected mud to get on the hands of the miners.

#### HEALTH CONSERVATION AT STEEL MILLS

Dr. J. A. Watkins, passed assistant Surgeon of the United States Public Health Service, recently completed technical paper No. 102, a Bureau of Mines publication on "Health Conservation at Steel Mills." The edition is not quite ready for distribution, but through the kindness of the Director of the Bureau I am permitted to make reference to it.

The number and seriousness of occupational health hazards have increased rapidly with the evolution of new machinery, the use of new materials and process of manufacture and the resulting new products. The attempted or forced adoption of the human body to this changed environment has resulted in many abnormal conditions. The importance of the prevention of disease among workers can be realized from the fact that the average loss of time due to illness among approximately 30,000,000

workers in the United States is 9 days a year. This is 270,000,000 working days or about 750,000 working years annually. If medical attention be estimated at one dollar a day and earnings at two dollars a day this loss amounts to \$880,000,000 annually.

Dr. Watkins urges medical supervision of employees and he makes the following suggestions:

The working man has a right to demand that he be not required to work beside men who are diseased or mentally deranged.

A plant hospital should be provided to give emergency relief to those injured or taken ill while at work. Fatigue lowers the vitality of the individual and thereby increases his susceptibility to the hazards of his occupation and to disease in general. There should be sufficient space for each employee in order that close proximity to dangerous machinery or undue exposure to heat, dust, fumes or gases or harmful material or products may be minimized.

Floorings affect health mainly through the liability of floors made of certain materials to retain germs of infectious diseases. Hard or elastic substances such as cement or steel make unsatisfactory floors for employees who have to be on their feet constantly.

He suggests that floor space should be kept clean and the floor should be so constructed as to permit easy and thorough cleansing. The workshop and factory should have proper lighting. It gives increased efficiency. The ill effects of bad lighting gives impaired vision and often is responsible for accidents. Noises cause lowered efficiency by having a deteriorating effect on the more sensitive functioning parts of the ear. Improper ventilation is responsible for general impairment of health.

The combination of high temperature and high humidity of the shops eventually affects the health of those exposed. The economic effect is a decrease in the efficiency of the worker, *i. e.*, a lowering in the character and amount of work performed. Continued exposure to high temperature and high humidity increase the susceptibility to disease and may cause muscular and joint pains, aches, cramps and in extreme cases, heat exhaustion and continued exposure will eventually cause anemia and skin eruptions and tend to induce premature old age.

The number of hours which a man actually works has a direct bearing on fatigue. After a certain amount of exertion for a given time, the efficiency of the employee fails.

Sanitary washing and dressing rooms are an aspect of this problem that should not be overlooked.

Water closets should receive proper consideration. Correct ventilation of these places consists not so much in the supplying of fresh air as in the rapid removal of disagreeable odors as they arise.

Drinking water should be pure and should be adequately supplied. The water should be of the proper temperature and should be so distributed as to preclude all possibility of contamination.

WASHINGTON, D. C.

#### DANGERS OTHER THAN ACCIDENTS IN THE MANUFACTURE OF EXPLOSIVES

By DR. ALICE HAMILTON  
U. S. Department of Labor

During the winter and early Spring of this year we began to get from England the reports of the Commission appointed by Parliament to inquire into the health of munition workers. Great Britain, engaged as she is in the greatest war in her history, a war in which the uninterrupted production of vast stores of munitions is vitally necessary, found time to turn her attention to the health and safety of the men and women engaged in munition work and appointed a group of well-known authorities to inquire into the dangers of overwork and of occupational diseases in these occupations. With such an example set us, it seemed as

if our country, peaceful and prosperous as she is, might do as much for the workers in our munition industry which has back of it no great national need, only the usual desire for profits. Consequently last April the Federal Bureau of Labor Statistics instructed me to begin a study of occupational poisoning in factories making high explosives, and by this term I mean all explosives aside from black powder, the making of which does not involve exposure to any poisonous substance.

In coöperation with the various state bureaus I have visited some forty plants so far but my study is not yet complete though it has covered the greater number of the most important. I have confined myself to the poisons used in the production of explosives, those evolved in the course of production and the explosives themselves. Accidents from explosions or burns I have not taken into account.

The list of poisons so far discovered I might run over hastily and then take them up more in detail.

There are some 30 to 35 poisonous substances which I have encountered so far, beginning with the three acids, hydrochloric, nitric and sulfuric. From these we get fumes of nitrogen oxides, of chlorine gas and of sulfur dioxide. Then there are benzene and toluene and their many derivatives, the nitrobenzenes and nitrotoluenes, phenol and sodium phenylate, the nitrophenols, ammonium picrate, aniline, diphenylamine, dimethylaniline, tetranitromethylaniline. More familiar substances also enter into this manufacture: sulfuric ether, ethyl alcohol, methyl alcohol, ethyl nitrite, amyl acetate. In making detonators we find mercury, mercuric nitrate and fulminate of mercury. In phenol manufacture I have seen caustic soda used in such a way as to be a decided danger. Finally there is the poison new to us medical people, especially on this side of the water, tetrachlorethane, used, not in the manufacture of munitions, but in a war industry, the varnishing of aeroplanes.

We may gain some idea of the industrial poisoning caused by these substances if we compare the British figures of occupational poisoning during the year just before the war with those of the first year of the war. In 1913,  $H_2S$  was responsible for 8 cases of poisoning with one death. In 1914, the number had risen to 22 with 3 deaths. This is something I cannot at all explain. I wish someone would tell me what war industry could be responsible for such an increase in  $H_2S$  poisoning. Surely it cannot be sulfur black. There was no nitrous fume poisoning in 1913 but in 1914 there were 9 cases with 2 deaths. Nitro and amido compounds of benzene in 1913 caused 2 cases, no fatalities; in 1914, 38 cases, with two deaths; and tetrachlorethane which in 1913 had given no trouble at all, produced, in 1914, 25 cases of poisoning with 4 deaths.

This looks like a startling record but it will not seem so in comparison with our own. I cannot give the full figures as yet but I can assure you that the 4 deaths from nitrogen compounds in the British report will be multiplied at least five times by our own record during the past year. I have records of fatal poisoning from the oxides of nitrogen, from benzene, nitrobenzene, trinitrotoluene, aniline, ether—a case of uræmic poisoning— $SO_2$ , and from sulfuric acid. The largest number of fatalities are from nitrogen oxides, next, but far less, from trinitrotoluene. I have found cases of poisoning from every substance enumerated in my list except ammonium picrate, not manufactured much now, methyl alcohol, which I have not found much in use, diphenylamine, dimethylaniline, and amyl acetate.

Now by far the most important of these poisons are the gases which we group together as the oxides of nitrogen—what the British call nitrous fumes. They are important in the first place because they are formed in all nitration processes and of course that means in the manufacture of all explosives. Then they are not irritating or corrosive, as are other acid fumes. Men will run from the chlorine gas liberated when nitric acid is being made from sodium nitrate which has the chloride as an

impurity, they will run from fumes of  $SO_2$ , but they often breathe enough nitrogen oxide fumes to cause severe, even fatal poisoning, without realizing that anything dangerous is happening.

I have found these fumes worst in the nitrating of cotton and of phenol, least in the nitrating of glycerine. In guncotton manufacture, especially when pot nitration is used, they constitute a constant and recognized danger. The more usual method of mechanical nitration in wringers is not productive of so much fume—as I understand it, higher nitration is done by the pot method—unless something goes wrong and there is a fire, a rapid decomposition with the formation of great clouds of fumes. It so happens that I have never been in a cotton nitrating plant in which at least one such accident did not occur, no matter how short my visit. In one case there were three in 7 minutes time and nobody seemed to think it unusual. I came to expect the sudden pouring out of the angry orange clouds, the men running for the platforms outside and waiting till the fumes had died down to what I always hoped was a safe point before going in again. I made a large part of my study in the hot weather of July and there were days when it would be 15 minutes before the air of a building would really clear up after a fire.

I do not know whether the manufacture of picric acid should be attended with even more excessive fume production than the nitrating of cotton, but in my experience it seems to be. Perhaps this is because I have seen so many hastily and poorly constructed picric acid plants, put up to fill a single war contract and carried on with what looks like reckless haste and I fear sometimes a good deal of ignorance, at least of the fundamental laws of hygiene. The so-called King method of nitrating phenol in pots into which the phenol is poured and the nitric acid siphoned in, has seemed to me a most dangerous method. In one plant no less than 100 of these siphons would be "shot off" as it is called at once and then the men expected to rush for the open, but, of course, if anything went wrong somebody must venture back into the long low shed now thick with orange fumes, and after two hours all must go in and break up the crust of picric that has formed and stir it up and raise more fumes. Still I have seen very dense fumes in plants using the more usual methods and one of the most spectacular orange clouds I have ever seen, visible for several miles, came from the drowning department of a synthetic picric plant.

Anyone who has been connected with work of this sort is familiar with the various forms of nitrogen oxide poisoning. The milder form, what the men usually mean to describe when they tell one that they were "knocked out by the gas," is an attack of choking and strangling for air quite like asthma, distressing but not serious. It may be accompanied by gastric pain and both usually yield to a few drops of chloroform given by the mouth. If the exposure has been greater, a bronchitis may follow, or an inflammation of the throat and larynx, some times even laryngeal oedema. This may pass into a consolidating pneumonia. Such cases I do not find listed as nitrogen oxide fume cases and I shall never be able to make any estimate of their number, for the Company doctors I have met refuse to admit that bronchitis or pneumonia may be caused by exposure to these fumes. They recognize the asthmatic attacks and they recognize fatal oedema, but nothing in between these two extremes. This is, of course, a pathological impossibility and Dr. Hudson, chief of the du Pont Company's medical staff and the man who knows more about the subject than anyone else in this country, says, on the ground of animal experiments, as well as observation of human cases, that consolidating pneumonia is one of the results of exposure to nitrogen oxide fumes. Fatal cases present a picture which one does not readily forget. In a typical case the man recovers from the first choking attack, goes home, eats his supper and goes to bed seemingly all right. During the night he wakes with a sudden intense dyspnoea, gasping and laboring for breath, and with increasing symptoms



of congestion of the lungs, going on to oedema and death. A very characteristic case came to my attention the other day, characteristic for several reasons. An enterprising group of men had taken a big war contract for picric acid, they had bought an old factory in a small country town, had imported foreign laborers from near-by towns and started in to manufacture at once. Presently the men began to be knocked out by the fumes and so many were frightened and quit that the force used to change about every fortnight. Of course, work could not be stopped till improvements could be installed, such as fans to carry off the fumes, but the managers, being kindly men, did what they could. They started putting in fans and got a local plumber to do the work. He had to place them where the fumes were thick and of course nitrating went on all the time. The plumber was overcome and had to be taken outside to revive. They advised him not to go back to finish the job that day but he insisted on doing so. He went home after a second "knock out," and was dead by morning. It seems a little ironical that the well-meant effort to improve conditions should have had such disastrous consequences and all because the management was in such a hurry.

These fumes are said by some to be more harmful in winter because the cold lowers the men's resistance, by others in hot weather because the air hangs heavy and takes so long to clear.

Perhaps it will be less confusing if instead of going on to the next most important poison I keep on with these two industries, the manufacture of guncotton and of picric acid. In guncotton manufacture, once the nitration is over, the only danger is from the solvents. I have not found wood alcohol in use as a solvent for guncotton as it is in celluloid manufacture. Grain alcohol I suppose we may ignore, though it is sometimes strong enough to make the men drunk just by inhalation. Amyl acetate, used for fine shot-gun powder, has not given rise to any trouble so far as I know. Ether does give enough trouble to be a decided inconvenience, especially in the winter when the pressing and cutting departments must be kept closed and the temperature at about 80° F. "Ether jags" are frequent and the men may even have to be sent to a hospital for a few days but they recover readily and either become more or less immune or usually they give up the job. Most company doctors, not all, deny that there is any chronic ether poisoning in such work, an assertion that on the face of it seems dubious. I have records of six cases of chronic nephritis, in men who had not the symptoms before they worked with ether. One ended in fatal uraemia. I have also records of 4 men in whom the fumes seemed to cause loss of appetite, chronic lassitude and drowsiness, loss of weight, all of which disappeared on leaving the ether atmosphere. These are few cases when one considers the large numbers employed, but they were happened upon accidentally and do not represent at all the real condition.

In manufacturing picric acid there are several poisons besides the nitrogen oxides. To begin with there is phenol, a very well-known poison. In the early days of antiseptic surgery there were many cases of carbolic acid poisoning in patients from too energetic irrigation of wounds, or from dressings soaked in carbolic solution and left on too long, and there was chronic poisoning among surgeons who would operate for hours daily in an atmosphere saturated by means of the carbolic spray. Also we know that severe systemic poisoning with dizziness, delirium, weakness and collapse may follow the spilling of phenol over a large surface of the body, and that chronic Bright's disease may follow long exposure to small quantities in the air. Phenol burns are often accompanied by general symptoms. Sodium phenylate is said to be quite as productive of burns as phenol itself.

If the picric acid is made by the synthetic method, there is dinitrochlorbenzol, capable of producing a very distressing form of dermatitis and there is caustic soda sometimes, which in one

instance at least was handled in such a way as to be decidedly dangerous to eyes and skin. Then there is the picric acid itself which causes severe infection of the skin and mucous membranes as well as bringing about gastric disturbances.

Benzene and toluene, the foundation for so many of the explosives, have given rise to several cases of severe and even fatal poisoning, death coming on almost instantly. In my experience these have all been due to repair work about stills necessitated by some accident. But accidents necessitating repairs seem so frequent in the manufacture of explosives that they really should not be regarded as exceptions; they should be taken as part of the day's work and provided for carefully, as indeed is done in some of the older plants.

The nitro and amido compounds of benzene and toluene give rise to a very well defined and characteristic form of poisoning, which consists in a direct action on the central nervous system and in the formation of methaemoglobin in the place of oxyhaemoglobin. As methaemoglobin is closely bound to the red corpuscles they cannot take up oxygen and the normal exchange of gases on which life depends is interrupted and a condition of internal suffocation comes on, a starvation for oxygen in the presence of abundance of air. The most striking symptom to the observer is the blue color, especially of the lips and mouth. Mild cases suffer from throbbing headaches, dizziness, and weakness. This also is known as a "jag" and I have talked to men who had had twenty or more "jags" and yet were apparently in good health. Occasionally there is a continual feeling of languor and nervousness. Foremen have told me that men in aniline work are always a bit grouchy, have to be handled gingerly and not hustled and that they really cannot work at a good pace.

The substances of this group which in the manufacture of explosives give rise to the most trouble, seem to be mononitrobenzene and trinitrotoluene. In severe cases of poisoning the color is livid, the heart is markedly weak and rapid, and coma may come on. The fatal case of nitrobenzene poisoning on my list had convulsions before death. I do not find as much trouble from nitrobenzene as from aniline but probably the poisoning, when it occurs, is severer.

Trinitrotoluene usually causes the same symptoms as nitrobenzene, aniline and the others, including the blue color, but severe cases may have no cyanosis; instead they may have a typical jaundice with yellow sclera, intense, uncontrollable nausea, inability to keep any food on the stomach and pain in the region of the liver. I have records of two fatal cases of toxic jaundice with changes in the liver exactly like those of acute yellow atrophy and another with oedema of the lungs which was, I suspect, caused by the fumes of nitration, not by the finished product. Trinitrotoluene, aniline or nitrobenzene may be absorbed through the skin or through the respiratory tract and I find many men with experience are beginning to lay more stress on the former method. The worst accidents from nitrobenzene and from aniline seem to come from spilling the fluid over skin or clothes. The fatal trinitrotoluene cases had been exposed to fumes, but another case, not fatal, occurred in a woman who was weighing and paring down charges for shells. In her case it was probably absorption through the skin though she may have breathed in dust fragments.

None of these poisons gives any warning of its dangerous nature by an irritating odor or a choking effect; they are rather pleasant than otherwise.

Nitroglycerine is a medical mystery, for apparently men may in the course of their work absorb many times what is considered a powerfully depressant dose, but they seem to suffer no ill effects once they have got past the stage of intense headache. There are some of the substances in explosive factories which have chiefly an action on the skin. Dry picric acid may cause a very distressing dermatitis; tetryl-tetranitromethylaniline is still

more irritating, and fulminate of mercury and dinitrochlorobenzene are also productive of skin inflammations, which may be quite serious enough to require shifting to other work. Individuals differ very much in their susceptibility to these skin affections; it is not only a question of personal cleanliness. Ethyl nitrate evolved in large quantities during the manufacture of fulminate, is a well-known depressant and may, especially on heavy hot days, cause faintness and feeble heart action for a while. Finally tetrachlorethane, used in the varnish for aeroplane wings, was found by the experiments of K. B. Lehmann, in 1911, to be about 4 times as poisonous as chloroform. Here, as with trinitrotoluene, it is toxic jaundice that develops. Fatal cases were reported from both England and Germany before the war and undoubtedly have occurred in both countries since the war. I am not able to say as yet how much this particular solvent is used in our flying machine construction.

There is no time to describe methods of prevention, some of which have been worked out with much care and knowledge by the older companies. Since it is a question of fume and dust prevention and of proper provision for bodily cleanliness, it is only the details that need to be solved in each instance. The larger number of men are not susceptible to these poisons unless conditions are very bad and the exposure excessive, but a minority is susceptible and a small group is over-susceptible and will suffer unless extraordinary precautions are taken, and unfortunately there is no way of picking out this group in advance.

One word as to occupational poisonings in general. Only last week I was challenged by one of the management of a large

munition factory for using the term occupational. He insisted that since the greater number of the men in a particular occupation do not suffer any ill effects, the poisoning that occurs is not occupational, being due to individual susceptibility. But individual susceptibility plays a part in all disease. Give 30 men typhoid-infected water to drink and you will not have 30 cases of typhoid fever—you may not have 15. But, if there are only two cases, you will still hold the water responsible for them. I find that this matter of immunity and lack of immunity is a great stumbling block to employers, who cannot believe that what is one man's meat may be another man's poison and this from no fault of his. The immune working man seems to be continually rising up to confront me and refute my statements. Never have I found a plant so bad that it could not boast at least one old and faithful employee who has breathed lead fumes, or arsenic dust, or wood alcohol, or benzene, or whatever, for years and never felt it. This is my usual experience. "You call this work dangerous. Now I'd like to show you a man here who has been at it for years and see what you think of him. Come over here John! Tell the lady how long you've been with us. Twenty years, isn't it, and never a sick day. Now what do you say to that?" And John's appearance justifies all that is said of him and still I persist in calling the work dangerous. If Nature had made all men really equal, it would be simple, but she has not and some men will suffer when most men escape. It is the susceptible man who must be taken as the rule if we are to prevent occupational poisoning, not the man who is immune and who does not need care.

HULL HOUSE, CHICAGO

## CURRENT INDUSTRIAL NEWS

### GAS ANNEALING FURNACES

A gas furnace newly installed by a Paris firm for the annealing of soft steel wire coils was described and illustrated in the *Journal des Usines à Gas* for August 5. The furnace consists of a masonry structure reinforced with external channel standards and fitted with counterpoised doors for the introduction and removal of the coils. The furnace is heated by 5 atmospheric burners arranged along the length of the base. These yield a temperature of 800° C. and consume about 20 cubic meters (700 cu. ft.) per hr. The furnace is continuous in action, one coil being inserted on one side and at the same time another removed by the opposite door. On this system, ten hours are required to anneal 75 coils, equivalent to 2½ kilos, of steel. The gas consumed per hour is thus 2.6 meters (cubic), costing about 52 cents. In comparison with the coal furnace previously in use, it is found that the results are better owing to the more exact regulation of the temperature and that there is no production of brittleness from faulty heating. Moreover, the wire is found to be heated uniformly throughout its entire length. The soft steel wire of 5 mm. diameter is annealed in coils, each weighing 35 kilos.—A. McMILLAN.

### PETROL SAFETY DEVICE

The *Petroleum World*, 13 (1916), 316, states that among the exhibits shown at the Easter show held at Sydney, N. S. W., this year, was a device which it is asserted affords the control of petrol. The inventor is Mr. M. G. O'Brien, an Australian by birth, and the device is known as the Tabrol Petrol Safety Device. Briefly, the device consists of a perforated brass tube in the form of a cylinder and a screw top fitted with an automatic safety valve. The former can be inserted into the tank of a motor car, motor boat, motor cycle, gasoline stove, or any receptacle for volatile oils and, while acting as a filler cup, prevents any spark or flame from entering the tank.—M.

### CUTCH PRODUCTION IN BURMA

The British demand for crude dyes is being met in part by increased shipments of cutch from Burma. In 1915, 1,234,140 lbs. of cutch were exported in contrast with 237,440 lbs. in 1914. In the manufacture of cutch no scientific processes are employed, the industry being carried on exclusively by the natives. It is obtained from the "acacia catechu," the trees being felled while green, the bark taken off and the timber chopped up and boiled in large cauldrons. The resultant liquid is drawn off and solidifies as it cools. In the better qualities of cutch only the heart-wood of the tree is utilized. Licenses for cutch manufacture are granted annually by the Government and the industry is more or less of a standby to the population in seasons of bad harvests. The Burmese Government increases or reduces the number of licenses as necessity arises. Cutch is used largely as a dye but, in addition to this, it is employed in some countries for tanning and as a preservative. Locally fishing nets and sails are steeped in it to preserve them from the action of sea water.—M.

### JAPANESE IRON ORE RESOURCES

It is reported that, owing to the greatly increased demand for iron and steel, the Japanese Government has been investigating sources of ore supply in their country and it would seem from the report recently issued, that the main source of supply within the Empire is the Kamaishi mine, the deposit of magnetic ore there being estimated at 35,000,000 tons. Deposits of similar ore are estimated to total between 5,000,000 and 6,000,000 tons from mines in the provinces of Rikuchu, Echigo, Iwaki, Iwashi, Kozuke, Yamato, Harima and Mimaska. Deposits of red iron ore, estimated to total about 30,000,000 tons, are located in the provinces of Echigo, Rikuchu, Tosa, Hyogo, Rikuzen and Izumo. Brown iron ore deposits believed to total 10,000,000 tons bring the estimated aggregate total to about 80,000,000 tons for the islands alone.—M.



## UTILIZATION OF COAL IN GREAT BRITAIN

In an article in the *Times Trade Supplement* for August, Prof. H. E. Armstrong, London, strongly urges that concerted action should be taken without delay for the complete association and organization of all the interests connected with the dyestuff manufacture in Great Britain. He points out that five-sixths of the coal raised in Great Britain is used direct for consumption, while the valuable volatile substances are conserved only from the remaining one-sixth. If the whole of the raw bituminous coal were submitted to the coking process at suitable temperatures, immense quantities of liquid fuel suitable for use in internal combustion engines would be recovered. In addition, there would be an ample supply of the raw material necessary for the now-important manufacture of high explosives, while the raw material for dyes would be more than sufficient to supply the whole world. Again, agricultural interests could be amply supplied by the large quantities of ammonia available and, by using the soft coke in open fires, soot and smoke would, to a great extent, be abolished. Prof. Armstrong goes the length of urging that the government should legislate forbidding the use of raw coal and should prevent its exportation to foreign ports. The necessary funds for the study of all problems relating to the development of coking processes and the utilization of the by-products might be conveniently raised by placing a tax of only one cent on each ton of coal taken from the ground.—M.

## PAPER PULP FROM BAMBOO

According to a report in the *Indian Trade Journal* by the paper pulp expert of Bansda State, the suitability of bamboo fiber for the manufacture of paper pulp has been fully demonstrated. Every one who has handled the finished material has agreed that it is admirably suited for the purpose, and especially so for paper used for high-class printing and illustration work requiring a close, even texture and surface, and a minimum of stretch and shrinkage under the damping operation. Again, it makes any kind of paper by itself and does not require blending with other fibers. The one serious objection advanced against it was the cost of bleaching. With the soda process, this difficulty is almost removed. The quantity of bleach required now is not 9 to 40 per cent but is only 5 to 10 per cent. Esparto boiled with 15 to 18 per cent soda requires 5 to 10 per cent bleach according to the standard of whiteness of the paper required. Bamboo is treated similarly to esparto except that bamboo requires a higher temperature, though lower than what is needed in boiling wood. Bleaching expenditure has been brought down to a figure which compares very favorably with esparto or any of the raw materials now in use. Bamboo is subject only to the chemical process of pulping and such methods employed are of two kinds, *viz.*, acid, of which the so-called sulfite process is typical, and the alkaline, exemplified by the well-known "soda" process.—M.

## INSULATING MATERIAL

Although it has been called both cotton and wool, the insulating material usually known as silicate cotton has nothing to do with either of these substances in their magnified conditions. It has been suggested by a writer in *Ice and Cold Storage* that some definite name for the material should be used and considers "silicate fiber" as a proper designation. Silicate cotton is prepared from slag procured from ironworks. In the treatment of ore in blast furnaces, lime, coal, coke, etc., are mixed with the substance and eventually intermingle in the molten condition. Subsequently such materials are rejected and form a boiling lather, as it were, which is discharged by the working of the mass and cools down as a slag, the constitution, consistency and color of which vary according to the exact nature of the ingredients. —M.

## COAL RESOURCES OF THE UNITED KINGDOM

An important paper on the coal resources of the United Kingdom was recently read at the South Wales Institute of Engineers by Mr. Arnold Lupton. From calculations made, Mr. Lupton showed that there were in reserve in the South Wales coalfield 35,690,000,000 tons of coal and, with an output of say 60,000,000 tons a year, that would last 595 years. But the maximum output, whatever it might prove to be, would not be maintained till the end; it would gradually decline. In Mr. Lupton's opinion, men could be working coal in South Wales 5000 years hence. In 1913, the amount of coal raised in the United Kingdom was 287,000,000 tons. Having regard to the character of the new collieries recently established and about to be established in different parts of Great Britain, there was every reason to suppose that the next decade would show an increase in coal production. The writer further thought it probable that the annual tonnage raised would increase until it reached the figure of 350,000,000 or even 400,000,000 tons.—M.

## PARAFFIN FOR MOTOR VEHICLES

According to the *Times Engineering Supplement* (No. 501 p. 120) a device, known as the Smith-King paraffin attachment, has been introduced by a London firm, with the intention of facilitating the use of paraffin oil as a fuel for motor-car engines. It takes advantage of the fact that in the Smith carburetor there are four jets, each fitting into a separate choke or port and controlled by a valve or dashpot sliding on a central spindle which brings them successively into action as the demand of the engine increases. With the King attachment two float chambers are provided, one for petrol and the other for paraffin, the former being in connection with the first jet of the carburetor and the latter with the three other jets. For starting and slow-running the engine is fed with petrol from the first jet, but, as the throttle is opened, the controlling valve rises and brings the paraffin jet into operation, the petrol supply being automatically cut off. It is stated that in average running the proportion of petrol consumed never exceeds 20 per cent and is generally less. To secure proper vaporization of the paraffin the float chamber allocated to the latter is heated by means of a jacket through which the hot water from the radiator circulates, or by an exhaust heating arrangement, while to prevent possible condensation of the vaporized paraffin as it passes to the cylinders the inlet pipe is jacketed in connection with the exhaust.—M.

## RAPESEED OIL TAR SOAP

For production of fluid soap, linseed oil may be substituted by rapeseed oil. The same applies to the oils formerly used for tar soaps. A tar soap, which resists cold and is perfectly soluble in water, is obtained according to the following recipe taken from *Oil and Color Trade Journal*, 50 (1916), 615: birchwood tar 25 parts, potash lye (35 per cent, freshly prepared) 18 parts, rapeseed oil 20 parts, spirits 25 parts, distilled water 12 parts. The tar is mixed with the lye, the rapeseed oil is added, saponification is effected and the soap mass dissolved in spirits. The soap mass is increased or the amount of alkali decreased according to requirements.—M.

## PERNAMBUCO WHALE FISHERY

According to a British Consular report, an important whale fishing station has been established on the coast of the State of Parahyba. Whales arrive in large numbers off the Brazilian coast from the polar regions, about the end of June. During the year 1914, 154 whales were caught. The animals are hauled ashore by a steam whaling boat, cut up and boiled with remarkable rapidity, three average sized whales being dealt with in one day and there is practically no waste, even the flesh and bones being converted into manure after the oil is extracted.—M.

### CANADIAN PETROLEUM IMPORTS

The total value of imports of petroleum and petroleum products to Canada in 1915 was \$8,047,781 as against a value of \$11,174,763 in 1914. The total imports of petroleum oils, crude and refined in 1915, were 236,923,765 gals., valued at \$7,979,264. The oil imports included crude oil, 192,588,487 gals. valued at \$3,678,021; refined and illuminating oils, 6,792,873 gals. valued at \$405,019; gasoline, 28,030,972 gals. valued at \$2,693,717; lubricating oils, 4,557,179 gals. valued at \$755,535; and other oil products of petroleum, 4,954,254 gals. valued at \$446,972. The oil imports in 1914 were as follows: crude oil, 195,207,210 gals. valued at \$5,750,971; refined and illuminating oils, 12,833,065 gals. valued at \$2,747,360; lubricating oils, 5,767,676 gals. valued at \$940,143; and other oil products of petroleum, 6,283,621 gals. valued at \$663,407, making a total of 244,487,973 gals. valued at \$11,072,362. The imports of petroleum products in 1915 included 980,662 lbs. of paraffin and paraffin-wax candles valued at \$68,517.—M.

### VEGETABLE WAX FROM MADAGASCAR

According to the *Chem. Trade Journal*, a product resembling carnauba wax is prepared in Madagascar from the leaves of the raffia palm which is the source of the bass used by gardeners. The wax is obtained from the residues of the leaves after the bass has been stripped off. It has approximately the same melting point (83° C.) as carnauba wax and behaves in the same way towards solvents.—M.

### PROHIBITED EXPORTS

The following have been added to the list of substances, the export of which from Great Britain is prohibited: cadmium, alloys of cadmium and cadmium ore (to all destinations other than British); cork and cork dust, fibers, linoleum (to all destinations in Europe other than France, Russia, Italy, Spain and Portugal); cryolite, dandy brushes, lead-coated sheets (to all destinations).—M.

### JAPANESE LEATHER INDUSTRY

According to accounts recently issued, the Japanese leather trade is passing through a period of prosperity hitherto unknown. Korean leather, which before the war scarcely existed, has developed considerably under Japanese management. Excellent military boots and cartridge belts are being made in the factories of Seoul. An establishment near Seoul recently supplied 40,000 pairs of military boots and 30,000 cartridge belts. Thousands of people in Japan are making various leather articles required by the Russian army.—M.

### DIESEL ENGINE CRANK SHAFTS

In a paper read recently before the Diesel Engine Users' Association, Mr. P. H. Smith tried to show that the life of crankshafts of Diesel engines depends to a great extent on the engineer in charge and may be prolonged indefinitely if certain reasonable and simple precautions are taken. He showed that all the failures investigated were due to lack of alignment of the main bearings, usually resulting from unequal rates of wear of the several shaft bearings, though attributable in some cases to negligence during erection or, in older engines, to defective foundations. The type of engine least liable to fracture is the three-cylinder and the worst is the four-cylinder, though the two-cylinder runs it very close if fitted with a heavy fly-wheel. Nearly always, the shafts give way through the webs, the cracks starting at the center and working outwards. In single-cylinder units either web may fail; in two-cylinder engines web 4 fails most frequently (the webs being numbered consecutively from the end farthest from the fly-wheel); in three-cylinder units the fracture occurs in either web 1 or 6 and in 1 as often as 6; in four-cylinder engines it is almost invariably web 4 that fractures.—M.

### A NEW IRISH INDUSTRY

A large factory, says *Engineering*, **111** (1916), 251, will shortly be opened in Dublin for the manufacture of electric dry cells and batteries of all kinds for pocket-lamps, telephones, household bells, automobile and other uses. This factory will give employment to over 200 hands, mostly girl labor. During the war, special attention has been drawn to the manufacture of electric dry batteries for pocket lamps. In the United Kingdom the yearly consumption was over 60,000,000 of which only 8,000,000 were made in England. Germany supplied over 40,000,000.—M.

### SUNFLOWER CAKE AS FUEL

Previous to the war, says the *Oil and Color Trade Journal*, quoting from a Petrograd newspaper, oil-cakes to the extent of tens of millions of poods (36.113 lbs. = 1 pood) were exported from Russia to foreign countries, chiefly to Germany, where the raising of cattle prospered at the expense of Russian bran and oil-cakes. From the beginning of the war, the export of these materials has practically ceased. For some time there was a panic in oil-cakes, it being difficult to know what to do with them, as the inland market was very poor. Afterwards, however, there was no difficulty in disposing of them. Industry in Central Russia was left without fuel as the railways did not bring coal and the price had risen to a very high figure. Factory owners began to turn their attention to the using of sunflower seed as a fuel to take the place of coal and now most of the industrial works have laid in stocks of the oil-cake to fuel them during the coming season. The Balashevsky mills sometime ago bought 200,000 poods of sunflower seed cake at 55 cents per pood for the winter season.—M.

### ARGENTINE WOLFRAM OUTPUT

The *Iron and Coal Trades Review*, **93** (1916), 184, reports that the total Argentine exports of tungsten ore from 1909-1913, inclusive, amounted to 3,319 tons. Of this amount, 3,309 tons went to Germany and only 10 tons to Great Britain. The exports to Germany for 1912 amounted to 637 tons; for 1913, 536 tons; and for 1914, 394 tons. In 1915, the United States became an importer, receiving 135 tons of ore from Buenos Aires out of a total of 158 tons exported during that year. In the first three months of the present year 146 tons of ore left that port for the United States. When war broke out, the German market was cut off and the Hausa mines, supposed to be connected with Krupp's, closed down part of their plant, thus reducing the production somewhat. They are now, however, working at full capacity and it is announced by the management that the entire output for 1916 has been contracted for in the United States.—M.

### AUSTRALIAN GOLD

According to statistics, the decline in the production of gold in the Australian Commonwealth, which has been noticed for several years, seems to have continued in 1915, the total output for the twelve months amounting to 1,942,835 oz. (fine) as compared with 2,048,905 oz. (fine) in 1914. The most serious decline occurred in Victoria where there was a falling off in output of 80,638 oz., while the amount for Western Australia was 22,868 oz. less than for the previous year. For New South Wales, the figure given shows an increase of nearly 1,000 oz. for the year. The present high rate of wages and the current conditions of working are regarded by capitalists interested in gold mining as rendering the industry more unprofitable as years go on. In December last, the Arbitration Court granted an increase of wages and, as a result of this decision, it is probable that some of the gold mines in Victoria may be closed down.—M.



### AUSTRALIAN GRASS TREE GUM

A report from the Trade Commissioner in Australia states that a merchant in Sydney is prepared to export to the United Kingdom a powder which requires only to be mixed with spirits to produce lacquer. This powder is made from grass tree gum which in turn is derived from plants found in the coastal districts of New South Wales. It is claimed that the powder is free from all impurities, that it dissolves instantly and that tests on wood and iron have shown better results than have been obtained from spirit lacquers of German manufacture. Samples of the yellow and brown gum may be seen at the Board of Trade Offices, London.—M.

### NEW FERTILIZER

Experiments have recently been made upon the fertilizing value of sodium ammonium sulfate as compared with ammonium sulfate. Owing to the scarcity of sulfuric acid, sodium bisulfate is being used to a large extent to absorb ammonia. The material with which the experiments were made contained 9 to 10 per cent nitrogen and the crops treated were rye, oats, barley and several varieties of beets and cabbage. In every case, ammonium and sodium ammonium sulfates gave practically the same yields when equivalent amounts of nitrogen were applied. —M.

### PLASTER OF PARIS

An article in the *Journ. Pharm. Chem.* 14 (1916), 78, describes the effect of various substances in the accelerating of the hardening of plaster of Paris. The various electro-negative elements have not an identical action. For the same base, the salts of the strongest acid have the greatest activity. Electro-positive elements behave in a similar manner; the strongest base most energetically accelerates the time of setting. The substances which modify the solubility of the plaster also modify its time of setting. Salts which increase the solubility accelerate the hardening; substances which decrease the solubility retard the setting.—M.

### BRITISH PULP

The investigation of possible new paper-making materials found within the British Empire continues to be carried on systematically at the Imperial Institute, London, and some of the latest results in this connection are published in the new number of the *Bulletin of the Imperial Institute*. One of the materials examined has been tambookie or tambookie grass, which grows luxuriantly over vast tracts of country in the Transvaal, particularly in the northerly parts. This grass has been found to produce, under the same conditions, more pulp than Algerian esparto grass but a little less than Spanish esparto. The pulp produced is of good quality and can be easily bleached. Paper-making trials were also carried out and it was shown that a satisfactory paper of fairly good strength can be made from tambookie grass pulp. The most economical use for the grass will probably be to convert it to half-stuff which can be exported to Europe or used for paper-making locally. Specimens of the grass and of the paper made from it can be seen at the Imperial Institute.—M.

### CANADIAN EXPORT OF PAPER

Some interesting facts are to be found in a report recently published in a Canadian contemporary, showing at what an enormous rate the export of paper from Canada has increased within the past twenty-four years. The first shipment of paper was made in 1892 and was valued at \$91; last year Canada exported over \$15,000,000 worth, while in the three months of this year, \$4,600,000 worth or \$1,000,000 more than for the corresponding months of 1915 has been sent abroad and it is expected that the exports of this year will reach the large figure of \$20,000,000.—M.

### SULFITE RESIDUE AS FUEL

Much interest is attached, says the *Chem. Trade Journal*, to the invention of Mr. R. W. Strehlenert, a Swede, of sulfite coal from the residue of sulfite wood pulp. A company has been formed in Norway to exploit the invention with a capital of \$450,000. The residue from sulfite manufacture is large, as the paper pulp accounts for only 45 per cent of the original weight of wood. The balance is neglected, except for what is used in sulfite spirit manufacture. For this purpose only about 15 per cent is accounted for, so that more than 50 per cent of the total weight of wood remains unused. In the Strehlenert process, the product is a coal or coal powder with a heating value of 12,400 B. t. u. per lb. It has been calculated that the production of cellulose in Sweden and Norway amounts to about 1,000,000 tons per annum of which three-quarters comes from Sweden and one-quarter from Norway. The first works are being commenced at Greaker, between Sargsborg and Frederikstad, with an initial capacity of some 6,000 tons per annum. The quantity of coal which the Greaker Cellulose Works use in the year.—M.

### PAPER-SIZING

The *Paper-Maker*, 52 (1916), 233, quoting from the *Chemiker Zeitung*, says that sodium bisulfate has been proposed as a partial substitute for aluminum sulfate in the sizing of paper but, while the impure by-products of the bisulfate are suitable for the sizing of the lower grades of paper, it is considered that only purified salts should be used for the finer grades. The most economical and convenient method of employing pure bisulfate is to prepare a solution as required by the addition of sulfuric acid to a solution of pure normal sodium sulfate which is less costly than the pure bisulfate and keeps better on storage. In sizing the paper, sodium bisulfate or aluminum sulfate should be added before the rosin size in order to acidify the pulp and to inhibit the action of the saline constituents of the water and fiber upon the dilute size-milk. An equally favorable result is obtained whether the whole or only a portion of the bisulfate or aluminum sulfate solution be added before the rosin size, but, if the rosin size be added first, as is the custom in many cases, the economical effect is not realized.—M.

### FIQUE-FIBER

The value of fique, *Nature*, 98 (1916), 55, the fiber of *Furcraea gigantea*, found in Colombia, is emphasized in a short article by Mr. M. T. Dawe, Director of Agriculture of Colombia. It is used for the soles of the natives' shoes or alpargatas, sacks, girths, ropes, matting and even for roofing of the houses. For the latter purpose, the green leaves are used. The article is illustrated by a photograph showing a cottage thatched with the leaves of fique. Hand-prepared fiber is sold in Bogotá market at 12 c. per lb. but, by using modern machinery, a profit of \$95 per ton might be readily expected if fiber sold at its present wholesale price of \$160 per ton. If the substance were exported and the selling price remained \$125 to \$150 per ton, a profit of \$25 to \$50 per ton should be realized.—M.

### NEW HYDRO-ELECTRIC WORK IN NORWAY

The Bremanger Power Company has decided to exploit the Svelgvassdrag falls at Bremanger which will have a capacity of 21,000 turbine horse-power. It is proposed to erect a factory for the manufacture of carbide and cyanamide with a production of 30,000 tons of carbide per annum, one-third of which will be used in the manufacture of cyanamide. There is also some thought of taking up the manufacture of ferro-silicon. The whole installation is likely to be taken in hand at one time. The share capital proposed will be \$950,000 in addition to which a loan of \$1,000,000 has been provisionally arranged.—M.

### FINE CHEMICAL MANUFACTURE IN AUSTRALIA

From a report sent by the Sydney Office of H. M. Trade Commissioner in Australia, it appears that the Government Laboratory attached to the State Railway Department in Victoria, has, for some time past, been carrying out experiments with a view to the manufacture of the necessary supplies of certain chemicals used in photography, which had formerly been obtained entirely from Germany. Among these substances are pyrogallol and amidol. A perfectly satisfactory pyrogallol has been produced in the laboratory in commercial quantities and, at a price, less than half the present market price. The substance, which is being prepared for the first time in Australia, is at present being used in the Railway Department with highly satisfactory results. Greater difficulties, however, were experienced in the manufacture of amidol as the process was in the hands of a German firm and was held a profound secret. It is stated that the difficulties have now been overcome and that the Australian-made amidol is quite equal to the German article in quality. It is being produced at a cost of one-half the current market price.—M.

### PALM PRODUCTS OF SIERRA LEONE

According to a report by the Colonial Secretary, the total quantity of palm kernels exported from Sierra Leone in 1915 amounted to 39,624 tons, valued at \$2,520,132, an increase in weight of 3,709 tons and a decrease in value of \$276,400 as compared with the figures for 1914. A noticeable point is the decrease in market value of this product. The price in Europe at one time fell as low as \$62 per ton whereas in 1914 it never fell below \$80 nor below \$105 per ton in 1913. Towards the end of the year prices increased and reached \$95 per ton in December, 1915. In 1913, Germany secured 43,016 tons of this product out of a total of 49,201 tons exported but, in 1915, the whole quantity went to the United Kingdom. Throughout the year the prices for palm oil were well maintained on the European market and increases were shown both in the quantity and value of oils. The volume of exported oil was 481,576 gals. valued at \$228,355 as compared with 436,144 gals. valued at \$192,685 in 1914. Of the total quantity exported, the United Kingdom received 384,006 gals., while 89,869 gals. went to France. In 1913, out of a total of 617,089 gals., 509,688 gals. went to United Kingdom, 69,786 gals. to Germany and none to France.—M.

### ANTIMONY DISCOVERY IN IRELAND

According to a report in a contemporary, antimony has just been discovered in County Monaghan, Ireland. The new mine is said to be a rich one and is situated four miles from Keady. Samples of the ore have been submitted to experts who state that it contains, on analysis, 80 per cent antimony, 10 per cent ammonium sulfate, 10 per cent pyrites and other materials. The mine has been tested in three places for about 100 yards and, in each place, signs of true lodes were shown.—M.

### CHLORATE MANUFACTURE IN JAPAN

From recent reports, it would seem that, since the war began, the potassium chlorate manufacture trade has developed considerably in Japan. At the present time, there are about 33 factories with a total monthly output of 7,000 bbls. The Nihon Kagaku Kokyo Kaisha heads the list with 3,000 bbls. per month. In normal times, the consumption is about 7,000 bbls., but, under prevailing circumstances, it is not expected that more than 6,000 bbls. will be used, thus leaving an excess in supply over demand of something like 1,000 bbls. per month. It seems that chlorate factories are still making extensions and, when these reach completion, it is thought that the output of chlorate of potash will exceed 10,000 bbls. per month.—M.

### AUSTRALIAN SMELTERS' WORKS

According to reports in the Australian press, the Associated Smelters will possess the largest works of their kind in the world, with a capacity to produce 140,000 tons to 150,000 tons of lead per annum. Upon this basis, the Company will be able to treat up to 250,000 tons 60 per cent leady-concentrates a year. With a view to eventualities, the nominal capital of the Associated Smelters' Proprietary, Ltd., was lately increased from £750,000 (\$3,750,000) to £1,000,000 (\$5,000,000). The issue of shares or stocks has, however, not yet been made. The present holders of interests, says the *Mining Journal*, are Broken Hill Proprietary \$1,000,000, North Broken Hill \$1,000,000, Broken Hill South \$1,000,000, and Zinc Corporation \$500,000, while \$250,000 in \$5 shares is in reserve. Steady progress is said to be going on in expanding and improving the Associated Smelters at Port Pirie, one of the alterations to attain increased economy in operating being the complete electrification of the works upon lines which will enable the various plants for supplying motive power to be operated from a central station.—M.

### GLASS MANUFACTURE IN ENGLAND

Since the appointment of the Glass Research Committee of the Institute of Chemistry in October, 1914, says the *Times Engineering Supplement*, No. 502 (136), Professor Jackson and Dr. Merton have reported 33 formulas for glasses of various kinds. Of these, 14, including soft glass for ordinary chemical laboratory ware, resistant glass, glass for combustion tubing, miners' lamp glasses, and lead glass suitable as an enamel for sealing platinum into soft glass, were the result of the first year's work. The remaining 19 have been prepared since October, 1915, the work having been assisted by grants from the Advisory Council on Scientific and Industrial Research. These latter include thermometer glass for high and ordinary temperatures; leadless opal glass suitable for working with certain thermometer glasses to form the enamel backing; opal glass that does not lose its opal character on repeated working in the blow-pipe flame; glasses having the same properties as "Fluor Glass;" glasses similar in properties to "Prism Crown" and "Heavy Flint;" glasses suitable for making the "shell," veins and lenses of artificial eyes; glasses for use in manufacture of electric lamps; an enamel glass suitable for sealing in various metallic wires including copper, iron, and nickel and which makes a satisfactory joint with soft soda glasses and with many lead glasses; lead glass of high density such as is required for X-ray shields. These formulas are being now used by British firms and examples of their products are to be seen at the house of the Institute in Russell-Square, London. An inquiry is also being made with regard to the clay used for making the pots employed in the manufacture of optical and chemical glass.—M.

### RUSSIAN ULTRAMARINE

About the middle of 1914 (*Oil and Color Trade Journal*) an ultramarine factory was established in South Russia. The article had previously been imported from abroad and partly furnished by factories in the north of the country. At present ultramarine is offered in exceedingly reduced quantities in consequence of which the price has risen considerably. This circumstance, as well as the proximity of Mariopol on the Eka terminsk Railway, where there are deposits of a fine quality of kaolin, which constitutes the principal raw material for the production of ultramarine, has induced one of the local contractors, who control the kaolin deposits, to set up an ultramarine factory at Mariopol. At first, the productivity of the new factory is being set on a modest basis, namely, 1000 poods per annum. The kaolin, which it is hoped to use in the new factory for the production of the article, has lately found a good market for the manufacture of porcelain in Moscow and other districts.—M.



## MINERAL WEALTH OF BRITISH COLUMBIA

Interesting information regarding the mineral wealth of British Columbia is found in the annual report issued by the Ministry of Mines of the province for the year ending December 31, 1915. Statistics are also given of the output of various minerals over a period of years ending with 1915. The following list gives the yields for last year.

Gold (placer).....	38,500 oz.	\$ 770,000
Gold (lode).....	250,021 oz.	5,167,934
Silver.....	3,366,806 oz.	1,588,991
Lead.....	46,503,590 lbs.	1,939,200
Copper.....	56,918,405 lbs.	9,835,500
Zinc.....	12,982,440 lbs.	1,460,524
Coal.....	1,611,129 tons	8,638,952
Coke.....	245,871 tons	1,475,226
Miscellaneous Products.....		1,571,181
		\$29,447,508

The report states that no marked advancement has been made with a view to making use of the numerous deposits of iron ore, which are distributed throughout the province. At the present time, there does not seem to be a market in the province for iron ore and, consequently, little development work has been done although it is a well known fact that a number of iron ore deposits exist in different districts, which are of considerable size and, as a rule, very free from injurious elements.—M.

## COCONUT TRADE IN FIJI ISLANDS

The area under coconuts cultivated by Europeans was estimated at 45,102 acres in 1915 as against 42,402 acres in 1914, the respective values of copra exported being \$1,169,795 and \$741,860, and the weight for 1915, 15,238 tons. The cultivation of coconuts continues to increase although the extraordinary conditions, which have prevailed during the year, have unsettled and restricted the copra market. Throughout the year, experiments were conducted at Laucala by the Department of Agriculture, with a view to improving the condition of coconut trees. A decided benefit has followed the cultivation of the trees and the application of manure. It has been arranged to extend these experiments by planting plots of trees at various places on the coast and carefully selected seednuts have been collected and distributed.—M.

## CANADIAN BEET CROP

It is estimated by the Canadian census and statistics office at Ottawa that in 1915, 18,000 acres were devoted to the cultivation of sugar beet roots in Canada, all in the province of Ontario, for the manufacture of beet sugar as compared with 12,000 acres in 1914. The total estimated yield of roots in 1915 was 141,000 tons as compared with 108,600 tons in 1914, the average yield per acre being 7.83 tons as compared with 8.98 in 1914. The production of refined sugar made from Canadian beets grown in 1915 was 36,838,267 lbs. as compared with 27,345,248 lbs. in 1914 and 23,964,272 lbs. in 1913.—M.

## BRITISH MADE THYMOL

According to the *Oil and Color Trade Journal* (Vol. 50, No. 925), thymol is being manufactured in England from the oil of red thyme, distilled in Spain. The quality is said to be fully up to the standard of German-made thymol and a specimen crystal has been preserved, weighing nearly an ounce and a half and measuring 2 1/4 in. by 1 1/4 in. by 1 1/4 in.—M.

## GRAPHITE DISCOVERED IN GREENLAND

A valuable vein of graphite is reported by the Board of Trade Journal to have been discovered at Anisok in Greenland and is now being worked. The last vessel arriving at Copenhagen from Greenland brought 800 tons of graphite. A factory for the utilization of graphite has been erected in Denmark.—M.

## RADIUM PRODUCTION IN BOHEMIA

During 1915, 25,720 lbs. of uranite prepared for smelting from the uranium ore, were produced in Bohemia. Of the different compounds of uranium, 2,325 lbs. of an average value of £50 (\$2500) per 100 lbs. were produced in the Government mine in Joachimsthal. The factory for radium compounds, which is under the government, prepared compounds containing 1.754 g. of radium elements having a total value of \$200,000. It is interesting to note that 0.879 g. more radium was produced in 1915 than in the previous year.—M.

## SANDAL WOOD OIL

The scarcity of this oil continues and is being accentuated by inquiries for large quantities coming in from France and Russia. For the latter, an order for 2000 lbs. is in the hands of agents but cannot be filled as no dealer has that quantity free on the spot. Oil in original distillers' packages is worth \$7 to \$8 and small quantities of indifferent quality are offered at \$7.—M.

## BOARD OF TRADE

During the month of August, the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles:

Agates	Hinges
Asbestos thread	Lamps, petroleum
Asphalt	Leather-board, cheap
Asphalt lac	Locks
Bags, suitable for holding a hard paste	Looms, for weaving canvas for balata beltings
Casks, for holding cement	MACHINERY:
CELLULOID ARTICLES:	Glass graduating machines
Dolls and Combs	Portable ice-making machines
CHEMICALS:	Automatic, for making cup and square hooks
Selenate of sodium	Baling-presses
Sulfate of iron	For button making
CUTLERY:	Plant, for distilling carboniferous shale
Cheap knives, razors and scissors	For oiling silk for surgical purposes
ELECTRICAL APPARATUS:	Winnowing machines
Plated metal fronts for hand lamps	Milk-powder
Foliage and grasses, dried	Oil for soap manufacture
GLASS AND GLASSWARE:	Oils, white, oleine
Lamp chimneys	Pens, fountain
Phials, 1, 2, 4 dram	Pitch, sulfite cellulose
Tumblers	Pots and pans of pure nickel sheet
Glue, fish, similar to German brand at \$7.50 per cwt.	Seaweed, dried
Gutta-percha composition, thin sheet	Slate pencils
	Studs, wire lever
	Typewriter ribbons

During the month of September, the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles:

Beads, for necklets	Jars, glass or earthenware for shipping chloride of lime
Blinds, green paper, for windows	Laces, boot and shoe, cotton
Bottles, champagne	MACHINERY AND PLANT:
Brushes, painting and sweeping	Embroidery machines
Brushes, wire for cleaning gloves	Machines for filling tins with powder and automatically weighing same
Bulbs, for electric lamps	Match-making machines
Buckets, papier maché, for electrical power station	Strawboard tube-making plant
Buttons, small fancy	Tooth-paste making machines
Canvas, artists'	Glass engraving machines
Charcoal iron sheets	Salt crushers and evaporators
Celluloid, clear, transparent in sheets about 55 1/4" by 24 1/4", thickness 25/1000, 30/1000 or 35/1000	Mouldings, picture frame
Cerium iron stones for automatic lighters	Nickel, sheets, pure
CHEMICALS:	Needles, knitting machine
Antimony pentachloride	Pins, safety
Antimony trichloride	Press-buttons
Tin oxide, white	Quartz, ground
Tartaric acid	Rims, foundation for solid rubber tires
Clocks	Sand, fine, siliceous to pass 150 to 200 mesh
Cooking utensils, earthenware, fire-proof	Scissors, tailors', cutting out
ELECTRICAL APPARATUS:	Sewing-machine parts
Smoothing irons for boot uppers	Soldering-paste
Stearite insulators	Strips, iron, suitable for hooping
Glass chimneys, jugs, tumblers	Thermometers, veterinary
Glass for thermometers	Tin-foil, thin
Gum bottles, bell-shaped	Tortoise-shell substitute

Firms which may be able to supply information regarding these articles are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall St., London, E. C.—M.

## SCIENTIFIC SOCIETIES

### DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS—MINUTES OF BUSINESS SESSIONS 53RD MEETING A. C. S.

The Division of Industrial Chemists and Chemical Engineers of the American Chemical Society met in Schermerhorn Hall at Columbia University on the 27th, 28th and 29th of September, 1916.

The meeting was called to order by the Chairman, Dr. H. E. Howe.

The minutes of the Urbana meeting were read by the secretary and approved by the Division.

The secretary had to report that Mr. R. J. Quinn of Morris & Co. has been appointed a member of the Committee on the Analysis of Oils and Fats in place of Mr. A. Lowenstein, resigned; also that the following members have been appointed a Committee on the Analysis and Specifications of Cotton Seed Products, which committee was authorized at the Urbana meeting: Thomas C. Law, Atlanta, Ga., *Chairman*; Archibald Campbell, St. Bernard, Ohio; and F. N. Smalley, Savannah, Ga.

The Division having had the required two weeks' notice of the proposal to amend Article IV of the By-Laws, the matter was brought up for disposal. The By-Law in question reads as follows:

"The Chairman shall with the advice and approval of the Executive Committee appoint from time to time standing committees of the Division to consider, conduct and report upon such special matters as may be delegated to them. The following committees shall be appointed at the annual meeting or as soon thereafter as may be expedient: (1) Committee on Definition of Trade Terms, (2) Committee on Trade Customs, (3) Committee on Official Specifications, (4) Committee on Research Problems, (5) Committee on Standard Methods, (6) Committee on Descriptive Bibliographies, (7) Committee on Advertising."

The Secretary explained that as some of the committees had never done any work and inasmuch as it had been found that some of the committees could do nothing along the lines laid down, the Executive Committee had decided that it was useless to reappoint continually these committees and as a consequence, the Division had voted at the Urbana meeting to bring the matter of amendment before the Division at the New York meeting. Consequently it is desired to amend the above Article to read as follows:

"The Chairman shall, with the advice and approval of the Executive Committee, appoint from time to time standing committees of the Division to consider, conduct and report upon such special matters as may be delegated to them."

There being no discussion the Chairman put the question and the Division voted to amend the article in the above manner.

The Chairman appointed the following members to constitute a Nominating Committee: Wm. Brady, *Chairman*; Chas. E. Coates and H. H. Tozier.

This committee, during the Friday session, brought in the following nominations: H. E. Howe, *Chairman*; R. F. Bacon, *Vice-Chairman*; S. H. Salisbury, Jr., *Secretary*. *Executive Committee*: M. C. Whitbrand, W. F. Hillebrand, C. H. Herty, H. K. Benson, J. R. Withrow and S. W. Parr. It was moved and seconded that the nominations be closed. Motion carried. It was moved and seconded that the secretary cast the ballot for the nominees. Motion carried. The chairman then declared the above nominees elected officers of the Division for 1917.

At this meeting the Division carried into effect the suggestions of the Executive Committee that

1—Every title sent in for the Divisional Program should be accompanied by an abstract, otherwise the title would not be printed on the program.

2—All titles and abstracts should pass through the hands of a committee before being programmed.

3—A paper should be limited to five minutes unless other arrangements were made with the Secretary.

This arrangement was found to be very satisfactory and it was the consensus of opinion of the Division that it should be adhered to in the future, the further suggestion being made that the papers themselves should be sent in to a proper committee and passed on before allowing the titles to appear on the program. The ideas of the members of the Division are desired on this point and these as well as any other suggestions tending toward making the meetings more interesting should be sent to the Secretary. It was further suggested that the Division should try to have more papers of an engineering nature presented at the meetings, as might well be expected from the name of the Division.

A report of the work of the Committee on the Analysis of Oils and Fats was presented to the Division. This was tabled for the time being.

The Executive Committee had no report to make to the Division and the remainder of the sessions was taken up with the reading of the papers which appeared in the official program

LEHIGH UNIVERSITY  
SOUTH BETHLEHEM, PA.  
October 4, 1916

SAMUEL H. SALISBURY, JR.,  
*Secretary*

### REPORT OF COMMITTEE ON FERTILIZER LEGISLATION FERTILIZER DIVISION AMERICAN CHEMICAL SOCIETY NEW YORK CITY SEPTEMBER 27, 1916

Your Committee has not much to report concerning legislation which has been enacted since the last meeting of the Division. On Sept. 1st an entirely new fertilizer law went into effect in Louisiana. With this exception there has been no legislation in any state which makes a complete revision of previous enactments.

Owing to the potash situation, some of the states enacted special legislation for relief of the manufacturers, which applies to the question of grades and guarantees. In other states, this question is handled by the fertilizer control officials. In the Northern states comparatively little legislation has been proposed in recent years; the tendency seems to be to adjust matters through Department regulations, rather than through statutes, and this plan is quite satisfactory inasmuch as the present laws are ample to protect both producer and consumer and we at least have the advantage of being able to discuss the matter with men who are competent from a technical standpoint, rather than with some well meaning, but ill-informed members of the legislature.

In the Southern states, the situation is somewhat different. The existing laws are adequate to meet all conditions and the agricultural departments, as a rule, are satisfied with the present regulations, but in some of the states there is hardly a session of the legislature in which there are not one or more fertilizer bills introduced. It is believed that this results largely from a desire of some of the overzealous rural representatives to do something which will appear to benefit their constituents. This is an unfortunate situation as the continual agitation and changes in laws cause a great deal of trouble and expense to the manufacturers. This condition of affairs emphasizes the desirability of a uniform fertilizer law which will be operative in all the states. This question, as you know, has been discussed by this and other organizations, and while it might be possible to formulate a law which would be acceptable to the manufacturers and agricultural departments, under the existing conditions, it



would be almost impossible to get such a law adopted in all the states. Unless the officials of the agricultural departments can control this class of legislation and furthermore, will exercise their authority regardless of political conditions, there is no hope of maintaining a uniform system of fertilizer control. Even with existing laws, there could be a standardization of the regulations agreed upon by the state officials, which would undoubtedly prove of considerable advantage to manufacturers. The question of uniform laws is of so much importance to the manufacturers that we should do everything we can to attain this end.

In previous reports we have referred to legislation which dis criminate against certain ammoniates which are known to have a definite value, even though this status be denied to them by the present empirical methods of testing for availability of organic nitrogen. Furthermore, the methods of stating the results of analysis in some states are very misleading as to the quality of the nitrogen which has been used. Many of the sources of organic nitrogen, which were formerly used for fertilizers are now utilized for other purposes and unless fertilizer manufacturers can utilize all such sources as are known to be valuable, or can be made so by chemical processes, the prices of organic ammoniates will get so high as to prohibit their use. There is a large demand for nitrogen from organic sources and it is the desire of the manufacturers to meet this demand, but such materials cannot be employed at a cost at which they cannot be profitably used by the consumer.

It has been the custom of some of the state departments to assume that samples taken by consumers are on a par with those taken by officials designated for the purpose. This procedure is manifestly unjust to the manufacturer, even though the samples are taken in the presence of witnesses. The average person, while he may have honest intentions, has no conception of the proper method of drawing a sample which will correctly represent the goods sampled. If a consumer desires to have a special analysis made of fertilizer which he has purchased and the department considers that there is good and sufficient reason why such an analysis should be made, an official inspector should be designated to draw the sample and under no other circumstances should the state departments test samples of manufactured fertilizers received from consumers. This whole question of sampling is of great importance and there should be some standard regulations adopted in the different states which will insure uniformity and accuracy in methods employed.

There is a tendency in some localities to impose unnecessary burdens on the manufacturer by requiring him to furnish information concerning his business and to comply with other regulations which can be of no possible use to the consumer, but serves to confuse and complicate the business in its relations to the trade and causes unnecessary trouble to the fertilizer control officials in carrying out their inspection work.

Fertilizer laws should embody only such requirements as are necessary to safeguard the interests of both consumer and manufacturer without imposing unnecessary hardships.

If this Division can formulate a law which will meet these requirements and have it adopted in all the states, it will have done a great service to the fertilizer industry.

F. B. CARPENTER, *Chairman*,  
H. A. HUSTON, J. E. BRECKENRIDGE, } *Committee on Fertilizer*  
H. J. WHEELER, PAUL RUDNICK, } *Legislation*

#### AMERICAN MINING CONGRESS

The 19th Annual Session of the American Mining Congress will be held at Hotel LaSalle, Chicago, during the week of November 13th.

The entire 17th floor of Hotel LaSalle will be set apart for exhibits, and the entire 19th floor of the hotel has been set apart for meeting rooms.

On Monday night Mr. Edward L. Doheny, of Los Angeles, will show a moving picture of the great Mexican oil gusher, Cerro Azul, and Dr. Henry Mace Payne will give an illustrated lecture on "Mining Frozen Gravels of Alaska and Siberia." The slides will portray features of mining in the far North which have never before been shown.

Mr. H. L. Ameling, of St. Louis, will deliver a lecture illustrated by moving pictures on the use of the core drill.

On Wednesday night there will be a smoker, and on Thursday evening the annual banquet will be held in the magnificent banquet hall of the hotel.

The opening addresses of welcome of Governor Edward F. Dunne, of Illinois; Mayor W. H. Thompson, of Chicago; and President J. W. O'Leary, of the Chicago Association of Commerce, will be responded to by representatives of every oil and mining State in the Union. These responses will not be the ordinary impromptu kind but in every instance a carefully prepared three-minute resolution embracing the State's most important mining issue, formulated to aid the Resolutions Committees in framing legislative demands which synthesize the needs of the mining sections of the country.

At the general meeting Tuesday, November 14th, the subject will be "Safety." Mr. Van H. Manning, director of the U. S. Bureau of Mines, will give an address on "The Past and the Future of Mine Safety Work."

At the general meeting, Wednesday, the topic will be "Efficiency in Mining Operation." Colonel George Pope, of Hartford, Conn., president of the National Manufacturers' Association, will speak on "Organized Capital and Organized Labor and Their Relation to Efficiency, Conservation, Better Wages, Better Living Conditions, Lawlessness, Strike Disorders and Industrial Freedom."

Hon. N. N. Hurley, chairman of the Federal Trade Commission, will speak on the subject of "The Federal Trade Commission and the Mining Industry." It is this commission which, through Mr. Hurley, established a uniform system of cost accounting for the coal industry, and he will present for consideration his ideas of needed legislation as developed in the course of the commission's investigation. Mr. Charles M. Moderwell, of Chicago, will present the report of the Committee on Relations with the Federal Trade Commission.

On Thursday the subject will be "Conservation." Mr. Jennings, of Washington, D. C., will speak on "The Accomplishment of Invention and Its Relation to Labor and Capital."

On Friday the local Reception Committee have arranged an excursion to Gary, where inspection will be made under the guidance of the Steel Company's experts.

Special topics will be taken up by the various Sections, as follows: Zinc and Lead, Precious Metals, Oil, and Coal.

#### FIFTH ANNUAL SAFETY CONGRESS NATIONAL SAFETY COUNCIL

The Fifth Annual Safety Congress met at the Statler Hotel, Detroit, Mich., on October 16 to 20, 1916. The various Sectional Meetings were: Chemical, Foundry, Iron and Steel, Mining, Public Utilities, Steam Railroad, Health Service, Electric Railway, Paper and Pulp Manufacturers, Textile, Cement, Employees' Benefit Association, Governmental Public Safety, and Logging, Lumbering and Woodworking.

The addresses presented at the Chemical Sectional Meeting were as follows:

Health Problems in the Chemical Industry. Dr. GEORGE M. PRICE, Director, Joint Board of Sanitary Control, New York City.

The Goggle Problem in the Chemical Industry. J. R. DE LA TORRE BUENO, Editor, General Chemical Bulletin, General Chemical Co., New York City.

Care of Workmen Employed in the Manufacture of Aniline and Benzol Products. A. B. MITCHELL, Benzol Products Co., Marcus Hook, Pa.  
Fume Poisoning from Nitric and Mixed Acids. L. A. DE BLOIS, Engineering Dept., Safety Division, E. I. du Pont de Nemours & Co., Wilmington, Del.

These addresses will be printed in full in our next issue.

## NOTES AND CORRESPONDENCE

### EFFICIENCY OF AIR DRYERS

*Editor of the Journal of Industrial and Engineering Chemistry:*

In his letter of Aug. 17th [THIS JOURNAL, 8 (1916), 853], Prof. Lewis takes exception to my statement that the consumption of heat in an air dryer is definite and that practically 1120 B. t. u. are required to evaporate 1 lb. of water. "In order to convince me of my error" he proceeds to describe an ideal dryer capable of evaporating 1 lb. of water with a considerably smaller expenditure of heat than I postulated.

Before examining the workings of this machine, let me say that as far as convincing me of error is concerned, the whole matter is quite beside the mark. I did *not* say this was the requirement "under even the most ideal conditions," the phrase in quotation marks being Prof. Lewis' and not mine. I believe that a careful perusal of my letter of June 24th will make it perfectly clear that in stating the heat consumption at 1120 B. t. u. I referred solely to single effect apparatus. Moreover, I specifically stated that it requires "practically" this amount and that I spoke in round (approximate) numbers.

I cannot understand how the performance of an ideal, multiple-effect apparatus as described, has any relation to my figures as to the requirements of a practical single-effect machine and I am somewhat surprised that such an illustration should have been presented to convict me of error, the more so as Prof. Lewis himself appeared to recognize in a later paragraph of his letter that I was discussing solely single-effect apparatus and admits that he has to invoke the aid of multiple-effect to show that I was mistaken. Certainly, I have not at any time questioned or failed to recognize the larger possibilities of heat utilization in multiple-effect apparatus.

It will be seen, therefore, that I was not "mistaken" in my original statement, which is substantially correct in the form and in the relation in which it was made.

But while Prof. Lewis' ideal double-effect dryer quite fails in its purpose of either convicting or convincing me of error, it is intensely interesting in other ways and well worthy of a little further analysis.

The expenditure of heat for evaporation in this ideal dryer is calculated by Mr. Lewis as 1104 B. t. u. per lb. of water as regards the first part of the machine—that is to say, as long as it is operating single-effect. This figure, correct for the temperature limits assumed, is the only one that can properly be compared with my approximate figure, and, of course, is in substantial agreement with it. It is 1.5 per cent less than the quantity I stated as a "round number" and without defining the temperature limits.

The first assumption regarding the ideal dryer is "a material that may be dried at temperature of 160° without injury." It is then specified that the air *leaving* the dryer has a temperature of 160°, a dew point of 140° and carries 0.1514 lb. water per lb. of dry air. In order to accomplish this result each pound of air passing through the dryer has to evaporate 0.1462 lbs. water (0.1514 - 0.0052). To do this the air must give up  $0.1462 \times 1102 = 161.2$  B. t. u. This quantity of heat is capable of heating the 1 lb. of air  $162 / 0.2373 = 683^\circ$ , and as the air is to leave the dryer at a temperature of 160°, it must enter at a temperature of  $160 + 683 = 843^\circ$ . This temperature is well above the melting point of zinc.

It is proper to say that while the required amount of heat would result in this high initial temperature, if supplied at one time, it is nevertheless conceivable that no such high temperature need obtain if the heat is supplied in small increments. Indeed, in order to comply with the stipulated requirements of our ideal machine (not to exceed 160°), it would be abso-

lutely necessary to supply the heat in differential increments. The method of supplying heat in increments is indeed practiced in certain forms of drying apparatus, usually by re-circulation of the air, and to some extent makes possible the use of a high discharge temperature, with a corresponding economy in heat, without necessitating an inconvenient, or in many cases impossible, initial temperature.

It is stated that "it is theoretically possible to reduce the heat consumption \* \* \* to 1102 B. t. u. per lb. of water evaporated." This is literally correct as expressing the heat used in evaporation, but it must not be overlooked that a further expenditure of heat is necessary to raise the temperature of the air from 50° to 60°. As 1 lb. of air is to carry off 0.1462 lb. water, each pound of water requires 6.8 lbs. of air, which must be heated from the inlet temperature of 50° to the discharge temperature of 160° and requires  $110 \times 6.8 \times 0.2373 = 177$  B. t. u.

Considering the second dryer, I think we shall find that Prof. Lewis' figures on this are not entirely correct. He states: "It is therefore possible in this dryer to evaporate 0.1223 lb. of water per lb. of dry air." This statement is at the least elliptical, for under the specified conditions 1 lb. of the air supplied to the second dryer (at 90°) could not possibly evaporate this much water. To do so the air must give up 132 B. t. u., or would have to cool to absolute zero. Doubtless what was intended to be conveyed was that the heat recovered from 1 lb. of the discharge of the first dryer would evaporate this much water. This heat (132.3 B. t. u.) would, by assumption, be distributed in 13.8 lbs. of air; that is to say, the 132.3 units recovered from the first dryer would heat 13.8 lbs. air from 50° to 90°, or, in other words, 13.8 lbs. air in the second dryer is the equivalent of 1 lb. discharged from the first.

Now in order to perform the evaporation postulated by Prof. Lewis, it is manifest that this air must be cooled to 50°; *i. e.*, it must give up all the heat supplied to it. But long before this occurs the air would be completely saturated, and it is therefore impossible that the entire 132 units recovered in the first effect could be utilized in evaporation in the second effect as assumed by Prof. Lewis. To give the complete figures, in order to give up 132.3 B. t. u., 13.8 lbs. of air must cool at 40° or to a temperature of 50°. If completely saturated at 50° the 13.8 lbs. of air can contain  $13.8 \times 0.0075697 = 0.10446$  lb. of water. But by hypothesis, the 13.8 lbs. of air start with a content of  $13.8 \times 0.0052 = 0.07176$  lb. water and consequently can absorb only  $0.10446 - 0.07176 = 0.0327$  lb. instead of the 0.1223 lb. predicted by Prof. Lewis.

The maximum possible result would be obtained by a discharge temperature for the second dryer of approximately 63°, that is cooling the air 27°, under which conditions it would give up for evaporation 89.3 B. t. u., theoretically capable of evaporating 0.0844 lb. instead of Prof. Lewis' 0.1223 lb. The discharged air would then leave the machine completely saturated.

In his reference to the discussion of 1910, Prof. Lewis makes some remarks that I believe are not warranted by the record. In that discussion I did not at all question the published figures, but only the use of the word "efficiency" as deduced from those figures. In the original report Mr. Ruggles quite correctly stated the heat necessary to evaporate the water, using, by the way, the figure of 1122 B. t. u. per lb., which is practically the same which I am so grievously mistaken in using.

The thing I questioned was the propriety of *crediting* the machine with the large amount of heat carried off in the dried material. In the report in question this entirely wasted heat



is made to contribute to the "efficiency" of the dryer. My sole contention was that the efficiency of a drying machine was in no way a function of its capacity for heating said. I did indeed point out that the published figures required that about 33 per cent of the discharged water must be in the form of mist or liquid water, and I said, "if this is possible it opens up a way to extraordinary possibilities in drying economies." This does not appear to me to differ from Prof. Lewis' attitude of "unlikely but not impossible."

The theory of re-condensation and fog formation has been advanced a number of times. I agree absolutely with Prof. Lewis about it, that it is by no means impossible, but is unlikely, and that the conditions under which it can occur are unusual. Personally, in a limited experience, I have not come across an instance where any large supersaturation could be positively demonstrated, even under conditions favorable to it.

In conclusion as to the dryer question, I hold no special brief for the retention of the word efficiency in connection with the performance of these machines although to me personally it is a very useful tool. It is very much easier for me, for instance, to think of a turbine as a more efficient machine than a water wheel, than it is to remember their respective outputs of power per unit of energy supplied. Very likely this is largely a mental habit only, but the consideration of machines on their efficiency expressed as a percentage of an ideal duty is pretty strongly rooted as a custom.

Neither am I deeply concerned as to whether air drying and evaporation are treated separately or as one subject. Prof. Lewis feels very strongly about this, so by all means let us treat them as one. Frankly it appears to me quite too trivial to develop any strength of feeling about. My suggestion to treat them separately was largely in the interests of convenience and expediency. Take only the matter of indexing. Prof. Lewis' original letter setting forth the theoretical possibilities of multiple evaporation contains very much of interest, but the student of the subject will seek it in vain under the heading of "evaporation" and will be indeed fortunate if he searches under the caption of "air dryers" for matter relating to vacuum, multiple-effect evaporators.

I appreciate Prof. Lewis' elucidation of the point that I was unable to understand about the evaporation of saline solutions. Of course, if the vapor temperature is the same as that of the boiling solution the difficulty disappears. As Prof. Lewis says, my understanding was that the temperature of the vapor is that of the pure solvent. This is stated to be the case by very many authorities, including Rankine, Box, and many others, and I supposed was an accepted and established law. I have happened on only one authority to the contrary, namely Mendeléeff, who states that the temperature of the vapor is the same as that of the solution from which it is generated. He proceeds to give the boiling temperatures of several solutions of salts and rather curiously adds, "if the temperature of ebullition be determined by immersing the thermometer in the liquid itself," \* \* \* This qualifying phrase appears to indicate that a correct thermometric indication cannot be obtained at all in the vapor.

I was so much interested in the divergent statements of authorities on this point that I endeavored to satisfy myself by a very crude experiment. I took a solution of caustic soda, boiling approximately at 120° C., in a large flask, starting with the thermometer bulb immersed in the liquid. When very actively boiling and with the thermometer practically stationary, I raised the bulb just clear of the liquid, when the temperature instantly dropped about 12°, and then remained fairly steady. In this case the thermometer bulb was at a temperature of 120° and the drop could hardly be due to condensation, and was in the center of the flask having a surrounding jacket of vapor of about 3 in. on all sides.

I then withdrew the thermometer and wiped the bulb clean of caustic soda solution and immediately replaced it in the vapor, when the indication was 100°, very slowly rising to about 110°. The 100° mark was reached almost instantly, while the subsequent rise to 110° was very slow, requiring many minutes. The same result was obtained by rapidly washing off the thermometer with boiling water and plunging into the vapor while still hot, so as to eliminate as far as possible condensation on a cold bulb. Again the temperature of 100° was reached, almost instantly followed by a very slow rise as before.

It will be observed: (1) that the clean bulb (free from the solution) in all cases indicated 100° in the vapor at first and that the subsequent very slow rise was coincident with the deposition of the boiling solution on the bulb, from the bombardment from the actively boiling surface; (2) in no case could a reading be obtained anywhere near the boiling point of the liquid, but a condition of equilibrium occurs about midway between the temperature of ebullition and 100°.

BAYONNE, NEW JERSEY  
September 10, 1916

W. E. WADMAN

## ANALYSIS AND MANUFACTURE OF RED LEAD

*Editor of the Journal of Industrial and Engineering Chemistry:*

It may be of value to those interested in the analysis and manufacture of Red Lead to know that a mixture of dilute nitric and tartaric acids is an excellent solvent for that substance. The hot solution of tartaric and nitric acids dissolves Red Lead almost instantly. The proportion of tartaric to nitric acid is very small. A convenient dilute solvent for Red Lead is prepared by dissolving 5 g. of crystallized tartaric acid in some water, adding to it 200 cc. concentrated nitric acid and the whole diluted to 1 liter. Stronger solutions for larger samples are made by increasing the nitric and tartaric acid contents; thus, 100 cc. of a solution containing 300 cc. concentrated nitric acid and 15 g. of crystallized tartaric acid per liter will dissolve 20 g. of Red Lead. Too strong nitric acid must not be kept with tartaric acid as the latter will decompose on standing.

The solvent should be used hot, pouring it over the sample and stirring; it is very much more efficient and also cheaper than hydrogen peroxide which is in general use for Red Lead analysis.

CLEVELAND, OHIO  
October 6, 1916

GREGORY TOROSSIAN

## DETERMINATION OF SMALL AMOUNTS OF ALCOHOL AND WATER IN ETHER FOR ANAESTHESIA—A CORRECTION

In our article printed under the above title in *THIS JOURNAL*, 8 (1916), 807, an error occurs in Table I. The fraction

$$\frac{\text{Wt. ether} + 1.040533 + 0.9970795}{49.8444 + 1.040550 + 0.9970770}$$

should read:

$$\frac{\text{Wt. ether} + 1.040533 \times 0.9970795}{49.8444 + 1.040550 \times 0.9970770}$$

Also, Heft VIII in footnote 2, page 807, should read Heft VII.

ST. LOUIS E. MALLINCKRODT, JR., AND A. D. ALT  
September 18, 1916

## A STUDY OF THE EFFECT OF STORAGE ON MIXED PAINTS—CORRECTION

In the paper by Mr. Ware and myself as printed in *THIS JOURNAL*, 8 (1916), 879, the last line, second column, Table I, should read " $\text{Na}_2\text{CO}_3$ , . . ." instead of " $\text{Na}_2\text{CO}_3$ , 3 g."

UNIVERSITY OF MICHIGAN  
ANN ARBOR, October 19, 1916

R. E. CHRISTMAN

## SYNTHETIC PHENOL RESINS

Editor of the Journal of Industrial and Engineering Chemistry:

It was our purpose to have closed this controversy on synthetic phenol resins with our last communication to the Journal, but as the reply by Dr. Baekeland to our communication seems studiously to avoid the essentials at issue, it is necessary to restate our position.

We are not concerned with the problem of explaining the fact that a factory is not built for manufacturing a substance in a commercial way as soon as the substance is known in the scientific world. The Doctor seems to conclude indirectly that materials are not known or discovered until they are being made commercially: a rather compromising position at least in which to place our pure scientists.

Our proposition briefly stated is as follows

The anhydrous reaction which takes place between anhydrous phenol and anhydrous hexamethylenetetramine is different in every essential from the wet formaldehyde process, which wet process has been known for many years in a scientific way, and which has been developed recently in a commercial way by Dr. Baekeland.

The anhydrous reaction between anhydrous phenol and anhydrous hexamethylenetetramine is a recent discovery both from a purely scientific standpoint and from its commercial application. The anhydrous reaction differs from the wet formaldehyde process both as to *by-products, intermediate products, temperature of reaction, methods of working*, and also the characteristics of the final product are quite different if the data published on the constants of the phenol formaldehyde resins (wet process resins) are correct.

Dr. Baekeland's ideas have evolved rapidly. He takes the position in June, 1916, that it is Tweedle-Dum and Tweedle-Dee between hexamethylenetetramine and formaldehyde. Will the Doctor explain the statements which he made in THIS JOURNAL and in his patents in 1909? For his convenience we have arranged them in three columns as follows (italics are ours):

EXTRACT FROM PATENT TO  
BAEKELAND  
FILED IN 1907  
ISSUED IN 1909

"The proportion of bases used as condensing agent has a preponderant influence on the nature of the ultimate products. For instance, if a large amount of ammonia be used, *hexamethylenetetramine* is formed which is a crystalline body of definite chemical properties.

"It is, therefore, essential that the proportion of base should not exceed certain definite limits, and the maximum permissible proportion has been found to be less than one-fifth of the equimolecular proportion of phenol body present. If larger proportions of base be used there are found in the mass such amounts of disturbing bodies as to serve to render the product technically inferior or worthless for the purpose of this invention."

BAEKELAND, THIS  
JOURNAL, VOL. 1  
MAY, 1909  
PAGE 155

"I wish it distinctly understood that in order to obtain my technical effect I use the bases in relatively small quantities, say less than one-fifth of the amount which would be required to transform the phenol in phenolate."

"If larger amounts of base be used, the results are technically inferior, in fact, the process changes gradually into such as to give phenol alcohols or compound condensation products of ammonia or amines, with formaldehyde, all products very different from those I desire to make."

BAEKELAND, THIS  
JOURNAL, VOL. 8  
JUNE, 1916  
PAGE 569

"That ammonia and formaldehyde added together form immediately *hexamethylenetetramine* is such a well known fact in chemistry that one of the first things which were tried in my laboratory during my early research work was to make sure that *hexamethylenetetramine* could be substituted in the reaction, and it was shown that it gave substantially the same infusible product."

ence of the Chief Examiner and our attorneys, namely, that if we would stick to the dry process he would stick to the wet process and that there would be no conflict in any way.

Also will the Doctor explain his statements made from the floor in the Organic Section of the American Chemical Society at the Rochester Meeting, Sept., 1913, that the anhydrous reaction could never be controlled commercially and the best skill and effort of his laboratory had produced by the anhydrous reaction samples which at best were much inferior to those which he did obtain by the wet reaction? In 1913, hexamethylenetetramine is "incomparably inferior" to formaldehyde and small traces of ammonia; in 1916 they are equal. It is tweedle-dum and tweedle-dee between these. And in the Doctor's last article it seems the hexamethylenetetramine is preferred to all other combinations. Between 1913-1916 the writers have published the results of their discoveries with hexamethylenetetramine and phenol in the anhydrous reactions.

Another point: In 1912 the Doctor prefers the fixed alkalis, in 1916 he prefers the volatile alkali ammonia; or the non-volatile compound hexamethylenetetramine. We submit these statements in the following columns arranged for convenience in order of publication:

BAEKELAND, THIS JOURNAL,  
VOL. 4, OCT., 1912  
PAGE 742

"The use of these fixed alkalis has enabled us to carry on hardening and molding at a faster rate than is possible with ammonia or hexamethylenetetramine, or other means, and at the same time to produce molded articles of better heat resisting qualities, of highest excellent dielectric properties. For many electrical purposes, the fact that no free ammonia exists in the mass is a further advantage."

BAEKELAND, THIS  
JOURNAL, VOL. 4  
OCT., 1912  
PAGE 741

"In this and other respects the fixed alkalis have decided advantages over ammonia or hexamethylenetetramine, as well as over acid condensing agents."

BAEKELAND, THIS  
JOURNAL, VOL.  
8, JUNE, 1916  
PAGE 568

"Ammonia, whether it is used directly as such, or combined to formaldehyde as hexamethylenetetramine is still preferred over other bases for the great majority of phenolic, resinous condensation products now in the market."

The Doctor has radically changed his opinions during the period that the writers were publishing the results of their researches on hexamethylenetetramine and phenol in the anhydrous reaction. This is significant.

May we add that ammonia was used for the production of an infusible synthetic resin from phenol condensation products, prior to the time when Dr. Baekeland employed the eminently valuable properties of ammonia for this purpose. Luft's American patent, 1903, states plainly that he may use any alkali or alkali carbonate after previously washing out the acid with water, which would include not only ammonia but any of the other alkalis, and if the Doctor reads Luft's patent carefully he will see that Luft washes the resin previous to the action of the alkali. Luft's failure to elucidate the *modus operandi* of the chemical reaction, the results of which he was patenting, though this failure may be due to lack of knowledge on Luft's part, does not in any way invalidate the patent. The exact working of Luft's patent reads: "In order to render the mass transparent it is boiled while in a fresh viscous condition AFTER PREVIOUS WASHING WITH WATER, in the presence of a substance which reacts on the acid—as, for example, an aqueous solution of alkali or alkaline carbonate." From the foregoing statement of Luft it is obvious that ammonia was used as a condensing agent, as early as 1902-3. And yet the Doctor maintains that no one previous to him used an alkali such as ammonia in their process. The authors have made this material following Luft's process exactly and know that it can be worked commercially.

636-678 W. 22ND ST  
CHICAGO  
September 14, 1917

L. V. REDMAN  
A. J. WEITH  
F. P. BROCK

It will be interesting also to have the Doctor explain his statement to the writer in 1912 in the U. S. Patent Office in the pres-



## PERSONAL NOTES

The National Research Council, established by the National Academy of Sciences at the request of the President of the United States, held its organization meeting in New York City on September 20, 1916. With Dr. M. I. Pupin as temporary chairman, the following elections were made: *Permanent Chairman*, Dr. George E. Hale; *First Vice-Chairman*, Dr. Charles D. Walcott; *Second Vice-Chairman*, Mr. Gano Dunn. By an agreement between the National Academy of Sciences and the Engineering Foundation, the foundation places its funds at the disposal of the Council for one year and its secretary, Dr. C. T. Hutchinson, has been appointed *Secretary* of the Council.

Chairman Hale announced the following appointments to the *Executive Committee*: Messrs. J. J. Carty, E. G. Conklin, Gano Dunn, A. A. Noyes, M. I. Pupin and V. C. Vaughan. Two meetings of the *Executive Committee* were held in New York on Sept. 21 and 29, 1916. J. J. Carty was elected *Chairman*, and C. T. Hutchinson, *Secretary* of the committee. A resolution was adopted inviting the American Association for the Advancement of Science to cooperate with the National Research Council and a committee consisting of Messrs. Welch, Conklin and Noyes was appointed to that end. Other committees appointed were: *Committee on Research in Educational Institutions*, G. E. Hale, *Chairman*; *Committee on the Promotion of Industrial Research*, J. J. Carty, *Chairman*; *Committee on a National Census of Research*, Dr. Stratton, *Chairman*.

Rutgers College has conferred the degree of Doctor of Science on Dr. J. L. R. Morgan, class of 1892, professor of physical chemistry in Columbia University.

Mr. Ernst Child has resigned his position as general sales manager for Eimer & Amend and accepted the presidency of H. Reeve Angel & Co., Inc., 120 Liberty Street, New York.

Dr. Thomas, of Yale, and Mr. Gerges, of Ursinus, are new members of the faculty of chemistry in the University of Pennsylvania.

Dr. Samuel P. Sadtler delivered an address on the "Early History of Chemical Industry in Philadelphia," at the regular meeting of the Philadelphia Section of the A. C. S. on October 19th. The address will appear in full in our next issue.

Mr. George A. Burrell, formerly in charge of research work in gas and related investigations for the Bureau of Mines, Pittsburgh, Pa., has resigned his position to enter consulting work. In leaving the Government, Mr. Burrell closes twelve years continuous service.

Edward Ray Weidlein has been appointed associate director of the Mellon Institute of Industrial Research of the University of Pittsburgh. Mr. Weidlein has been an Industrial Fellowship incumbent since 1910, and, during the past four years, has been in active charge of the hydrometallurgical investigations of the Mellon Institute.

R. Lewis Morris, vice-president of Herman & Herman, Inc., the New York chemical house, sailed October 14th, from New York to open English offices for the corporation. Messrs. Herman & Herman are also opening offices in Petrograd, Moscow, Genoa and Barcelona; and still others will shortly be opened in the Far East. In November an officer of the company will sail from New York for Brazil and Argentina, to establish headquarters in those countries.

Mr. T. R. L. Loud entered upon his new duties as vice-president and general manager of the New York Quinine & Chemical Works, on October 2nd.

E. C. Franklin, professor of chemistry,<sup>5</sup> Stanford University, has been elected member of the Executive Committee of the Pacific Division of the American Association for the Advancement of Science.

Dr. Ferdinand Fischer, professor of chemical technology in the University of Göttingen, has died at 74 years of age.

Northwestern University has appointed Dr. Wallace J. Murray and Martin W. Lisse instructors in the department of chemistry.

The Barber Asphalt Paving Company has established at Harvard University and the Massachusetts Institute of Technology, a fellowship for research in asphaltic materials and their uses, to be known as "The Clifford Richardson Fellowship."

Prof. Carl T. Dowell, instructor of chemistry at the University of Texas, has been elected associate professor of chemistry at Tulane University.

The University of Illinois announces the following appointments and changes in the department of chemistry: Prof. Cullen W. Parmelee, sometime professor of ceramics at Rutgers College, professor of ceramic engineering; Prof. Richard C. Tolman, professor of physical chemistry, to succeed Prof. E. W. Washburn, now head of the department of ceramics. Dr. Roger C. Adams, assistant professor of organic chemistry, to succeed Dr. C. G. Derick who is organizing a research laboratory for the Schoellkopf Aniline and Chemical Works at Buffalo. Dr. Horace G. Deming, associate in chemistry, to assist in instruction of general chemistry and qualitative analysis. Prof. C. W. Balke, formerly head of division of general chemistry and qualitative analysis, is organizing a research laboratory for the Pfanstiehl Company in North Chicago.

Director Joseph E. Ralph of the U. S. Bureau of Engraving and Printing has made public the plan of the Bureau of Chemistry in its establishment of an experimental dye laboratory, for which Congress appropriated \$50,000, the location of which will be on the government's property in Virginia, just across the Potomac from Washington. Director Ralph has arranged with Dr. Alsberg to give a practical test to all the colors produced by this experimental laboratory.

President C. H. Herty has appointed a committee consisting of J. Merritt Matthews, *Chairman*, Allen Rogers and E. F. Roerber, to act on the resolutions dealing with the purchase and use of "American dyestuffs" by the U. S. Bureau of Engraving and Printing, which were adopted at the Dyestuffs Conference held during the New York Meeting of the A. C. S. [See THIS JOURNAL 8 (1916), 952.]

Owing to protests received from New York importers of German dyestuffs and German manufacturers, Secretary of Commerce Redfield has ordered the proof sheets of the census on dyestuffs compiled by the Bureau of Foreign and Domestic Commerce withdrawn from public inspection. American chemists and color manufacturers are protesting against the withdrawal of the data.

On September 19th, twenty members of the Civilian Navy Consulting Board, headed by Thomas A. Edison, took the oath of allegiance to the United States, as officers of the federal government. At the subsequent meeting the naval research laboratory and other questions were discussed.

Dr. C. E. Caspari addressed the St. Louis Section of the A. C. S. on "The New United States Pharmacopoeia" at their meeting on October 2nd.

# GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

## BUREAU OF MINES

**Construction and Operation of a Single-Tube Cracking Furnace for Making Gasoline.** C. P. BOWIE. Technical Paper 161. 12 pp. Paper, 10 cents. "It is the purpose of this report to outline briefly the general principles involved in the cracking of oils and distillate by the Rittman process, to describe the construction of a one-tube experimental plant, and to give in some detail those methods of operation that have given the best results."

"This paper is intended primarily for those who have obtained a license for the use of the process. It is assumed that such persons have a working knowledge of the modern processes of refining oils, and have read the bulletin<sup>1</sup> recently published by the Bureau of Mines on the results of experiments with this process."

**Methods of Sampling Delivered Coal and Specifications for Purchase of Coal for the Government.** GEORGE S. POPE. Bulletin 116. 64 pp. Paper, 15 cents. This outlines the procedure followed by the laboratory of the Bureau of Mines in analyzing and testing samples of coal deliveries.

**Ore-Sampling Conditions in the West.** T. R. WOODBRIDGE. Technical Paper 86. 88 pp. Paper, 15 cents. "In this report the subject of ore sampling is considered under five divisions, as follows: A definition of ore sampling; the condition of the ore as affecting sampling; description of the various methods of sampling used in the West, with flow sheets showing their application, and a criticism of certain details of practice; discussion of the methods investigated; and recommendations. The report deals principally with the first three of these divisions, although it may occasionally encroach upon the other two. Under various headings it has seemed necessary to repeat or discuss more fully some of the conditions of ore sampling in order to emphasize their effects on certain sampling processes."

"An exhaustive review or criticism is not attempted, and such deductions and suggestions as are made are offered with the knowledge that there must necessarily be some difference of opinion among well-informed and honest operators. It is therefore hoped that this paper will be freely discussed by those who can offer constructive criticism."

**Black Damp in Mines.** G. A. BURRELL, I. W. ROBERTSON AND G. G. OBERFELL. Bulletin 105. 77 pp. Paper, 10 cents. "The Bureau of Mines, in pursuing investigations looking to greater safety in mining, has analyzed samples of the air in many different coal mines in the United States, and has studied the analyses. This report presents the results of one phase of this study and shows how atmospheric air, after entering a coal mine, loses oxygen and gains carbon dioxide with resulting formation of so-called black damp. Also the report discusses the effects of the constituents of black damp on men, on the

burning of oil and acetylene lamps, and on the explosibility of methane."

**Methods of Sampling Delivered Coal and Specifications for the Purchase of Coal for the Government.** GEORGE S. POPE. Bulletin 116. 56 pp. Paper, 15 cents. "This bulletin is a revision of Bulletin 63 and is published by the Bureau of Mines in order that purchasers of coal for government, state, municipal, or private use may be informed regarding advances or refinements in sampling coal deliveries and preparing specifications for the purchase of coal."

## NAVY DEPARTMENT

**Carbon Dioxide Gas.** Contract Bulletin No. 3 of Fiscal Year 1916, as issued by the Bureau of Supplies and Accounts, specifies that carbon dioxide gas delivered to the Navy Department for use in refrigerating machinery must be "guaranteed at all times 99.5 per cent pure and be furnished in drums of an approved type."

## WAR DEPARTMENT

**Tests of Metals and Other Materials.** War Department Document 477. This is the Annual Report on tests made at the Watertown Arsenal, Massachusetts, during the year ending June 30, 1914. There are included a large number of analyses and micrographic illustrations of steels and metal samples which were subjected to various physical tests.

## SUPERINTENDENT OF DOCUMENTS

**Agricultural Chemistry Price List 40,** 7th edition, gives the complete list of government publications on Agricultural Chemistry which are for sale by the Superintendent of Documents, corrected to July, 1916. 16 pp.

## BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**Paper and Stationery Trade of the World.** GROSVENOR DAWE. Special Consular Report 73. 458 pp. Paper, 50 cents. This report is a compilation from Consular Reports and special investigations made with a view to giving complete statistics as to the condition of the paper and stationery trade throughout the world. The subjects are discussed for each locality under the following headings: (1) General statement as to character and source of the paper supply with special reference to the possibility of selling American products. (2) Market requirements, amount of each kind of paper consumed, standard sizes and general classification of paper needs. (3) Local product, including description of the raw materials, the number and character of output of paper and pulp mills, costs, and source of mill equipment. There are also included under this head certain summaries of prices. (4) Import paper statistics.

## BUREAU OF THE CENSUS

**Statistics for Alaska.** 41 pp. Paper, 10 cents. This is a separate from the 13th Census Report giving population, agriculture, manufacturing, and mining data.

## DEPARTMENT OF INTERIOR

**Regulations Covering Coal Land Leases in Alaska.** Interior Department unnumbered publication. Paper, 20 cents. This includes information relative to the operation and development of Alaska coal fields with copy of the law and regulations and approved form of proposed lease. Maps of areas are also included.

## GEOLOGICAL SURVEY

**The Lignite Field of Northwestern South Dakota.** DEAN E. WINCHESTER, C. J. HARES, E. RUSSELL LLOYD AND E. M. PARKS. Bulletin 627. 158 pp. and 2 plates. Paper, 25 cents. "In computing the probable amount of lignite available in northwestern South Dakota, only those areas are considered which are known to be underlain by lignite of sufficient thickness

<sup>1</sup> W. F. Rittman, C. B. Dutton, and E. W. Dean, "Manufacture of Gasoline and Benzene Toluene from Petroleum and Other Hydrocarbons," Bureau of Mines, Bull. 141 (1916), 268 pp., 9 pls. and 45 figs.



to be classified as coal land by the Geological Survey. The lignite of this field has a heating value on air-dry analysis of \$8,000 to \$8,300 B. t. u. as shown by the chemical analysis and, according to the regulations of the Department of the Interior, a bed of lignite with this heating value must be 2 ft. 10 in. thick in order to be considered sufficiently valuable for classification as coal land.

"In calculating the tonnage of any lens of lignite its area is determined and the average of the several measurements along the outcrop is assumed to represent the average thickness of the bed. The total content of the lens is determined by multiplying the area in square miles by the average thickness in feet, and this by 1,152,000, the number of short tons of lignite in a square mile of land underlain by a bed 1 ft. thick and having a specific gravity of 1.3. By this method it is estimated that there is in Perkins and Harding Counties minable lignite amounting to about 1,096,480,000 tons."

**The Chisana-White River District, Alaska.** STEPHEN R. CAPPS. Bulletin 630. 117 pp. and 2 plates. Paper, 20 cents. The bulk of this report refers to gold placer deposits, but gold loads, copper deposits and lignite fields are also briefly discussed.

**Lode Mining in the Quartzburg and Grimes Pass Porphyry Belt, Boise Basin, Idaho.** E. L. JONES. Bulletin 640-E, from Contributions to Economic Geology, 1916, Part I, pp. 83-111. Published July 25.

**The Alaskan Mining Industry in 1915.** ALFRED H. BROOKS. Bulletin 642-A. 66 pp. and 1 plate. Separate from Contributions to Mineral Resources of Alaska, 1915.

**Mineral Resources of the Upper Chitina Valley, Alaska.** FRED H. MOFFIT. Bulletin 642-C. 8 pp. Separate from Mineral Resources of Alaska, 1915.

**The Turnagain-Knik Region, Alaska.** STEPHEN R. CAPPS. Bulletin 642-E. 48 pp. Separate from Mineral Resources of Alaska, 1915.

**Gold Mining in the Willow Creek District, Alaska.** STEPHEN R. CAPPS. Bulletin 642-F. 6 pp. Separate from Mineral Resources of Alaska, 1915.

**Preliminary Report on the Tolovana District, Alaska.** ALFRED H. BROOKS. Bulletin 642-G. 10 pp. Separate from Mineral Resources of Alaska, 1915.

**Antimony Deposits of Alaska.** ALFRED H. BROOKS. Bulletin 649. 60 pp. and 1 map. "As a consequence of these (recent war) conditions the exploitation of the known stibnite ores of Alaska was begun in 1914 and active search was made for new deposits. In 1915 the production of antimony ores began at four mines in the Fairbanks and two in the Nome district, and there was much prospecting for stibnite in other parts of the Territory. All the operations were on a small scale, and at most of the mines they consisted principally in digging out rich ore shoots occurring near the surface by open cuts, together with breaking and hand sorting the ore. There is no record available of the ore mined, but the total shipments of antimony ore from Alaska in 1915 were 833 short tons. Exact information is lacking as to the antimony content of these shipments, but they probably averaged about 58 per cent metallic antimony. It is difficult from the information at hand to determine the value of this product, but the producer probably received from \$1.25 to \$1.75 a unit of antimony. The best information available indicates that this antimony ore sold at an average of about \$86 a ton in San Francisco, where all the Alaska product was marketed. Therefore the total value of crude antimony ore shipped from Alaska during 1915 was probably about \$74,000.

"Though the antimony mines of Alaska that were productive in 1915 were all located in the Fairbanks and Nome districts, yet many stibnite deposits in other parts of the Territory were also prospected. Such development work is reported from the Nizina, Port Wells, Kantishna, and other districts. The out-

look for profitable exploitation of Alaska antimony ores under normal conditions of the market is not very encouraging. It is possible, however, that the larger lodes which carry rich ore and are favorably located for transportation may furnish a field for permanent mining ventures."

**Reconnaissance of the Conconully and Ruby Mining Districts, Washington.** EDWARD L. JONES, JR. Bulletin 640-B, from Contributions to Economic Geology, 1916, Part I, pp. 11-36. Published August 12.

**Mining on Prince William Sound, Alaska.** BERTRAND L. JOHNSON. Bulletin 642-D, from Contributions to Mineral Resources of Alaska, 1915, pp. 137-145.

**Bibliography of North American Geology for 1915 with Subject Index.** JOHN M. NICKLES. Bulletin 645. 76 pp.

**Water Supply Papers.** A list of the publications of the Geological Survey on this subject has been prepared, indicating the papers which are still available either for free distribution or for sale by the Superintendent of Documents.

**Platinum and Allied Metals in 1915.** JAMES M. HILL. Separate No. 6, Mineral Resources of the United States, 1915, Part I, 19 pp. Published August 15. "The production of crude platinum in California and Oregon in 1915 was 741.91 oz. (troy), having a value of about \$23,500. This was an increase of 171.91 oz. over the production in 1914. Most of the crude platinum came from California; only one mine in Oregon reported a production in 1915.

"The estimated world's production of crude platinum in 1915, in troy ounces, was as follows:

Borneo and Sumatra.....	(a) 100
Canada.....	18,000
Colombia.....	303
New South Wales and Tasmania <sup>(b)</sup> .....	124,000
Russia.....	742
United States.....	143,145
Total.....	143,145

(a) No basis for estimate.

(b) Tasmania, osmiridium.

"Notwithstanding the embargo placed upon the exportation of platinum by all the allied governments, the imports of platinum and allied metals into the United States during 1915, as compiled by the Bureau of Foreign and Domestic Commerce, Department of Commerce, were only 10 per cent below imports in 1914.

"The average price of platinum for several years shows a rather uniform increase up to 1913, when a slight decline took place. In 1914 the price regained a high level of about \$45 an ounce, which decreased during the first part of 1915 to \$38 in June and July. In September when it was realized that supplies from Europe would be difficult to obtain, prices naturally responded. The high level, \$85.50 in December, 1915, has been surpassed during the first months of 1916, and there seems little likelihood of any immediate return to normal conditions.

"Prices reported for the refined metals of the platinum group, by different companies, have varied widely during 1915, but what seem to be fair average values are given in the table below, which values have been used by the United States Geological Survey in all computations:

Platinum.....	\$55
Iridium.....	\$83
Iridosmine.....	\$35
Palladium.....	\$56

"No prices of osmium, rhodium, and ruthenium, are available."

**Bauxite and Aluminum in 1915.** W. C. PHALEN. Separate No. 7, Mineral Resources of the United States, 1915, Part I. 16 pp. Published August 16. "The production of bauxite in the United States in 1915 was 297,041 long tons, valued at \$1,514,834, an increase of 77,723 long tons, or 35 per cent, in quantity and of \$445,640, or 42 per cent, in value as compared with 1914. The increase for 1915 is abnormal in the bauxite industry and is accounted for by the increased activity in the

production of metallic aluminum. The great bulk of the bauxite from which aluminum is produced comes from Arkansas, which in recent years has produced about 80 per cent of all the bauxite mined in the United States and in 1915 produced more than 90 per cent.

"The average price of bauxite per long ton at the mines was \$4.81 in 1912, \$4.75 in 1913, \$4.87 in 1914, and \$5.10 in 1915.

"The United States leads the nations in the production of metallic aluminum, and the marked increase in production in the United States is well illustrated by the figures given in the accompanying table.

ALUMINUM PRODUCED OR CONSUMED IN THE UNITED STATES, 1885-1915

	Pounds
1885.....	283
1895.....	920,000
1905.....	11,347,000
1910.....	47,734,000
1915.....	99,806,000

"The aluminum market in 1915, like that for most of the metals, went through a series of very radical changes. The price per pound ranged approximately from 19 cents at the beginning of the year to nearly 60 cents at the end."

**Lead in 1915.** General Report. C. E. SIEBENTHAL. Separate from Mineral Resources of the United States, 1915, Part I, pp. 187-205. Published September 23. "The following tabular statement gives the general items regarding domestic production and consumption of lead, from figures compiled by the Survey for 1915:

U. S. PRODUCTION	Short tons
Refined lead.....	550,055
Desilverized lead.....	388,594
Soft lead (including desilverized soft).....	205,462
Antimonial lead.....	23,224
Lead from domestic ores.....	507,026
Secondary lead.....	78,900
Consumption of lead in the United States (disregarding stocks).....	431,252

"The output of refined lead in the United States from domestic ores in 1915 was valued at \$47,660,000, at the average price of refined lead in New York, as compared with \$39,998,000."

**Sand and Gravel in 1915.** R. W. STONE. Separate No. 17, Mineral Resources of the United States, 1915, Part II. 13 pp. Published August 7.

**Lime in 1915.** G. F. LAUGHLIN. Separate No. 19, Mineral Resources of the United States, 1915, Part II. 20 pp. Published August 19. "The lime manufactured and sold in the United States in 1915 amounted to 3,589,699 short tons, valued at \$14,336,756. This was an increase of 208,771 tons, or 6 per cent, in quantity, and of \$1,067,818, or about 9 per cent, in value compared with sales in 1914. It nearly equaled the record output of 1913.

"The lime sold in the United States in 1915 may be classified by uses as follows:

	Quantity (Short Tons)	Price Av. per ton
Building lime.....	1,136,696	\$4.23
Chemical works.....	492,870	3.36
Paper mills.....	216,819	3.61
Sugar factories.....	34,025	6.77
Tanneries.....	47,104	4.06
Fertilizer.....	653,686	3.31
Dealers—uses not specified.....	595,128	4.22
Other uses(a).....	413,371	4.82
Total.....	3,589,699	\$3.99

(a) Includes lime for sand-lime brick, slag cement, alkali works, steel works, glassworks, smelters, sheep dipping, disinfectant, manufacture of soap, cyanide plants, glue factories, purification of water, etc.

**Cement in 1915.** ERNEST F. BURCHARD. Separate No. 16, Mineral Resources of the United States, 1915, Part II. 24 pp. Published August 12. "The cement industry showed no unusual features in 1915. In view of the experiences of 1914, when the production of Portland cement was checked for the first time, manufacturers exercised considerable caution, the result of which was a slight increase in the volume of shipments, a small decrease in the quantity of cement manufactured, and a

considerable decrease in the stocks of cement on hand—all indicating a correction of the tendency toward overproduction that has manifested itself at times during the last few years.

"In general, prices averaged 6.7 cents lower per bbl. in 1915 than in 1914, though toward the end of the year they were considerably higher. The statistics show that the general volume of business was about the same as in 1914, though it was not uniformly distributed throughout the year."

#### PUBLIC HEALTH REPORTS

**Present-Day Control of Drugs and Medicines.** MARTIN I. WILBERT. Public Health Reports, 31 (August 4), 2072-6. The variation in purity and strength of widely used drugs and preparations is discussed as a matter of difficulty in prescription writing and as a menace to patients. The magnitude of some variations discovered is pointed out.

The following five reprints from Public Health Reports are again available:

(1)—**Bread as Food, Changes in Its Vitamine Content and Nutritive Value with Reference to Occurrence of Pellagra.** CARL VOEGTLIN. M. X. SULLIVAN AND C. N. MYERS. Reprint No. 333. Paper, 5 cents.

(2)—**Cosmetics as Drugs, Review of Some of Reported Harmful Effects of Ordinary Constituents of Widely Used Cosmetics.** MARTIN I. WILBERT. Reprint No. 305. Paper, 5 cents.

(3)—**Practical Use of Disinfectants.** H. E. HASSELTINE. Reprint No. 287. Paper, 5 cents.

(4)—**Recent Legislation Designed to Restrict the Use of Narcotic Drugs.** Reprint No. 321. Paper, 5 cents.

(5)—**Vatamine and Nutritional Diseases.** ATHERTON SEIDELL. Reprint 325. Paper, 5 cents.

#### SANITARY LEGISLATION

**Production, Care, and Sale of Milk and Milk Products.** Indianapolis Ordinance adopted May 23, 1916, includes standards for the quality of milk.

#### COMMERCE REPORTS, SEPTEMBER, 1916

The 1916 sugar crop of Cuba is 3,000,000 tons, about 500,000 tons above the largest previous production. (P. 833.)

Experiments in Hawaii have shown that manganese in soils prevents the growth of pineapples, etc., through its rendering the iron content of the soils insoluble. Spraying of the pineapple plants with FeSO<sub>4</sub> solution has proven an efficient remedy. (P. 836.)

Efforts are being made to produce pig iron in New Zealand from the extensive deposits of iron-bearing sands. (P. 859.)

A new zinc smelter will soon be opened in Japan. (P. 879.)

The soy bean, extensively cultivated in Manchuria, contains 18 per cent of oil, used as an edible oil, as a lubricant and illuminant, and in the manufacture of soap and varnish. The oil is largely exported, and the bean cake is used as cattle food and fertilizer. (P. 886.)

The first electrolytic copper refinery in Canada has just been opened at Trail, B. C. (P. 887.)

Among Japanese products that are making rapid progress are dyestuffs, drugs, sheet glass, celluloid, paper, phosphorus, potassium chlorate, soda, and porcelain. (P. 892.)

Arrangements are being made for the smelting of Australian zinc concentrates in Great Britain, as well as for the erection of additional smelters in Australia. (P. 892.)

The exports of rubber from the Amazon district to the United States in July, 1916, are somewhat less than in July, 1915, while those to Europe are greater than last year. (P. 914.)

The output of sulfate wood-pulp in Sweden has been reduced by lack of fuel and sodium sulfate, most of which is now imported from Germany. (P. 938.)

The output of tin from Siam shows a slight increase. (P. 941.)



Arrangements are being made for increased transportation of Mexican **petroleum** to the United States. (P. 946.)

The **tungsten** deposits of California are now being developed, consisting of scheelite ores, containing about 2 per cent of  $WO_3$ . (P. 953.)

Owing to increased production and improved shipping facilities, Japan is becoming overstocked with numerous articles of which there had been a shortage; as a result there have been some losses, especially on **wood-pulp** and on **potassium chlorate**. (Pp. 964, 965.)

Production of **nitrate** in Chili is again normal and exports are greater than in former years. (P. 995.)

Exports of **Cascara bark** from Canada to the United States show a marked increase. (P. 966.)

Promising **tungsten** deposits are being opened in New Brunswick. (P. 970.)

**Carbolic acid** in large amounts is now being exported from the United States to Japan. (P. 973.)

The mineral output of Bolivia includes **tin**, **copper**, **silver**, **antimony**, **bismuth** and **tungsten**. (P. 973.)

Exportation of **manganese ore** from India is increasing. (P. 987.)

**Kaig grass** from India is proposed as a new source of **paper pulp**, being similar but slightly inferior to **esparto**. (P. 991.)

Experiments in South Africa upon the use of a **molasses distillate** as a motor fuel have been very promising. The fuel contains considerable **ether**, and alkali was present to absorb any acids produced in combustion and thus prevent corrosion. (P. 999.)

The output of **platinum**, **asbestos**, and **pyrites** from the Urals is below normal. (P. 999.)

Most of the world's supply of **nux vomica** is obtained from British India. In addition to **strychnine** and **brucine**, the seeds yield a light **brown dye**. (P. 1012.)

The United States' output of **chemical products** in 1914 was about 20 per cent in excess of that in 1909. (P. 1016.)

Owing to the curtailment of **sulfur** exports from Italy, the exports of sulfur from Japan have increased over 50 per cent. (P. 1019.)

Steps are being taken toward the establishment of a large **iron foundry** in Japan. (P. 1022.)

**Lemon-grass oil**, obtained in India by distillation of native lemon grass (*cymbopogon citratus* and *flexuosus*), contains 70 to 80 per cent of citral. It is used extensively in the United States in artificial **perfumes**, furniture polish, etc. (P. 1064.)

Efforts are being made to introduce Brazilian **piteira fiber** as a substitute for Mexican **henequen**. (P. 1075.)

Prospects for **petroleum** near Port Elizabeth, So. Africa, are promising. (P. 1084.)

Extensive deposits of **bauxite** have been found in Dutch Guiana. (P. 1098.)

In Japan a non-combustible "**celluloid**" has been invented made from **soy bean cake**. (P. 1115.)

New processes have been devised in England for the direct preparation of hydrated **sodium carbonate** in a stable powdered form, and also of **sodium silicate** in a solid soluble form, readily powdered. (P. 1126.)

Scarcity of **fertilizers** in Spain has led to the use of the residues obtained by evaporation of the mother liquors from solar salt beds. The product known as "**marine kainit**" is high in **potash**, and especially valuable for dry farming on account of its hygroscopic properties. It is also said to assist nitrification. (P. 1127.)

In a report on "Foreign Markets for American Chemicals" by T. H. Norton, the statistics for **exports of chemicals** show

the following totals for the fiscal years ending June 30, 1914, \$27,079,092; 1915, \$46,380,986; 1916, \$124,362,167. The principal items of increase are **sulfuric and other acids**, **dyes**, **copper sulfate**, **sodium compounds**, and **tanning extracts**. (P. 1129.)

The mineral products of Peru include **gold**, **silver**, **copper**, **lead**, **mercury**, **bismuth**, **zinc**, **vanadium**, **tungsten**, **molybdenum**, **borates**, **salt**, **coal**, and **petroleum**. (P. 1141.)

**Turmeric root** occurs in India in two forms, one used as a **dye** and the other as a **condiment**. (P. 1144.)

**Sumac leaves** are obtained in Sicily from both the wild and cultivated plants. The **tannin** content is greatest in a hot dry soil. (P. 1177.)

Among the **gums** obtained from India is **Kino**, obtained by solar evaporation of the juice from "*Pterocarpus marsupium*." The gum is proposed as a **tanning material**. (P. 1178.)

Many varieties of **castor seed** are grown in India, one of which, produced by selection, is said to produce an edible oil with no poisonous principle. Both the seed and oil are exported. The oil is used as an illuminating oil, for **preserving leather**, in **dyeing**, and **medicinally**. (P. 1187.)

**Zinc ores**, principally **sphalerite** and **calamine**, are now being exported from French Indo-China to the United States. (P. 1224.)

Marseille is the world's greatest **oil seed** crushing center, the principal oils being **peanut**, **cocoanut**, **sesame**, **castor**, **linseed**, **cottonseed**, and **palm kernel**. (Supplement 5-E.)

## SPECIAL SUPPLEMENTS ISSUED IN SEPTEMBER

FRANCE—5e	BRAZIL—40c
GERMANY—6c	PERU—46a
SWITZERLAND—17a	CHINA—52d and e
UNITED KINGDOM—19j	AUSTRALIA—60a
CIBALTAR—20a	BELGIAN KONGO—64a
GUATEMALA—29a	BRITISH EAST AFRICA—65a
NEWFOUNDLAND—33a	BRITISH SOUTH AFRICA—66a
DANISH WEST INDIES—37a	ZANZIBAR—78a

## STATISTICS OF EXPORTS TO THE UNITED STATES

SANTO DOMINGO — 166	BRISTOL, ENGLAND— Sup. 19j	LONDON—1011
Divi-divi	Animal charcoal	Rubber
Hides	Celestite	Tin
Mangrove	Ammonia	Hides
Copper	Bleaching powder	Indigo
Sugar	Fullers earth	Creosote oil
Wax	Iron oxide	Platinum
Logwood	Hides	Copper
Fustic		NEWFOUNDLAND — Sup. 33a
MARSEILLE—Sup. 5e	HULL, ENGLAND— Sup. 19j	Fish oils
Aluminum	Carbolic acid	Glycerine
Citric acid	Alum	Guanos
Glycerine	Creosote, etc.	Copper pyrites
Bauxite	Naphthalin	Iron ores
Copper matte	Glue	Flint pebbles
Phosphate	Glycerine	BRAZIL—Sup. 40c
Glue	Fertilizer	Diamonds
Grease	Hemp	Hides
Hides	Gum copal	Ipecacuanha
Rubber	Vegetable oils	Rubber
Nickel matte	Pigments	Caranaba wax
Paper stock	Rubber	Glycerine
Graphite	Tin	Castor seed
Soap		Sugar
Tin	CHINA—Sup. 52d and e	Whale oil
GERMANY—Sup. 6c	Antimony	Tonka beans
Caffeine	Beeswax	Copahiba balsam
Fertilizer	Albumen	PERU—Sup. 46a
Glass	Aniline dyes	Antimony
Hides	Camphor	Petroleum
Linoleum cement	Gall nuts	Silver
Lithophone	Indigo	Potash
Peanut oil	Licorice	Lead
Photographic paper	Musk	Cochineal
Tin	Rhubarb	Copper
Wool grease	Gold	Cottonseed cake
Manganese	Hides	Gold
Glue	Pig iron	Guanos
SWITZERLAND— Sup. 17a	Vegetable oils	Rubber
Perfumes	Zinc ore	Hides
Chemicals	AUSTRALIA—Sup. 60a	Molybdenum ore
Gelatine	Coke	Mercury
Glass	Copper	Tungsten ore
Glue	Copra	Vanadium ore
Hides	Gold	Zinc
Artificial silk	Hides	Peruvian bark
Aluminum	Nickel matte	BRITISH SOUTH AFRICA — Sup. 66a
Aniline dyes	Cocoanut oil	Aloes
Indigo	Stearin	Buchu leaves
Argols	Tallow	Diamonds
Glycerine	Eucalyptus oil	Chrome ore
	Zinc ore	Hides

## BOOK REVIEWS

**Diseases of Occupation and Vocational Hygiene.** Edited by GEORGE M. KOBER AND WILLIAM C. HANSON. xxi + 918 pp., 46 figures. P. Blakiston's Son & Co., Philadelphia, 1916. Price, \$8.00 net.

The subject matter of this noteworthy presentation of the basic data regarding the diseases of occupation, is grouped in three parts. Part I deals with the specific and systematic diseases of occupation (occupational intoxications; occupational infectious diseases; compressed air illness; effects of diminished atmosphere upon health; dust diseases of the lungs; diseases of the blood, circulatory system and kidneys; fatigue and occupation neuroses; occupational affections of the nose, mouth, throat, eye and ear; occupational affections of the skin; cancer and occupation; X-ray and radium; and electrical injuries and shock); the sections of this part were written by specialists of international reputation and contain accurate information relating to the pathology, symptomatology and treatment of the various occupational diseases recognized at the present time. Part II treats of the etiology and prophylaxis of occupational diseases and contains Dr. Kober's fourteen scholarly chapters on occupations involving exposure to conditions injurious to health. This part should be of especial interest to chemical manufacturers since it gives complete information on the prevention of avoidable occupational hazards; it presents a comprehensive list of industrial poisons and of industries and processes in which poisoning may occur, and also tables of occupational mortality and morbidity statistics. Part III is devoted to a consideration of the relation of clinics, statistics, governmental study and legislation to occupational diseases, and it should, as intended, stimulate instruction in the prevention of these diseases, which is, of course, of much more economic importance than their cure.

The editors state that they have endeavored to make the work "a safe and convenient guide," and it is the reviewer's opinion that they have been remarkably successful. The high reputation of the thirty-one contributors is impressive testimony of the editorial plan of thoroughness and reliability—a guarantee that no pains have been spared to make the work what it actually is, accurate, authoritative and comprehensive.

W. A. HAMOR

**Inventions and Patents.** By PHILIP E. EDELMAN. viii + 299 pp. D. Van Nostrand Co., Price, \$1.50 net.

The author states that the volume "is intended particularly for all persons interested in patents, either as inventors, investors, or manufacturers." It is the purpose of the book to give such persons an understanding of their rights, to show the steps necessary to take advantage of the commercial opportunities of patents and the mistakes to be avoided.

The book contains some hints valuable to beginners but is too technical for the inexperienced reader. The author presupposes a considerable knowledge of the subject and the average reader will find much that is beyond him. It is not free from mistakes and its suggestions should not be too literally acted upon, although a careful reader will learn much to guide him in seeking further advice. Upon the whole it is suggestive and should prove helpful to those to whom it is addressed.

The book is divided into sixteen chapters as follows: I, The Development of the Patent System. II, The Patent Office. III, Patent Attorneys. IV, The Germs of Invention. V, The Fields of Invention. VI, Preliminary Steps to Secure a Patent. VII, Patentability and Practicability. VIII, Application for and Prosecution of a Patent. IX, Protecting an

Invention. X, Points of Patent Procedure. XI, Patent Rights and How They are Utilized. XII, Disposing of Patent Rights XIII, About Infringements. XIV, Points about Foreign Patents. XV, Thoughts on Invention and Inventors. XVI, The Present Status of Inventions.

There is an appendix containing some sixty pages of abridgments of decisions which is of little, if any, practical value for the class to which the book is directed. At the back of the book are given a few forms for preparing assignments, etc.; those relating to Patent Agreements with Employees are of value and would save much confusion and bad feeling if universally followed.

S. C. MASTICK

**The Flotation Process.** By T. A. RICKARD. 364 pp. Illustrated. Mining & Scientific Press, San Francisco. Price, \$2.00.

This book has been prepared to meet the need of the hour, and the author can be congratulated on having so satisfactorily filled the requirement. Flotation is of such importance in the metallurgical treatment of ore that this compilation by Rickard will be a most welcome addition to the literature on the subject.

In the opening chapter, the paper entitled "The Flotation Process," written by the editor, we find a most interesting description of the process given in such a way that the theory of the subject can be readily understood even by the uninitiated. The paper covers the physics, the various processes used in different times, patents, practical development, theory, and litigation. It is an excellent review of the flotation process.

Then follow a number of papers on the various phases of the process by eminent writers and practical operators, including the following subjects: Flotation Tests at Mount Morgan; Oils Used in the Flotation Process; Flotation of Copper Ores; Preferential Flotation; Flotation at the Inspiration Mine, Arizona; Flotation in a Mexican Mill; Froth and Flotation; Flotation at Washoe Reduction Works, Anaconda; Flotation at the Central Mine, Broken Hill; What is Flotation?—I; Why is Flotation?—I; What is Flotation?—II; Surface Tension and Salts in Solution; Air-Froth Flotation—I; Why do Minerals Float? Why is Flotation?—II; Air-Froth Flotation—II; Cyanide Treatment of Flotation Concentrate; Flotation on Gold Ores; The Electrical Theory of Flotation—I; Notes on Flotation; Disposal of Flotation Residue; The Electrical Theory of Flotation—II; Effects of Soluble Components of Ore on Flotation; Flotation—A Paradox; Flotation of Gold Ores; Testing Ores for the Flotation Process—I; Testing Ores for the Flotation Process—II; Molecular Forces in Flotation; Flotation Tests in Separating Funnel; Flotation Principles; The Electrostatics of Flotation; On the Science of a Froth; Smelting Flotation Concentrate; Flotation on Dump Ore; Simple Problems in Flotation.

While a certain amount of repetition is unavoidable in such a collection of papers, the benefit of having them compiled in this manner for ready reference is obvious, and this book can be recommended to any interested in flotation.

As the editor has very aptly stated in one of his articles, "The metallurgist has in the past been dependent on chemistry to guide him in considering flotation processes; he must now go back to school and acquire something more than a smattering of physics if he expects to understand the problems involved in this new process."

Not the least valuable part of the work is a carefully compiled glossary of terms used in flotation, at the beginning, and a complete index at the end.

A. L. WALKER



**A Method for the Identification of Pure Organic Compounds by a Systematic Analytical Procedure Based on Physical Properties and Chemical Reactions.** Vol. II. Containing classified descriptions of about 4000 of the more important compounds of carbon with the elements nitrogen, hydrogen and oxygen. By SAMUEL PARSONS MULLIKEN, Ph.D. ix + 327 pp. John Wiley & Sons, Inc., New York, 1916. Price, Cloth, \$5.00 net.

The general principles of classification of compounds, and the descriptions and definitions of the terms order, genus, division, section and species, and of ordinal, generic, specific and co-ordinating tests, are the same as those given in Vol. I, with which all organic chemists are familiar.

Vol. I covered the more important compounds of carbon with hydrogen or oxygen, or both; Vol. III, the dyestuffs, natural and synthetic. The present volume covers the difficult field of the nitrogenous organic compounds; and it is expected that one more volume will complete this laborious undertaking.

As compared with the previous volumes, certain changes have been made, the most important of these improvements, in the estimation of the author, being: (1) a reduction in the number of genera in Order II as contrasted with Order I, (2) an increase in the proportion of carefully verified specific characterizations, and (3) a more convenient and flexible notation and arrangement for both specific characterizations and for numbered tests.

Order II, with which this volume deals, includes all compounds of carbon and nitrogen, with or without hydrogen or oxygen, and is divided into a colorless and a colored sub-order. The colorless sub-order is composed of three genera—comprising, respectively, acidic, basic and neutral compounds; and each of these genera has a solid (Div. A) and a liquid (Div. B) division. In the case of the colored sub-order, a classification by genera is unnecessary, and the different species are arranged as elsewhere according to ascending melting-point or boiling-point.

The substances described in this volume include a large proportion of our most important drugs, many of the most interesting constituents of living organisms and their transformation products, the nitro explosives, a large number of important intermediates of the dyestuff industry, valuable photographic developers, some perfume substances, and numerous other compounds of peculiar interest.

The labor of gathering, assorting, classifying and verifying such a huge mass of material must have been enormous, and it has all been done with the most painstaking care and attention. An undertaking of this kind must obviously be largely a labor of love, for the financial return can never be at all commensurate with the immense amount of time devoted to the work. All organic chemists should express their appreciation to the author whenever opportunity offers, as he has rendered a service to his profession which those who have used the books know best how to value. No laboratory concerned with the substances with which this book deals can afford to be without it.

MARSTON TAYLOR BOGERT

**The Chemical Examination of Water, Fuel, Flue-Gases and Lubricants.** By S. W. PARR. Published by the author at Urbana, Illinois. Price, \$1.50.

This little book is avowedly a "Course for Engineering Students" at the University of Illinois, but it will appeal to many practicing engineers and chemists who wish just the essentials of these important subjects explained briefly and very simply. The title hardly does justice to the contents of the book for more than 60 per cent of the text is utilized for what is really the chemical technology of boiler water, fuel and lubricants. The second division of the book is a laboratory manual giving the simplest methods of chemical analyses. The principles of

water softening are explained, methods of calculations given and illustrations of typical plants included. The problems of combustion are discussed and especial attention is paid to the proper valuation of coals of the Illinois type with their high vein moisture and ash. The book bears silent testimony to the many contributions which Professor Parr has made to our knowledge of coal. The subjects—Classifications of coal, unit coal, corrected ash, peroxide calorimeter, bomb calorimeter, photometric sulfur determination, total carbon determination, sampling deterioration in storage, spontaneous combustion, purchase of coal on specification—are all treated with a knowledge arising from special researches which have been made by Professor Parr. The salient features of all these investigations, originally published in many journals and bulletins, are here brought together in compact form. The book is to be commended to those who, with a slight knowledge of chemistry, desire to understand the problems connected with the utilization of fuel and the generation of steam, and especially to those who are so located that they must consider whether they shall buy their coal from the Mid-continental or the Eastern field.

ALFRED H. WHITE

**Mechanical Technology.** By G. F. CHARNOCK, Professor of Engineering, City of Bradford Technical College. D. Van Nostrand Co., New York City. Price, \$3.00.

Those interested in good books on technical subjects will find this book worth reading. The author's simple treatment of the subject of woods and metals for the Arts and Crafts will appeal especially to those in shop or factory. The treatment is especially suited to industrial, technical, trade, vocational and engineering schools where students are required to become familiar with the processes for converting raw materials into workable products. The author has carefully correlated the subject matter of the text and treats methods and processes so as to group like materials. The liberal use of illustrations helps to make clear the descriptions given.

A general description of the processes used in the rolling mills, the details of wire drawing, and the rolling of steel, copper, brass and iron, and the use of the mill in shaping larger bodies of metal is included. The operations and machines are fully illustrated, and in many cases the processes of rolling metals are shown by selected cuts.

The author explains how the raw material is prepared for the rolling mill, dealing with the ore charge in the blast furnace, physical, chemical and mechanical changes which take place during the conversion of the ore to pig iron, the use of the pig for Bessemer converter, open-hearth wrought iron, and the preparation of the furnace products for making alloy steels. The chapters are brimful of illustrations of furnaces, machinery, and processes which are used for converting the raw material into useful products.

In foundry processes his descriptions include the following: green sand molds, dry sand molds, loam work, preparation of sands, and the entire processes of molding and casting. The author includes also the more modern methods of pouring all metals in cast steel and cast iron bronze, brass and aluminum; how steel dies are used for casting interchangeable parts; and a description of the alloys used for this most interesting new art of molding.

Chapter III takes up the methods of treatment that depend for their success on the properties of malleability and ductility, as possessed by wrought iron and soft steels. The machines used, such as steam hammer, drop hammer, presses and other tools, are all described and a number of illustrations are presented.

The author is to be especially complimented on the variety of the illustrative problems presented and the skill shown in describing their solutions.

C. C. STEFFEL

# NEW PUBLICATIONS

By IRENE DeMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

- Alternating Current Machinery.** R. R. LAWRENCE. 12mo. 614 pp. Price, \$4.50. McGraw-Hill Book Co., New York.
- Calcium Carbide: The Manufacture of Carbide of Calcium.** CHARLES NINGHAM. 8vo. 220 pp. Price, 5 s. Raggett & Co., London.
- Catalogue of Scientific Papers, Vol. 15.** ROYAL SOCIETY OF LONDON. 4to. 1012 pp. Price, \$12.25. University of Chicago, Chicago.
- Centrifugal Pumps and Suction Dredges.** E. W. SARGEANT. 8vo. 188 pp. Price, \$3.25. J. B. Lippincott Co., Philadelphia, Pa.
- Chemistry: A Laboratory Manual of General Chemistry.** W. C. BRAV AND L. ROSENSTEIN. 8vo. 51 pp. Price, \$0.50. Lederer, Street & Zeus Co., Berkeley, Cal.
- Chemistry of the Garden.** H. H. COUSINS. Rev. Ed. 18mo. Price, 1 s. The Macmillan Co., London.
- Dyes: A Book of Vegetable Dyes.** E. M. MAIRREY. 8vo. 153 pp. Price, 5 s.
- Electrical Engineering.** E. J. BERG. 8vo. 332 pp. Price, \$3.50. McGraw-Hill Book Co., New York.
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## INORGANIC CHEMICALS

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Alum, lump ammonia.....	100 Lbs.	4.00	@
Aluminum Sulfate, high-grade.....	Ton	70.00	@
Ammonium Carbonate, domestic.....	Lb.	9 1/2	@
Ammonium Chloride, gray.....	Lb.	10 1/4	@
Aqua Ammonium, 26°, drums.....	Lb.	5 1/2	@
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Litharge, American.....	Lb.	9 1/4	@
Lithium Carbonate.....	Lb.	1.02	@
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## ORGANIC CHEMICALS

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Acetic Acid, 56 per cent, in bbls.....	Lb.	6 1/4	@
Acetic Acid, glacial, 99 1/2%, in carboys.....	Lb.	17	@
Acetone, drums.....	Lb.	21	@
Alcohol, denatured, 180 proof.....	Gal.	60	@
Alcohol, grain, 188 proof.....	Gal.	2.70	@

Alcohol, wood, 95 per cent, refined.....	Gal.	75	@
Amyl Acetate.....	Gal.	4.00	@
Aniline Oil.....	Lb.	25	@
Benzoic Acid, ex-toluol.....	Lb.	8.50	@
Benzol, 90 per cent.....	Gal.	58	@
Camphor, refined in bulk, bbls.....	Lb.	80 1/2	@
Carbolic Acid, U. S. P., crystals, drums.....	Lb.	55	@
Carbon Bisulfide.....	Lb.	7	@
Carbon Tetrachloride, drums, 100 gals.....	Lb.	16 1/4	@
Chloroform.....	Lb.	50	@
Citric Acid, domestic, crystals.....	Lb.	67	@
Cresol, U. S. P.....	Gal.	1.36	@
Dextrine, corn (carloads, bags).....	100 Lbs.	3.95	@
Dextrine, imported potato.....	Lb.	12	@
Ether, U. S. P., 1900.....	Lb.	15	@
Formaldehyde, 40 per cent.....	Lb.	10	@
Glycerine, dynamite, drums included.....	Lb.	52 1/2	@
Oxalic Acid, in casks.....	Lb.	56	@
Pyrogallie Acid, resublimed bulk.....	Lb.	3.00	@
Salicylic Acid.....	Lb.	1.25	@
Starch, cassava.....	Lb.	—	@
Starch, corn (carloads, bags) pearl.....	100 Lbs.	2.65	@
Starch, potato.....	Lb.	6	@
Starch, rice.....	Lb.	8	@
Flour, sago.....	Lb.	4 1/2	@
Starch, wheat.....	Lb.	6	@
Tannic Acid, commercial.....	Lb.	65	@
Tartaric Acid, crystals.....	Lb.	67	@

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Beeswax, pure, white.....	Lb.	40	@
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Ceresin, yellow.....	Lb.	10	@
Corn Oil, crude.....	100 Lbs.	\$11.25	@
Cottonseed Oil, crude, f. o. b. mill.....	Gal.	normal	@
Cottonseed Oil, p. s. y.....	Lb.	11 3/4	@
Creosote, beechwood.....	Lb.	2.75	@
Cylinder Oil, light, filtered.....	Gal.	21	@
Fusel Oil, crude.....	Lb.	3.75	@
Japan Wax.....	Lb.	15	@
Lard Oil, prime winter.....	Gal.	1.12	@
Linsed Oil, raw (car lots).....	Gal.	87	@
Menhaden Oil, crude (southern).....	Gal.	53	@
Naphtha, 68 @ 72°.....	Gal.	33 3/4	@
Neat's-foot Oil, 20°.....	Gal.	1.10	@
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Paraffine Oil, high viscosity.....	Gal.	29 1/2	@
Rosin, "F" Grade, 280 lbs.....	Bbl.	6.90	@
Rosin Oil, first run.....	Gal.	38	@
Shellac, T. N.....	Lb.	31	@
Spermaceti, cake.....	Lb.	24	@
Sperm Oil, bleached winter, 38°.....	Gal.	80	@
Spindle Oil, No. 200.....	Gal.	24	@
Stearic Acid, double-pressed.....	Lb.	13 1/2	@
Tallow, acidless.....	Gal.	88	@
Tar Oil, distilled.....	Gal.	35	@
Turpentine, spirits of.....	Gal.	47	@

## METALS

Aluminum, No. 1, ingots.....	Lb.	64	@
Antimony, ordinary.....	Lb.	13	@
Bismuth, N. Y.....	Lb.	3.05	@
Copper, electrolytic.....	Lb.	27 1/2	@
Copper, lake.....	Lb.	27 1/2	@
Lead, N. Y.....	100 Lbs.	7.00	@
Nickel, electrolytic.....	Lb.	45	@
Nickel, shot and ingots.....	Lb.	50	@
Platinum, refined.....	Oz.	85.00	@
Silver.....	Oz.	67 1/2	@
Tin.....	Lb.	41 1/2	@
Zinc, N. Y.....	100 Lbs.	\$10	@

## FERTILIZER MATERIALS

Ammonium Sulfate.....	100 Lbs.	4.00	@
Blood, dried F O B Chicago.....	Unit	3.30	@
Bone, 4 1/2 and 50, ground, raw.....	Ton	28.50	@
Calcium Cyanamid.....	Unit of Ammonia	—	@
Calcium Nitrate, Norwegian.....	100 Lbs.	—	@
Castor Meal.....	Unit	—	@
Fish Scrap, domestic, dried, f. o. b. works.....	Unit	3.80	@
Phosphate, acid.....	Ton	10.00	@
Phosphate rock; f. o. b. mine:			
Florida land pebble, 68 per cent.....	Ton	2.75	@
Tennessee, 78-80 per cent.....	Ton	5.00	@
Potassium "muriate," basis 80 per cent.....	Ton	450.00	@
Pyrites, furnace size, imported.....	Unit	15 1/2	@
Tankage, high-grade; f. o. b. Chicago.....	Unit	3.00	@

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## EDITORIALS

### THE NEW EDITOR

The editorship of the JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY passes with this issue to Charles Holmes Herty. Every officer and counselor of the Society present at the meeting at which the future policy and management of the Industrial Journal were under serious consideration, will remember with pride the genuine and deep-seated enthusiasm which greeted the announcement that Dr. Herty would accept this important duty. The perplexing problems of the future of this publication and the relations it should hold to those inside and outside of the great and growing chemical profession became clearly defined and took form and direction with his unselfish response to the demands of the Society.

Dr. Herty does not assume the duties of the editorship for the purpose of enhancing his personal reputation, but purely in a spirit of generous desire to advance the interests of chemistry in America. His achievements in education, business, public service and the Presidency of the American Chemical Society admirably demonstrate capacity for leadership. Such a record of distinguished service in the profession is a firm foundation upon which to build a useful and highly successful editorial career. In addition there is his charming personality, a wide and cordial acquaintance, a familiarity with the aims and needs of his fellow chemists, decision, action, the courage of his scientific and common-sense convictions, and a sincere desire to do constructive service in the interests of his profession. These are priceless assets for an editor.

A measure of credit is due those who have worked so faithfully, and at times without a full appreciation of the difficulties involved, to bring the Journal to its present state of development. To Dr. Richardson, who started the Journal from the nebulous suggestions which always accompany the launching of such an enterprise, and who sifted out the meager supply of real building material and resources for development which were then available, the Society owes the greatest debt. A successful enterprise requires as essential elements of its success, a definite policy, an organization, and ample resources. The most conspicuous characteristic of this enterprise during its early history was the absence of the two last-named elements.

Our present state of progress has been due entirely to the patient indulgence of the officers and members of the Society during the developmental stages of the Journal; the unselfish and often thankless task of the *Associate Editors* who have improved, by their expert study and criticism, the original papers; the *Assistant Editor* who has standardized the management of the editorial office work; the *Advertising Managers*, who have shown the Society how to realize upon the advertising possibilities of its publications; the printer and his remarkable staff of expert technical compositors, proof-readers and printers; the regular staff writers; and most of all those investigators and

chemical engineers who publish with us the results of their observations and researches.

This is an auspicious occasion for the American Chemical Society. A broadening business sense is discernible in the development of its publications. For the first time in its history the Industrial Journal is working to a definite creed, formulated, considered and adopted by the governing body of the Society. The publication is now given financial support, an adequate office for the transaction of its editorial and advertising business, a permanent organization and a policy—all essential elements in building up a technical publication fittingly to represent the interests of the American chemical profession.

Under the guidance of Dr. Herty, so eminently qualified to direct its editorial policies into channels which will inure to the benefit of the chemical profession in its broadest sense, the future of the Industrial Journal seems assured.

### OUR NITROGEN DEMAND AND SUPPLY IN THE EVENT OF WAR

We have carefully followed the discussion of the nitrogen question, in which general public interest has been intensified by the recent Nitrogen Bill appropriating \$20,000,000 for a Government nitrate plant. The purpose of this legislation was to insure the country a dependable supply of nitric acid for military explosives in the event of war.

Public discussion of the question has developed so little in the way of a quantitative analysis of the relation between the nitrogen supply and demand, in the event of war, that we believe our readers will be interested in a graphic presentation of this relation under normal conditions, and a forecast of what may be expected in the event of war.

The situation which Congress and the Administration planned to meet is that condition where, by reason of enemy attack at sea, by the scarcity of ocean craft, or for other reasons, the country is cut off from importations of nitrogenous materials.

The accompanying diagram is for the most part self-explanatory: the sources of information are indicated for every figure given, while the few simple assumptions made are clearly set forth in the references.

The figures show unmistakably that in the event of war, the United States will face an imperative demand for over 309,000 tons of nitrogen with a prospective supply of only 77,000 tons. Thus the demand is seen to be four times as great as the supply. Our belief that this condition will not be radically altered by development of by-product ammonia is based upon the published statements of recognized coke-oven authorities. Such estimates indicate that the country's annual production cannot exceed, within a period of time pertinent to this discussion, 100,000 to 140,000 tons of nitrogen. The obvious and available remedy is the establishment of an adequate air-nitrogen industry in the United States.

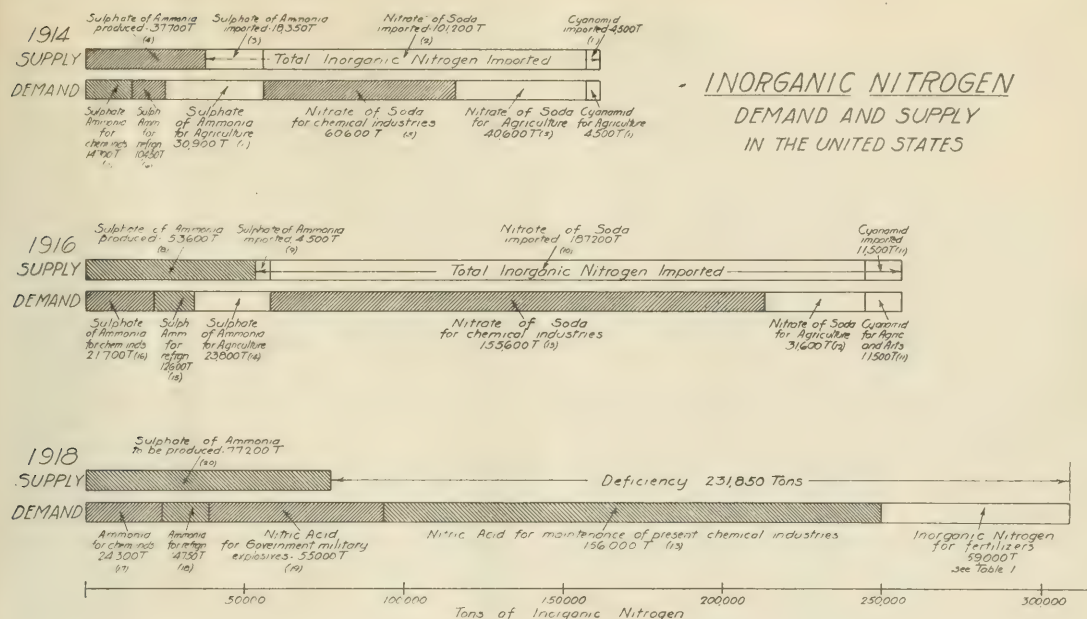


TABLE I.—PRODUCTION AND REQUIREMENTS OF NITROGEN FOR AGRICULTURE IN TONS OF NITROGEN

REQUIREMENTS	1914 Ref.	1918 Ref.
<b>Cottonseed Meal</b>		
Feed.....	63,500 (5)	
Fertilizer.....	54,400 (5)	
<b>Other Organic Ammoniates</b>		
Feed.....	8,000 (5)	
Fertilizer.....	69,700 (22)	
<b>Inorganic Ammoniates</b>		
Nitrate of Soda.....	40,600 (5)	
Sulfate of Ammonia.....	30,900 (1)	
Cyanamid.....	4,500 (1)	
<b>Summary:</b>		
Feed.....	71,500	71,500 (23)
Fertilizer.....	200,100	178,000 (24)
<b>Total.....</b>	<b>271,600</b>	<b>249,500</b>
<b>PRODUCTION</b>		
Cottonseed Meal.....	164,500 (5)	123,500 (26)
Other Organic Ammoniates.....	61,700 (25)	67,000 (27)
Sulfate of Ammonia.....	12,600 (28)	*
	237,800	
<b>IMPORTS (Net)</b>	<b>33,800 (29)</b>	
<b>TOTAL SUPPLY.....</b>	<b>271,600</b>	<b>190,500</b>
<b>DEFICIENCY which must be supplied as inorganic nitrogen... 59,000 Tons</b>		

\* Assumed all used in arts.

## REFERENCES

- (1) "Bureau of Commerce Census of Manufactures—Fertilizer Industry," released July 6, 1916.
- (2) "American Fertilizer Handbook," 1916, p. 31.
- (3) *Ibid.*, p. 43.
- (4) *Ibid.*, p. 42.
- (5) "Federal Trade Commission Report on Fertilizer Industry," issued August 19, 1916, pp. 29, 30.
- (6) "Mineral Resources of the U. S., 1914," p. 408.
- (7) Total consumption less amount used in refrigerating industry—(Ref. 6).
- (8) 1915—45,300, Ref. 2, p. 42, plus 8,300 increase for 1916, W. H. Childs, *Mel. & Chem. Eng.*, July 1, 1916, p. 39.
- (9) Basis 21,950 short tons sulfate of ammonia imported during fiscal year ending June 30, 1916. See Foreign Commerce Reports—quoted, *The American Fertilizer*, September 16, 1916.
- (10) 1,200,335 short tons nitrate of soda imported fiscal year ending June 30, 1916. See *Oil, Paint & Drug Reporter*, August 26, 1916.
- (11) Basis production of 64,000 tons cyanamid at 18 per cent nitrogen.

## INORGANIC NITROGEN

### DEMAND AND SUPPLY

#### IN THE UNITED STATES

(12) Basic Total Fertilizer Consumption as follows in tons:

	1914	1915	1916*
Northern States.....	2,742,133	2,833,829	3,120,000*
Southern States.....	4,887,095	3,036,854	2,828,000
<b>Total.....</b>	<b>7,629,228</b>	<b>5,870,683</b>	<b>5,948,000</b>

\* Estimated normal 10 per cent increase from 1915 forward.

See also U. S. Dept. of Agric., *Monthly Crop Report*, July, 1916, and Ref. 2, p. 41. Assume 1916 Nitrate of Soda consumption in agriculture is to 1914 consumption as total fertilizer tonnages in these years, or 78 per cent. This gives 200,000 tons nitrate of soda consumed in agriculture in 1916. Regarding latter assumption see *Monthly Crop Reporter*, October, 1916, p. 100.

(13) Imports minus consumption in agriculture, Refs. 10 and 12. That consumption in the arts is at least at this rate is substantiated by export statistics on explosives, and by private information on the rate of nitric acid consumption by munitions manufacturers.

(14) Assume sulfate of ammonia consumption in agriculture proportional to total fertilizer consumption in 1916 and 1914, respectively, as in Ref. 12. 78 per cent of 149,924 equals 115,500 tons sulfate of ammonia for agriculture in 1916.

(15) Ref. 6, assuming 1914–1916 increase same per year as from 1909 to 1914, U. S. Census of Manufactures, 1910, p. 546.

(16) Imports plus production, minus consumption in agriculture and refrigeration.

(17) 1916 consumption (Ref. 16), plus average annual increase 1909–1914 (U. S. Census of Manufactures, 1910 and Ref. 7) of 1300 tons of nitrogen per annum for 2 years.

(18) Ref. 15 plus two years average annual increase 1914–1916.

(19) Germany's requirements at the outbreak of the war, as determined by the U. S. War Department; now very greatly increased.

(20) W. H. Childs, *Mel. & Chem. Eng.*, July 1, 1916, p. 39.

(21) Assuming all imports cut off.

(22) Consumption organic ammoniates, excluding cottonseed meal (Ref. 1).

	Tons	Value
Tankage and ammoniates not elsewhere specified.....	887,934	\$20,131,141
Fish.....	250,110	3,111,991
Bone, raw, ground, steamed, etc.....	148,191	3,410,545
Guano.....	120,128	445,416

Assume average value of 33.20 per unit of ammonia including P <sub>2</sub> O <sub>5</sub> present (Ref. 5, p. 147)	1,406,363	\$27,099,093
	Per cent N	Units N:H
	4.95	8,460,000
		Tons N, 69,700

(23) Assumed same as in 1914.

(24) Ref. 12, assume 10 per cent increase per annum from 1916 in North, as before war, and assume 1918 war basis same as 1915 in South, or total 6,780,000 tons = 89 per cent of 1914.

(25) Ref. 22—deduct for imported organic ammoniates a value of \$6,200,000 (Ref. 2, pp. 21, 24, 26, 32) 1,950,000 units of ammonia = 16,000 tons nitrogen. Add 8,000 tons for feed. Ref. 5, p. 73.

(26) Taken same as 1915 (Ref. 2, p. H-6).

(27) Ref. 25 plus normal annual increase (Ref. 1).

(28) Consumption in agriculture (Ref. 1) minus imports, Ref. 2, p. 43.

(29) Imports of agricultural nitrate of soda, sulfate of ammonia, cyanamid and "other organic ammoniates," minus exports of cottonseed meal.



## ORIGINAL PAPERS

THE PRODUCTION OF THE LOWER CHLORIDES OF METHANE FROM NATURAL GAS<sup>1</sup>

By CLAYTON W. BEDFORD

Received July 21, 1916

The large amount of methane available in the form of natural gas has made the transformation of the same into chloroform an attractive problem. The low cost of carbon tetrachloride from other sources, along with the fact that in the chlorination of methane half of the halogen goes to form hydrogen chloride, has made the formation of the tetrachloride from methane less interesting.

Baskerville and Hamor<sup>2</sup> have very completely covered the literature on this subject, as well as the manufacture of chloroform from materials other than methane. The following references, however, are repeated, since they are closely related to this article. Berthelot,<sup>3</sup> in 1858, showed that unless the reaction between chlorine and methane was carried out with extreme slowness, explosions and the separation of carbon easily resulted. Phillips,<sup>4</sup> in 1893, tried to avoid explosions by chlorinating methane, without the access of light, in a tube heated to 300–400° C., and finding that only the first and last chlorides of the series were formed in appreciable amounts, he questioned<sup>5</sup> the successful chlorination to intermediate products. Tolloczko,<sup>6</sup> in 1912, also working in hot tubes, obtained results similar to Phillips. Walter,<sup>7</sup> in 1909, states that water vapor cuts down the speed of chlorination considerably, and if the chlorine is added gradually that it reacts more readily with the partially chlorinated methane than with the original hydrocarbon, the result being the highest chlorine substitution possible. Baskerville and Riederer<sup>8</sup> cite the work of Phillips and Walter and seek to obtain chloroform indirectly by chlorinating methane to the tetrachloride and then reducing. They also show that the blue end of the visible spectrum is more suitable for use in chlorination than ultraviolet rays. Graul and Hanschke,<sup>9</sup> in 1912, state that the chlorination of ethane in diffused daylight, as carried out by Schorlemmer,<sup>10</sup> in 1869, is impractical, since at low temperatures the halogen reacts very slowly.

Thermochemical calculations<sup>11</sup> predict a rise of over 2000° C. for the reaction of a mixture of methane and chlorine in the proportions to form carbon tetrachloride, provided all the heat of reaction goes to increase the temperature of the reaction products;

for equal volumes of methane and chlorine, the rise calculated for  $\text{CH}_3\text{Cl}$  is over 1700°; for a mixture of 5 vols. methane : 1 vol. chlorine, the theoretical rise is nearly 600° so that even with this high dilution of the gases, if the reaction were carried out in a tube already heated to 400°, the resulting temperature would approximate 1000° C. At or above 1000° C., methane and its derivatives will decompose, and Phillips states that he frequently observed the deposition of carbon inside his heated tube.

A mixture of 4 vols. of chlorine with 1 vol. methane, the theoretical proportions to form carbon tetrachloride, when exposed to direct sunlight in glass tubes of small diameter, will not give a violent reaction and if the air is cold, the reaction will proceed slowly. The gases are so closely in contact with the tube walls that any heat liberated is radiated at once and the temperature cannot rise to that of speedy reaction even in direct sunlight. A mixture of chlorine and methane, in the same proportions in a large balloon flask and in direct sunlight, will explode with great violence. The interior of the gas body, being heat-insulated by the surrounding layers of gas, quickly comes up to the temperature of speedy reaction and then rises suddenly to 1000° C. or higher, where carbonization begins to take place.

At temperatures even as low as 100° C., all of the chlorine derivatives of methane will remain in the vapor state and with chlorine showing a preference for the partially chlorinated hydrocarbon, the intermediate compounds cannot easily be obtained. The problem, therefore, is to obtain a speedy chlorination of methane while maintaining an average temperature low enough to condense out the chloroform before it can be chlorinated further.

At high temperatures no light is necessary to induce the reaction between chlorine and methane. In order to maintain a low temperature, the amount of free chlorine in the gases at any time must be correspondingly low, and the lower the content of the chlorine, the stronger the light necessary to induce a speedy reaction at this low temperature. It therefore became evident, from a few preliminary experiments, that the successful solution of the problem was partly dependent on the use of a sufficiently powerful light. The "White Flame Arc," as described by Mott and Bedford,<sup>1</sup> was found to be the most satisfactory source of light and was used in all of the following work.

One volume of chlorine in seven volumes of natural gas will react quickly in the presence of light from the "White Flame Arc" but without explosion. If reactions with fresh quantities of chlorine be repeated, the speed of the reaction finally slows down as the residual gas becomes diluted with chlorine, hydrogen chloride, nitrogen, air, etc., until finally no more reaction will take place without the aid of external heat.

The effect of concentration of free chlorine on the

<sup>1</sup> Mott and Bedford, *THIS JOURNAL*, **8** (1916), 1029.

<sup>1</sup> Patent applications have been made, covering the work outlined in this article.

<sup>2</sup> *THIS JOURNAL*, **4** (1912), 216.

<sup>3</sup> *Ann. chim. phys.*, [3] **52** (1858), 98.

<sup>4</sup> *Am. Phil. Soc.*, March 17, 1893.

<sup>5</sup> *Am. Chem. J.*, **16**, 362.

<sup>6</sup> *Abhandl. Krakau. Wiss.*, **1912**; *J. Soc. Chem. Ind.*, **32** (1913), 742.

<sup>7</sup> German Patent 222,919, November, 1909.

<sup>8</sup> *THIS JOURNAL*, **5** (1913), 5.

<sup>9</sup> U. S. Patent 687,454.

<sup>10</sup> *Ann.*, **150**, p. 217.

<sup>11</sup> Using 21,000 as the heat in the formation of carbon tetrachloride. (See "Thermochemistry," Thomsen-Ramsay series, p. 246.) Berthelot and Matignon give 68,500 as the heat of formation of carbon tetrachloride, which gives a value of over 3000° C. in the above calculation.

chlorination of methane was studied in the following manner: Natural gas was confined in a bell jar over water at about 20° C. and chlorine was added by bubbling it in through the water. A uniform mixture of the gases was obtained by shaking the jar and splashing the water. The access of diffused daylight, during the short period, produced little or no reaction as long as the percentage of chlorine in the gases was low. Upon suddenly exposing to the light from the "White Flame Arc" there was an instantaneous expansion of the gases, even when the chlorine content was small. After the reaction, the water was shaken up through the gases, thereby cooling them, removing the hydrogen chloride and condensing such reaction products as were liquids at the temperature of the water.

Fig. 1 shows the results of chlorinating natural gas, while confined over water at room temperature, the chlorine being added in increments of either 500, 250,

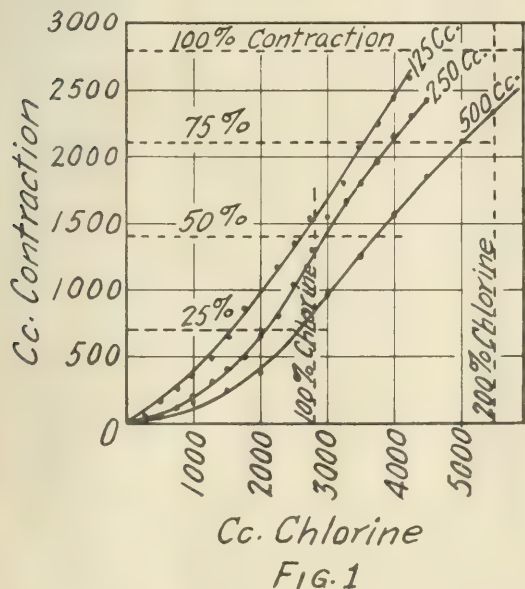
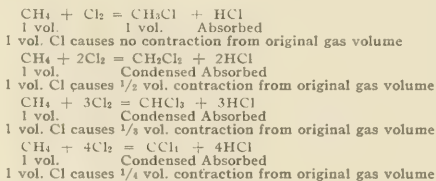


FIG. 1

or 125 cc. After mixing the gases, they were exposed to the light and then cooled by shaking up with the water. After each cycle of operations, the volume of the residual gas was noted and its contraction from the original gas volume calculated. Before the experiments were started the water was saturated with chlorine and with natural gas; the slight increase in temperature of the water, during the reaction was found to aid rather than hinder the process. Starting with three liters of natural gas, there was always an unreactive residue of about 200 cc., showing that about 2800 cc. would react with the chlorine under these conditions.

The horizontal dotted lines in Fig. 1 represent percentages of the total contraction obtained and aid in the study of the curves. The vertical dotted lines represent volumes of chlorine equal to and twice the total contraction in gas volume.

By the following equations, it is shown that the greater the contraction of the original gas, caused by a given amount of chlorine, the greater will be the amount of low boiling constituents in the reaction product.



It therefore becomes evident that since methyl chloride is a gas, a given volume of chlorine should not produce a contraction from the original gas volume of more than one-half the volume of the chlorine added. In the curve obtained by using 125 cc. of chlorine at a time, this actually took place, 4000 cc. of chlorine producing a gas contraction of nearly 2500 cc. This was evidently due to the solution of methyl chloride in water, in which it is quite soluble and with which the water had not been saturated, previous to the experiments.

It is noted from the curves, that the reaction of 125 cc. of chlorine at a time, with the more frequent coolings and the lower average temperature, caused a greater contraction for the same amount of chlorine than when 250 or 500 cc. were added at each time. Theoretically, therefore, for the production of the lower chlorides of methane, the chlorine should be added in extremely small increments and the reaction should be complete and the heat of reaction dissipated before the addition of the fresh chlorine. This condition is closely approximated by the continuous addition of chlorine in the presence of excessive cooling and under the influence of a very powerful light.

It is true that the presence of ethane in the natural gas, as used, somewhat complicates the study of the curves, but since ethyl chloride is gaseous above 12° C. and the di-chlor product is easily liquefied, very little difference is to be expected in the character of the lower parts of the curves.

These curves also prove that the lower chlorides of methane may be condensed out and removed from the field of action before the tetrachloride is formed. Moreover, the analysis by distillation, of the reaction product which separated out under the confining water, showed the liquid to be about half chloroform. A second experiment with the natural gas confined over water at about 80° C. resulted in a product containing almost entirely carbon tetrachloride as far as the methane derivatives were concerned. A third experiment, using water at from 10° to 15° and shaking it up through the gases during the reaction, gave a product which consisted of 6 parts of chloroform to every 5 parts of carbon tetrachloride, besides ethane chlorides.

These, along with many other preliminary tests, led to the following conclusions:

1—At low temperatures, each of the four chlorides of methane form in turn from the preceding member



of the series, chlorine showing a slight preference for chlor-methanes over the hydrocarbon itself.

2—The heat liberated by the reaction of dilute mixtures of methane and chlorine may easily raise the temperature of the gases to the decomposition point where different laws govern the reaction.

3—Efficient cooling will condense the chloroform and remove it from the field of reaction before it chlorinates further.

4—The lower the temperature at which the reaction takes place, the more actinic the light required to maintain the reaction for a given concentration of free chlorine.

5—Water does not hinder the reaction but on the contrary speeds it by removing the reaction products and bringing the reacted gases into more intimate contact.

6—The slightest trace of ammonia or similar nitrogen compounds stops the reaction until a high concentration of free chlorine overpowers the negative catalyst, when a disastrous explosion results.

#### ICE AS A COOLING AGENT

The attempt to obtain better cooling in order to prevent entirely the formation of tetrachloride, finally led to the carrying out of the reaction in the inter-

many trials and variations in the apparatus, the one shown in Fig. 2 solved the difficulty.

An 8-liter, two-neck Woulfe flask, with the bottom removed, was placed over a single ice cake chipped to nearly fill the flask. As the ice melted in the top of the reaction chamber, the flask settled upon it keeping ice in the top of the chamber where the cooling is most needed, until the bottom of the flask touched the bottom of the vat, whereupon the ice melted away from the top of the flask and allowed gradual increase in the volume as well as in the temperature of the gas above, until carbonization took place. The dotted lines show the points of highest temperature as shown by the melting of the ice. Upon starting the reaction, by means of the White Flame Arc light, with the chlorine content of the gases about 1 in 8, the circulation was found to be rapid and violent. The gases passed upward on the side next to the light, drawing the cold gases from around the ice cake below. The ice did not melt on the side of the light as fast as had been expected, due to the high velocity of the gases. The addition of fresh and cold chlorine gas at the top and back of the apparatus aided in the downward motion at the rear, due to the high specific gravity of the chlorine. Fresh gas was added at the top and front. The reaction was continuous and speedy, the

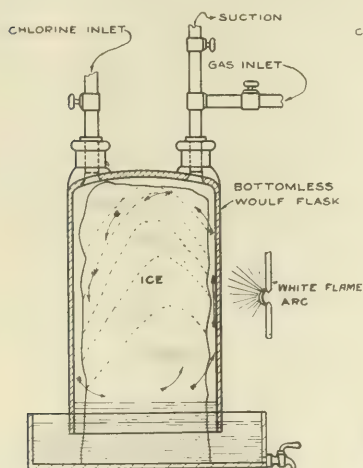


FIG. 2

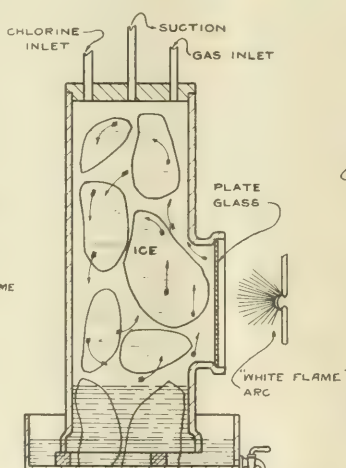


FIG. 3

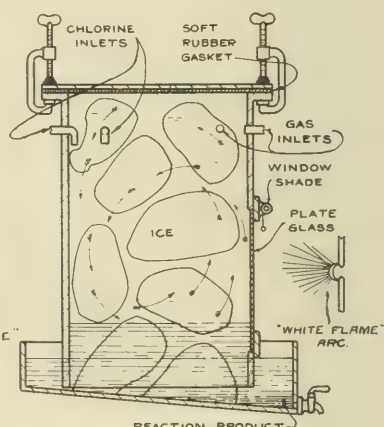


FIG. 4

stices between cakes of ice. It was predicted that by filling the reaction chamber with cracked ice, we should obtain only the di- and tri-substitution products, since methyl chloride is a gas at the temperature of ice and the others should condense out before forming the tetrachloride.

The first experiment in the chlorination of methane in the spaces between cracked ice presented the difficulty of improper gas circulation. The gases directly exposed to the light would react at once but further action took place only as the chlorine slowly diffused toward the light. The content of chlorine was increased until with a mixture of 4 vols. chlorine : 1 vol. methane, an explosion resulted, even in the presence of ice cakes the size of hen's eggs or smaller. After

amount of the two gases admitted being regulated according to the height of the water level below. As the gas was chlorinated and condensed the volume grew less and more gas was added. When the volume continually increased it indicated that either too much gas or too little chlorine was being admitted. A balance was easily obtained and the reaction proceeded until the ice had melted too low to be effective. It was found that 2.6 cu. ft. of natural gas gave 166 cc. of reaction product which is equivalent to about 17 gal. per 1000 cu. ft. This included the methylene chloride and chloroform dissolved in the water, which were separated by distillation. The methyl chloride in the water was not recovered.

The apparatus shown in Fig. 3 was designed to

prevent the access of light to the large volume of gas left in the top of the reaction chamber by the melting of the ice and also to furnish a larger supply of ice per charge. A 10 in. sewer pipe "tee," with the side outlet near the bell end, was supported on three bricks and set in a vat of water. The side outlet was closed with a circular piece of plate glass sealed in with litharge-glycerine cement. The tile was filled with pieces of ice the size of coconuts or larger and the top closed with a wooden lid made gas-tight by rubber coverings. After removing the air by suction through an opening in the lid, natural gas and chlorine were admitted at the same relative points as in Fig. 2. The use of large pieces of ice left larger spaces between them and the gas circulation was not interfered with. Immediately after or even during the reaction, which started next to the glass, the gases passed up into the dark ice chamber above and any reaction product higher than methyl chloride was removed by condensation; the unreacted gas then mixed with a fresh supply of chlorine, passed down at the rear to be drawn forward and upward into the light for a second reaction. The melting of the ice in the upper part of the tile and the increasing amount of the gases collecting there, in no way interfered with the reaction or the circulation of the gases. The warm gases rose at the front and on being cooled and mixed with the heavy chlorine, they dropped down at the rear only to be drawn forward to replace the reacted gas in front of the window. At first it was feared that the ice might deflect the light rays upward into the gas chamber above and cause an explosion or at least undesirable reactions, but no trouble in this respect was experienced and not until the ice had melted down below the level of the window was it necessary to interrupt the reaction to supply a fresh charge.

The capacity of the tile was found to be about  $3\frac{1}{4}$  cu. ft. of gas per hr. and a total of 18.5 cu. ft. gave 1.1 liters of product having the following composition by volume (percentages).

Methylene Chloride	Chloroform	Carbon Tetrachloride	Ethane Products
35.5	47.5	4.0	13.0

The reaction is necessarily an intermittent one as all non-reacting gases collect in the chamber and must be removed from time to time. The ice also must be replaced but this might be accomplished without interrupting the process.

Fig. 4 shows a large wooden reaction chamber, 28 in.  $\times$  28 in.  $\times$  44 in. inside dimensions, built for the carrying out of the reaction on a larger scale, and duplicating that of Fig. 3 with the addition of a shade for the covering of the upper part of the glass window and with the sloping of the vat for the better separation of the reaction product. Instead of removing the air by suction it was replaced by running in natural gas for some time before the admission of the chlorine. The wooden apparatus was made gas-tight and also protected from the action of chlorine by the application of several coats of cellulose acetate dissolved in methylene chloride or chloroform. It may be said here that only very pure methylene chloride

or chloroform will dissolve cellulose acetate and that the reaction product inside of the chamber had very little effect on the coating.

In one experiment using 250 cu. ft. of natural gas, the rate of consumption varied from 14 to 30 cu. ft. per hr. and several gallons of product resulted. The analysis of the liquid reaction product separating out under water was as follows, percentages being by volume:

Methylene Chloride	Chloroform	Carbon Tetrachloride	Ethane Chlorides
35	35	5	20

The analysis of the part soluble in the water and separated by distillation was:

Methylene Chloride	Chloroform	Carbon Tetrachloride	Ethane Chlorides
61	28	1.5	6

About 14 per cent of the reaction product dissolves in the water produced from the melting of ice by the heat of the reaction. This soluble portion may be entirely recovered by distilling off 5 per cent to 10 per cent of the water, the methane chlorides coming over with the distillate, and the residue being about a 5 per cent solution of hydrochloric acid provided no water has been added except that produced by the melting of ice. About 135 lbs. of ice are necessary for the production of one gallon of product having the composition as given above and the HCl from the reaction is thereby greatly diluted.

#### WATER AS THE COOLING AGENT

With the object of recovering the HCl in a concentrated form, experiments were made using water as the cooling agent and dripping or spraying it through the gases during reaction. By repeated use and re-cooling of the same water it was hoped that a concentrated acid could be obtained. The reaction proceeded as before but the method was found to be inferior to ice cooling for the following reasons:

1—The latent heat of melting ice is not available when using water as the cooling agent.

2—Efficient contact between the water and the gases is necessary but difficult to obtain.

3—It was found impossible to obtain strong acid and at the same time remove all of the HCl from the gases as fast as it was formed.

4—The use of the water as the cooling agent greatly complicates the apparatus necessary for the reaction.

#### REACTION PRODUCTS OTHER THAN CHLOROFORM

Methylene chloride, which can be made in large quantities by this method, is valuable in and of itself, being an excellent solvent for cellulose acetate and very nearly duplicating the properties of chloroform in every respect. As an anesthetic it is said to excel chloroform because of its higher volatility and lesser action on the heart. The U. S. Dispensatory, 19th edition, says that for anesthesia "it is probable that methylene chloride has advantages over chloroform, but the high price of the pure drug must interfere with its use."

The greatest value of methylene chloride will probably lie in the production of chloroform. In a liquid state, methylene chloride is easily transformed into



chloroform by passing in chlorine gas assisted by sunlight or even by the light from 150 watt tungsten lamps. The temperature cannot rise above the boiling point of the liquid and no catalysts are necessary. The formation of carbon tetrachloride is avoided by chlorinating until only about 10 per cent of the methylene chloride has been reacted upon and then separating the chloroform by distillation.

Methyl chloride up to 40 per cent has been found in the gases removed from the ice chamber during the first few minutes after starting to chlorinate natural gas. It is easily isolated by compression or by solution in water or other solvents and this method presents a commercial method for its manufacture. Its use would probably be greatly increased by the development of a cheap and easy method of production.

RESEARCH LABORATORIES  
THE GOODYEAR TIRE & RUBBER COMPANY  
AKRON, OHIO

### THE RELATION BETWEEN THE TOXICITY AND THE VOLATILITY OF CREOSOTE OILS

By ERNEST BATEMAN  
Received October 18, 1916

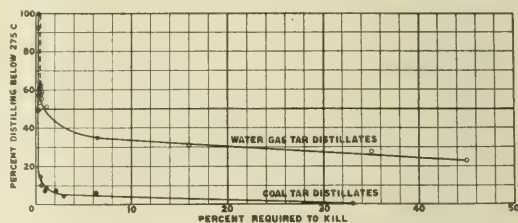
During the last few years considerable attention has been given by various workers on creosote oils and other wood preservatives to the question of toxicity. J. M. Weiss,<sup>1</sup> Dean and Downs,<sup>2</sup> Humphrey and Fleming,<sup>3</sup> and others have accumulated considerable data on this subject.

The two most important sources of oils used for wood preservation are coal tar and water-gas tar. The oils obtained from these by distillation are usually called creosotes or distillates. In the course of a study of the literature on the toxicity of these oils the writer was struck by the fact that it depended a great deal on the boiling point, or, more properly speaking, on the volatility of the oils used, whether or not coal-tar creosote was more toxic than water-gas tar distillates. For instance, J. M. Weiss showed that American creosote (77 per cent distilling at 270° C.) was slightly more toxic than German creosote (36 per cent distilling at 270° C.) but that they both were more toxic than water-gas tar distillate (50 per cent distilling at 270° C.). In another article he shows that water-gas tar distillate No. 21 (50 per cent distilling at 270° C.) was more toxic than coal-tar creosote No. 10 (8.5 per cent distilling below 270° C.). Dean and Downs showed that coal-tar creosotes marked "A" (58 per cent distilling at 300° C.) and "B" (distillation limits not given) and water-gas tar distillate marked "C" (78 per cent distilling at 300° C.) had about the same toxicity, while water-gas tar distillate marked "D" (distillation limits not given) was slightly more toxic than all three. But all four of above oils were more toxic than expressed anthracene oil (distillation limits not given but certainly much less volatile than the other oils). Humphrey and Fleming show that water-gas tar distillate No. 2235 (62 per cent dis-

tilling below 275° C.) is much more toxic than Fraction IV coal-tar creosote (4.7 per cent distilling below 275° C.) or Fraction V coal-tar creosote (O distilling below 275° C.) and the carbolineum No. 1843 (6.1 per cent distilling below 275° C.). On the other hand, they also show that all the coal-tar products tested were more toxic than water-gas tar distillate No. 1101 (16.3 per cent distilling below 275° C.).

A study of all of the toxicity data available show that out of these apparently conflicting results a very definite and logical order can be established if the volatility of the oils in question is coordinated with their toxicity. It is the purpose of this paper to show this relation.

For all practical purposes the percentage of oil distilling below 275° C. is a good measure of the comparative volatility of creosote oil.<sup>1</sup> This point has been taken as a measure of the volatility of the creosotes and a curve has been plotted using this figure as one coordinate and the killing point against *Fomes annosus* (Humphrey and Fleming) as the other coordinate. As a result, two curves are obtained—one for coal-tar creosote and the other for water-gas tar distillates. These are shown in the accompanying cut. Data from other sources could not be included because different organisms have a somewhat different action.



A careful study of tests using other organisms, however, shows that the general finding is the same, although the numerical values may be quite different.

The accuracy of these curves has been proved in a measure in the following manner:<sup>2</sup> Creosotes whose toxicity has not hitherto been tested were analyzed and their toxicity was predicted from their volatility, with the following results:

Kinds of Creosote	KILLING POINT	
	(As estimated from curve)	(As determined by test)
Coal-tar oil No. 1.....	0.6%	-0.5%
Coal-tar oil No. 2.....	0.75%	0.8%
Coal-tar oil No. 3.....	1.0%	1.1%
Water-gas tar oil No. 1.....	17.0%	16.0%

The above indicates that the killing point can be determined as accurately from a consideration of the distillation as it can be from toxicity tests, provided that the authenticity of the oil is without question. The curves are of considerable interest aside from merely predicting the toxicity. They suggest—first, a possible method of determining the purity of oils, perhaps by some short test as the Rideal-Walker test on the high boiling fractions; and second, that much

<sup>1</sup> See Forest Service, *Circ.* 112.

<sup>2</sup> My thanks are due to Miss Ruby Tiller and Mrs. Ruth Fleming, Assistants in Pathology, Bureau of Plant Industry, of this laboratory, for supplying me with the data on toxicity which were necessary to prove the correctness of the relationship here shown.

<sup>1</sup> *J. Soc. Chem. Ind.*, 30 (1911), 190 and 1348.

<sup>2</sup> *Proc. Internat. Congr. App. Chem.*, 1912.

<sup>3</sup> Department of Agriculture, *Bull.* 227; *This Journal*, 6 (1914), 128; 7 (1915), 652.

of the toxicity of coal-tar creosote is derived not from the hydrocarbon oils and solids but from the high boiling tar acids and tar bases. These lines of work will be followed up by this laboratory in the near future.

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### OZOKERITE FROM THE THRALL OIL FIELD<sup>1</sup>

By E. P. SCHUCH  
Received August 5, 1916

Ozokerite owes its use and value to the fact that it combines the great chemical inactivity or resistivity of paraffin with the physical properties of beeswax, namely, the property of being "doughy" or "kneadable." Its value is enhanced by the fact that its melting point is higher than that of paraffin or of beeswax.

Ozokerite and ceresine are used industrially in the manufacture of candles, in cable insulation, in shoe, stove and floor polishes. They are rather expensive—particularly at the present time because ozokerite is mined chiefly in Galicia. One New York firm, which buys large amounts of this material, stated that before the war Galician ceresine was worth 25 cents per lb., and that at present it was probably worth three times that amount. Ozokerite is found in the Caucasus, and in the Wasatch Mountains, Utah.

Some dark brown, waxy material, which is obtained together with crude petroleum at Thrall, Texas, has recently been analyzed in the Chemical Division of the Bureau of Economic Geology, and has been recognized as being *ozokerite* of an exceptionally good quality, as the following data show:

The crude material is soft, sticky, and of a dark brown color, with a sp. gr. of 0.875. It has a strong odor of crude petroleum. Heated to remove the latter, the crude material loses 14.72 per cent in weight up to 100° C., and 8.42 per cent more (or a total of 23.14 per cent) up to 180° C.

For refining, this heated material was treated with 18 per cent of its weight of concentrated sulfuric acid and the mixture heated at 180–200° C. until SO<sub>2</sub> ceased to be evolved. Then the mass was mixed with animal charcoal and "extracted" sawdust, the mixture heated for 20 min., then cooled and extracted with gasoline. On evaporating the gasoline, a material of the consistency of beeswax varying in color from orange-yellow to white was obtained. The white samples were practically free from the odor of petroleum, so that the color in the yellow samples was probably due to the presence of a trace of the original impurities. The amount of refined material thus obtained varied from 54 to 77 per cent of the weight of the crude material employed. Such refined ozokerite is technically known as *ceresine*.

Since the material might be either paraffin or ozokerite, a comparison with paraffin of the same consistency or hardness was made. The Thrall ozokerite is perfectly "doughy" and can be "kneaded," while paraffin is "flaky" and brittle.

<sup>1</sup> Published by permission of the Director of the Bureau of Economic Geology and Technology of the University of Texas.

Ceresine is distinguished from paraffin by means of its lesser solubility in carbon tetrachloride, carbon bisulfide, and chloroform:<sup>1</sup> 100 cc. portions of carbon tetrachloride dissolved 3.08 g. of Thrall ceresine, and 24.15 g. of "Texaco" paraffin, respectively.

The melting point of ozokerite<sup>2</sup> varies "from below 60° C. in the poorer grades to 68–75° C. in the normal quality, but may go as high as 84° C. (marble wax)." The Thrall ozokerite (unrefined) had a melting point of 79.5° C., while the refined material (the Thrall ceresine) melted at 75° C. The melting point of paraffin of the same consistency varies from 50 to 58° C., and that of "Texaco" paraffin was found to be 55° C. Thus melting point determinations indicate that the Thrall ozokerite is of fine quality.

The specific gravity<sup>3</sup> of paraffin (solidification point 44–58° C.) is 0.867–0.915 at 15° C., and of ceresine (solidification point 56–84° C.) it is between 0.912 and 0.943. The Thrall ceresine had a specific gravity of 0.926 to 0.928.

Various investigators have found that the indices of refraction of paraffins with melting points 50–58° C., range from 1.4220 to 1.4275 at 90° C., while the indices of refraction of pure ceresine range from 1.4212 to 1.4354, and even to 1.4415. The index of refraction of the Thrall ceresine was 1.4414 to 1.4420 at 90° C.

The purity of ceresine (particularly the absence of paraffin in it) is established by "fractional" dissolution and precipitation which, with a mixture of ceresine and paraffin, yields consecutive precipitates and a non-precipitable residue containing different proportions of ceresine to paraffin. This variation in the proportions of ceresine to paraffin can be ascertained by taking the indices of refraction of the consecutive precipitates and of the non-precipitable residue. With a pure ceresine, the indices of refraction of all the different precipitates should be well above the index of refraction for paraffin. On dissolution in chloroform, and precipitation with alcohol,<sup>3</sup> the Thrall ceresine gave, on an average, the following indices of refraction:

First Precipitate	Second Precipitate	Residue
1.4400	1.4470	1.4420

This indicates that the Thrall ceresine is totally free from paraffin.

A sample of Galician ozokerite, secured in the open market for purposes of comparison, showed itself to be less "doughy" or kneadable than the Thrall ozokerite, and yielded a more flaky or brittle ceresin than the Thrall ceresine. Its melting point was low (55° C.); its index of refraction, 1.4420 at 90° C. This sample seems to be of a less desirable material than the Thrall ozokerite, but we do not know that it is a fair sample of Galician ozokerite.

These determinations show, beyond the question of a doubt, that the "Thrall" material is ozokerite, free from paraffin, and of a fine quality.

BUREAU OF ECONOMIC GEOLOGY AND TECHNOLOGY  
AUSTIN, TEXAS

<sup>1</sup> Lewkowsitch's, "Analysis of Oils, Fats and Waxes."

<sup>2</sup> Holde-Mueller's "Examination of Hydrocarbon Oils."

<sup>3</sup> Holde-Mueller, p. 246.



# ON THE MISCELLANEOUS VEGETABLE FIBERS AS THE RAW MATERIAL FOR CELLULOSE

By H. NISHIDA

Received July 9, 1915.

Although the most ordinary source of cellulose for manufacturing of celluloid is cotton fiber, many other vegetable fibers can be employed. Some of them give products with excellent properties, but their practical application is much restricted by their respective state of occurrence or by economic conditions. After very extensive researches, however, from the scientific, as well as the practical side, the author has found that certain particular fibers quite satisfy the requirements of a raw material for the celluloid.

Among them the bamboo fiber is especially recommendable for a certain class of celluloid. Certain bast fibers growing in Japan (Mitsumata, Kozo, Gampi) and wood fiber, even at the state of mechanical wood pulp, can also be recommended for some classes of celluloid, but straw fiber from rice gives a much better result.

The most important feature of the cotton fiber as the best raw material is, of course, its purity as cellulose; but lignocellulose can hardly be neglected as an important raw material for celluloid.

Nitrocellulose for guncotton, must, of course, possess well-known stable properties proved by the heat test: on the other hand, nitrocellulose for celluloid need not always have the maximum stability, it being converted to quite a stable composition by means of camphor or its substitutes, which act as "stabilizers." Lignocellulose, sometimes even that containing much pectin substance, and which is nearly hopeless as a raw material for guncotton,<sup>1</sup> can be well employed for celluloid.

In this research, the author took the more reasonable fibers which can certainly be obtained in Japan and determined what particular properties are to be obtained from each particular fiber, which form is most suitable for the purpose, how we must treat them to convert them into the final commercial product, and lastly, their economical values.

## LIST OF FIBERS TREATED

1. Raw cotton staple, American.
2. Waste cotton from spinning mill, scoured.
3. Waste cotton yarn from weaving mill, scoured.
4. Tissue paper from colored cotton rags, bleached.
5. Tissue paper from white rags.
6. Tissue paper from cotton fish nets waste.
7. Scoured and perfectly cleaned surgical loose waste.
8. Mercerized cotton bleached.
9. Mercerized cotton unbleached.
10. Tissue paper from linen rags.
11. Paper from Mitsumata fiber, specially made.
12. Paper from Kozo fiber, specially made.
13. Paper from Gampi fiber, specially made.
14. Chemical wood pulp.
15. Tissue paper from chemical wood pulp.
16. Tissue paper from mechanical wood fiber, specially manufactured.
17. Tissue paper from straw fiber, specially prepared.
18. Half stuff from bamboo fiber.
19. Tissue paper from bamboo fiber, specially made.

The author has been very much obliged to the firms and gentlemen mentioned below who have kindly supplied him with the raw materials required, and to whom he wishes to offer special thanks:

The Nippon Celluloid Zineo Kensei K. K.  
Messrs. Iwai Shoten, Osaka and Kobe.  
Mr. Otomune, cotton broker.  
Mino Paper Syndicate, Gifu.  
Yokkaichi Paper Mill.  
Yusa Paper Syndicate, Kochi.  
Mitsubishi Paper Mill, Takasago.  
Neda Paper Mill.  
Nagoya High Technical College.

## PREPARATION OF THE RAW MATERIALS

Among the above mentioned raw materials, the raw, loose cotton staple was the only one which was not purified. The raw American cotton still contained much husks and dirt, but the cellulose itself was absolutely uninjured, either mechanically or chemically. The waste cotton from the spinning mill was severely scoured and the fiber, therefore, was too much tendered to withstand the action of strong acids. It contained much oxy- and hydrocellulose. Among the waste cotton from the weaving mills, that from Waka-yama flannelette factory was superior and was well cleaned and perfectly scoured. But still it contained no less oxycellulose.

Tissue paper from colored cotton rags was made in the following manner: The colored rags were first sorted according to the nature of the fiber and that containing any trace of animal matter was discarded; they were then further assorted according to their colors, so that no aniline black or indigo blue was left. After being digested with lime and caustic soda, washed carefully, bleached by bleaching powder, and beaten in a rather wet way, they were made up into web, without adding any sizing material. The final sheet weighed 31.5 g. per sq. m. The manner of beating has a great influence on the result of celluloid manufacturing, as will be seen later. What is known as "wet-beating" gives a much better result than what is known as "free-beating."

Tissue paper from white rags was made in a similar way, but it was not so severely scoured, and not bleached. The fiber is much purer and was not tendered. On tissue of this kind, however, the water used in the paper mill has a greater influence than in the ordinary tissue, since any dirt, turbidity or any suspension causes a more or less colored tint that spoils the resultant celluloid.

The tissue paper from worn fish net made of cotton, which is chiefly used in Northern Japan, is one of the better class tissues, since it contains no coloring matter. But its darkness in the shade and its higher percentage content of oxy- and hydrocellulose makes it second to the tissue from purer white rags. These two kinds of good tissues weighed 30 g. and 31.5 g. per sq. m., respectively.

Well cleaned pure cotton, commonly used for surgical purposes, was used. Although this ought to be perfectly pure cellulose, it is generally cleaned by pretty rough treatment, so that chemically it often contains a rather high percentage of oxy- and hydrocellulose.

Mercerized cotton yarn, both bleached and unbleached, gives a highly viscous camphor-alcohol solution from its nitrocellulose, resulting in a much more elastic celluloid. W. Vieweg's so-called "Mercerisationsgrad" was in both cases 1.45.

<sup>1</sup> von K. A. Nitzelnadel, "Versuche ueber die Verwenbarkeit aus Sulfzellulose und Strohstoff hergestellter Nitrozellulosen."

Tissue paper from linen fiber belongs to the better raw material, so far as the physical nature of the fiber is concerned. The product from wetly beaten linen fibers gives a very stiff tissue, which causes very little mechanical loss in the washing and bleaching operation of the nitrocellulose. On the other hand, however, it requires a more prolonged mixing and kneading manipulation, using more camphor-alcohol solution to bring it to the same stiffness, than does the ordinary cotton tissue. The tissue used weighed 26 g. per sq. m.

Papers from bast fibers native to Japan, *viz.*, Mitsumata, Kozo, Gampi, were practically made by hand without using any sizing materials, and without mixing any other fibers. Their respective thicknesses were rather too large for the material to be reckoned as tissue paper:

Mitsumata, 0.007 in.	106 g. per sq. m.
Kozo, 0.010 in.	200 g. per sq. m.
Gampi, 0.004 in.	95 g. per sq. m.

The nitrating acid, however, could well penetrate the fiber, on account of its free capillary. These fibers are well-known, long stout ones, and gave paper as wet beaten tissues, and highly viscous solutions with camphor-alcohol.

The chemical wood pulp treated, was that from the sulfite process. Since tissue paper therefrom was too difficult to make on the paper machine, on account of the shortness of the fiber, 30 per cent cotton fiber was added and it was then made up to a sheet weighing 16 g. per sq. m., without any sizing material. A second tissue was also made from the same mixture without using any sizing material; the sheets weighed 23 g. per sq. m.

Straw fibers were especially difficult to make into tissue form, and after repeated trials at the Kochi-paper research works, they were finally finished thus: dried straw from rice-plant was cut into chips and carefully sorted and the part obtained which is free of knots, technically known as "Subé" in Japan. This was boiled in an open digester with 18 per cent caustic soda, washed, beaten and bleached with 15 per cent bleaching powder, and washed again perfectly, then made into sheet by hand, after "Tama-zuki." The paper weighed 41.5 g. per sq. m.

Halfstuff from bamboo fiber, delivered after passing through the wet-machine in the paper-mill, was dried gently and nitrated. The web had, of course, the large average thickness of 0.016 in. But its many folds increased the relative surface coming in contact with the acid, and was rather completely and smoothly nitrated, in spite of its thickness.

Tissue paper from bamboo fibers was made only by mixing carefully with about 10 per cent rag fibers; the sheet weighed 42 g. per sq. m. A thicker paper with bamboo fibers only, was made with a slight amount of starch size, giving 119 g. weight per sq. m. Bamboo paper sized in the ordinary way with rosin and alum was also tried.

#### CHEMICAL COMPARISON OF THE RAW MATERIALS

The raw materials thus prepared were then tested as to their copper numbers (Schwalbe), acid numbers

(Vieweg) and oxycellulose content.<sup>1</sup> Oxycellulose was tested by the author's volumetric method, using titanous chloride solution and methylene blue.

TABLE I

RAW MATERIAL	COPPER No.	ACID No.	OXYCELLULOSE Per cent	ASH Per cent
Raw loose cotton.....	1.10	0.93	0.09	1.0
Spinners' waste.....	1.75	1.33	3.85	0.87
Weavers' waste.....	2.23	1.20	2.12	0.67
Tissue from colored rags.....	2.3	2.10	1.83	0.10
Tissue from white rag.....	0.49	0.533	0.50	0.07
Tissue from fish net.....	0.93	1.00	2.22	0.09
Surgical cotton.....	0.36	0.28	5.10	0.07
Linen tissue.....	0.72	2.02	1.50	0.60
Mercedized cotton, unbleached.....	1.07	1.22	5.67	0.15
Mercedized cotton, bleached.....	0.93	0.33	3.17	0.13
Mitsumata paper.....	1.11	1.32	5.82	0.60
Kozo paper.....	1.09	1.25	5.75	0.73
Gampi paper.....	1.13	0.97	5.92	0.66
Chemical wood pulp.....	1.85	2.09	6.15	0.10
Tissue from chemical wood.....	1.92	2.30	6.28	0.15
Tissue from mechanical wood.....	2.57	3.73	6.41	0.48
Tissue from straw.....	3.10	3.69	6.62	3.80
Bamboo pulp.....	2.35	3.20	5.35	4.10
Tissue from bamboo.....	2.23	2.16	6.45	3.30
Tissue from wet beaten.....	2.20	3.06	5.99	3.45
Bamboo paper, starch sized.....	2.97	3.06	6.00	3.76
Bamboo paper, resin sized.....	4.29	2.66	6.59	5.20

The results in Table I show that the fibers severely treated with chemicals or by mechanical manipulation for a long time, contain more oxycellulose. Further we know: (a) That every compound-cellulose shows a higher copper number and absorbs more methylene blue than pure cellulose; (b) that the fiber consisting of lignocellulose accompanied with impure pectous substances (as with the case of mechanical wood pulp and bamboo pulp) shows the highest copper and acid numbers; (c) that the presence of any amount of sizing or loading material increases these numbers *e. g.*, cigarette tissue containing certain inorganic salts, showed copper number 6.25, acid number 4.94 and oxygen content 8.25 per cent, when estimated directly without the stripping, the sizing and the loading materials, in spite of the fact that it consists of best class linen fibers only: also the above given results for bamboo paper sized with rosin and alum confirmed the same fact. This is why the papers giving higher percentages of ashes show the higher numbers, and are not desirable in our case.

#### PHYSICAL NATURE OF THE RAW MATERIALS

As to the physical natures of the raw materials, capillary absorption is to be first considered, but this can be often controlled by variation of the dipping time in the nitrating operation. Actually, the papers for the celluloid factory being free from sizing materials, their capillary absorptions are not remarkably different. In practice they are usually steeped in the acid bath in small pieces, which makes the difference of their absorbing speed more negligible, provided the thickness is the same. The thinner the paper, the better the penetration of acid is effected. In practice a thickness giving 15-40 g. per sq. m. is moderate. According to my experiments, when the fiber is beaten in the free state, 15-30 g. per sq. m. would be the limit weight, while when well-beaten in the wet state (and also for long fiber) even 200 g. or more weight per sq. m. could be allowed. This is, however, just the opposite requirement from the standpoint of the papermaker. The long steeping of the fiber in a nitrating bath often causes tremendous loss of the fiber,

<sup>1</sup> Dr. W. Schultz, "Zur Kenntniss der cellulosearten," Dr. C. Schwalbe, "Die Chemie der Cellulose."



especially with the short fibrous materials. This causes an extraordinary loss in a celluloid works, cuts down the daily output of the nitrocellulose, increases the loss of the  $\text{HNO}_3$  content in the working acid, and often makes the waste acid quite turbid with fine organic matter, which makes it unrecoverable. For this reason, "the thinnest paper from wet-beaten fiber is the best raw material for celluloid. In fact, the length of the individual fiber, and the beating manipulation are the two most important features for the tissues used by a celluloid factory. As we can afterwards see, the actual loss of the nitrocellulose, and the viscosity of its camphor-alcohol solution, and the luster as well as the physical properties of the finished celluloid, are quite intimately related to the length of the fibers originally used and the hydration of the fibers, *i. e.*, the manner of beating in the paper mill.

#### NITRATION

The nitrating acid for celluloid purposes has been fully discussed in a previous article<sup>1</sup> by the author,

1,500 for cotton or purer cellulose  
2,100 for linen and allied bast fibers  
2,400 for wood and straw cellulose  
2,700 for mechanical wood and fibers most difficultly nitrated.

And further, we must take the thickness of the raw material into consideration, as explained before. The above constants hold good for a thickness weighing up to 40 g. per sq. m., and when thicker tissue or paper is used it increases as follows:

$$\text{Constant} \times 0.9 \sqrt{\frac{D}{40}} \dots \text{up to } D = 100 \text{ g.}$$

$$\text{Constant} \times 0.85 \sqrt{\frac{D}{40}} \dots \text{up to } D = 200 \text{ g.}$$

where D is the number of g. per sq. m.

#### COMPARISON OF THE NATURES OF THE FIBERS

The most important results of the nitrations of the various fibers were: (a) the yields of the nitro-compound, or loss in the pot, together with the degree of the contamination of the working acid; (b) the solubilities and viscosities in camphor-alcohol solution; (c) the stabilities as celluloid, provided exactly the

TABLE II

No.	FIBER	YIELD Per cent Nitro-Compound	SOLUBILITY in 36% Camphor-Alcohol Solution	VISCOSITY (Engler) 20° C.	Kind of Celluloid Made	STABILITY Heat Test Min. Sec.	Flash Point ° C.	TENSILE STRENGTH (See Text)	BENDING STRESS (See Text)
1	Raw Cotton.....	80	100	5.0	Amber	3-12	166.5	0.95	1.0
2	Spinners' Waste.....	40	98	5.1	.....	.....	.....	.....	.....
3	Weavers' Waste.....	150	97	20.2	Shell	3-52	152	0.98	1.1
4	Tissue from Colored Rags.....	155	100	6.0	Fancy	15-20	182	0.99	1.08
5	Tissue from White Rags.....	149	100	7.8	Horn	12-41	182	1.1	1.0
6	Tissue from Fish Nets.....	155	100	8.3	Horn	12-17	183	1.1	1.0
7	Tissue from Fish Nets.....	155	100	8.3	Transparent	12-12	181.5	1.1	1.0
8	Surgical Cotton.....	155	100	12.4	Dark Marble	10-5	179	1.0	1.0 standard
9	Linen Tissue.....	153.3	100	32.7	Transparent	15-14	185	1.1	0.95
10	Mercerized Cotton, Unbleached.....	145	100	31.5	Shell	18-22	171	1.25	0.90
11	Mercerized Cotton, Bleached.....	165	100	33.8	Transparent	5-2	169	1.22	0.95
12	Mitsumata.....	86.2	98.5	19.0	Amber	10-38	173	1.18	0.92
13	Kozo.....	85.3	97.5	21.7	Amber	9- 0	175	1.15	0.91
14	Gampi.....	91.8	99.0	45.7	Amber	8-12	170.5	1.20	0.90
15	Gampi.....	91.8	99.0	45.7	Tube	4-43	166.5	1.20	0.90
16	Chemical Wood.....	105	95.5	3.8	Fancy	5-29	177	0.98	1.00
17	Tissue from Chemical Wood.....	121.6	97.0	7.7	Amber	8-17	177	0.99	1.00
18	Tissue from Mechanical Wood.....	130	89.0	12.3	Shell	13-56	166	0.90	1.00
19	Tissue from Straw.....	100.8	97.0	3.4	Shell	5-46	169	0.90	1.10
20	Tissue from Bamboo Pulp.....	110	99.0	25.0	Amber	5-13	152	0.92	1.13
21	Tissue from Bamboo.....	127	99.0	24.4	Shell	9- 5	167	0.81	1.20
22	Tissue from Bamboo.....	127	99.0	24.4	Amber	7-30	171	0.81	1.20
23	Paper from Wet-beaten Bamboo; without Sizing.....	132	100	10.0	Amber	3-42	152.4	0.95	1.25
24	Paper with Starch Sizing.....	116.8	96.0	27.6	Transparent	4-48	171	0.90	1.25
25	Paper with Resin Sizing.....	100	97.2	12.4	Shell	6-11	141	0.92	1.15
26	Cigarette Paper.....	143.2	98.5	5.85	Amber	8-15	170	1.09	0.93

- (1) Contained much dirt from cotton husks.
- (2) Contained much dirt from husks and spinning mill; the fiber was injured so that it caused too great a loss, and was not practicable.
- (3) Certain insoluble parts formed specks in the celluloid.
- (4) A slightly turbid solution.
- (5) Did not give a clear solution.
- (6) A perfectly clear, very viscid solution.
- (7) Very dark; contained insoluble sediments.
- (8) Dark; insoluble sediments.
- (9) Dark brown gallette; dissolved imperfectly. The celluloid sample

and as a conclusion therefrom he always uses as a working acid a mixture of the following percentage composition:

$\text{H}_2\text{SO}_4$	$\text{HNO}_3$	$\text{HNO}_2$	Water
64.0 to 65.5	15.0 to 16.5	0.8 to 1.0	18.0 to 19.0

The nitrating temperature and time duration must be varied according to the variety of the fibers. After repeated experiments, it was found that the product of the temperature ( $^{\circ}\text{C}.$ ) and the time duration (min.) should be kept constant in order to produce the same degree of the nitration; or,  $\text{Temp. } (^{\circ}\text{C.}) \times \text{Min.} = \text{Const.}$ , where the constant varies according to the nature of the fiber; *e. g.*,

<sup>1</sup> "Étude sur la Viscosité des Dissolutions de Nitrocellulose dans les Solutions alcooliques de Camphre," *Le Caoutchouc & La Gutta-Percha*, des 15 Mars et 15 Avril, 1914.

therefrom shows the fiber at only its brownish part, while the amber part consists of the fiber from ordinary rags.

- (19) Slightly turbid light brown solution.
- (20) Contained very fine specks, perhaps  $\text{SiO}_2$  (?), from the knots, but otherwise the solution looked almost clear.
- (21) Similar result to (20). Celluloid extremely hard and brittle.
- (22) Dissolved perfectly.
- (23) Some insoluble matter remained.
- (24) Gave much more brownish solution than (23). Contained more insoluble matter.
- (25) Contained very fine insoluble substance. Gave a turbid solution.

same washing, kneading, rolling and drying manipulations were used for all; (d) the physical properties of the resultant products as celluloid.

In Table II "Yield" refers to the rate of output of the nitro-compound from the raw fibers which often partly dissolve in the working acid, and partly form fine sediments when severely disintegrated.

"Solubility" means that of the nitro-compound obtained in 36 per cent camphor-alcohol solution. Generally by the "solubility" of nitrocellulose, we are accustomed to understand its solubility in ether-alcohol mixture, but nowadays, we must consider the nitrocellulose for celluloid in quite a different way from that for explosives. In our case, we prefer naturally the camphor-alcohol solution as its solvent. According to the author's experiments, a 36 per cent

solution (by weight) is the most suitable solvent for the purpose. To prepare this dissolve 36 g. pure camphor crystals in 126 cc. absolute alcohol of sp. gr. 0.79425. Take exactly 2 g. of the nitro-compound, and dissolve in 100 cc. of the 36 per cent camphor-alcohol solution by careful agitation, and let it stand for one day in a stoppered 100 cc. measuring flask. Take 25 cc. from clear part and evaporate to dryness in a weighed dish at about 45–50° C.; weigh its residue, which gives the dissolved nitrocellulose and camphor contained in the 25 cc. solution by calculation, and therefrom gives the solubility. The best nitrocellulose for celluloid purposes dissolves as much as 99–100 per cent and gives a perfectly clear solution, without any turbidity, sediment, or even transparent gelatinous lumpy masses.

"Viscosity" was determined by measuring with the Engler viscosimeter. Dissolve the 6 g. nitrocellulose

to boiling in  $1\frac{1}{2}$  hr., and then boiled for ten minutes. Now add 1 g. pure recrystallized potassium iodide dissolved in 250 cc. distilled water, stir well and cool. The best filter paper, which has been well washed by distilled water and completely dried, is passed through the mixture for about 10 cc. and then hung in a dark room kept free from any acid fumes. After drying, cut into narrow strips, and keep in a brown bottle tightly stoppered and placed in the dark for about six weeks.

Now take 1.3 g. of the finely scraped celluloid in a heat-test tube and hang the starch iodide paper at the inner end of a glass rod passed through the rubber stopper, as used in Abel's heat-test apparatus. The paper is half dipped in glycerine beforehand. The whole arrangement is now warmed in a water bath at 80° C. Note the time required to give the change of color at the glycerine boundary, comparing the shade with that of a standard tint paper.

(2) The flashing temperature was found similarly to that of nitrocellulose for guncotton or explosives. We took 0.3 g. scraped celluloid, which was placed in a heat-test tube, and raised the temperature of the heating oil bath 3° C. per min., reading the flashing temperature on a thermometer inserted in the test tube.

"Tensile strength" was determined by putting the celluloid rod or log of a known sectional area in a special testing machine (Fig. I) designed by the author and Mr. I. Sakai, his assistant mechanical engineer. This testing machine was operated by hydraulic pressure so that the stress and strain could be very accurately and easily read. The celluloid from surgical cotton was used as the unit and the others calculated on that basis. The unit reading for stress was 5.1 kg. per sq. mm., *i. e.*, nearly 5 tons per sq. in., the elongation being 0.03.

"Bending moment" was similarly tested in our own special testing apparatus (Fig. II), and again the celluloid from surgical cotton was used as a unit.

Of course, the physical properties are much affected by the several operations during the finishing of celluloid from its gallette stage, and especially by the nature and quantity of the loading materials.

#### CONCLUSIONS

I—As to the chemical and physical properties and the stability and appearance of the finished celluloid: Any trace of acid appreciably lowers the stability. An acid celluloid often undergoes fading of color, change of shade, and even remarkable alteration of nature, and is to be treated as an inferior variety. The heat test and ignition temperature give a correct hint on this point and we can value their chemical quality rather easily when the celluloid is nearly dried up.

Among the physical properties, strength is apparently proportional to viscosity, or in other words, to the conditions of their original fibrous material and their beating manner in the paper mill, where they were converted into tissue. The higher elasticity is always accompanied by the higher viscous nitrocellulose-

### Celluloid Bending Stress Testing

#### Machine

Working pressure 500 lb./sq. in.

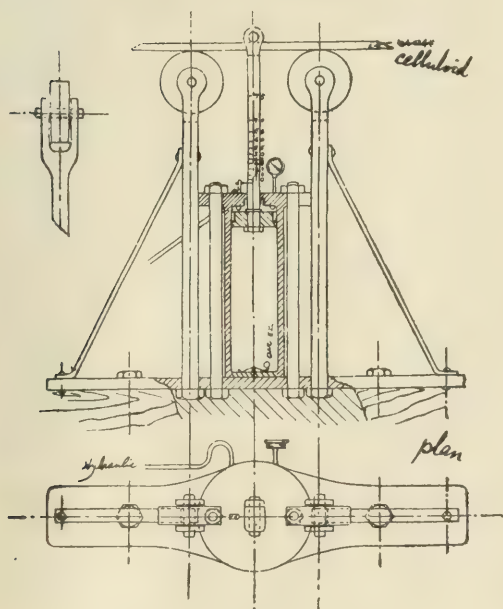


FIG. I

in 300 cc. of 36 per cent camphor-alcohol solution in a conical cup, stir well and let it stand over night; then measure the viscosity at 20° C., which is compared with that of distilled water.

"Stability" was examined according to Will's method,<sup>1</sup> modified as follows:

(1) The "heat test" was determined by the use of our standard starch iodide paper prepared in the following manner: 3 g. of refined starch are made into a paste by mixing with 350 cc. distilled water, and warmed under continuous stirring, so that it is brought

<sup>1</sup> "Untersuchungen ueber Zelluloid," *Z. angew. Chem.*, Heft 32 (1906).



galette. It seems to be true that the physical nature of the celluloid, when not mixed with particular ingredients, depends on the nature of the fibers, rather more so than is the case with paper.

The shade of the galette itself differs with the raw material; generally, the more impure cellulose gives a browner shade (but not darkened); fiber from colored

Bamboo and straw must be specially treated, since it is quite difficult to free them absolutely from the adulteration coming from their knots. Translucency is often caused by an incomplete drying of the nitro-cellulose after washing with water, but it results mostly from incorrect nitration, leaving certain insoluble nitrocelluloses, or sometimes from too much oxycellulose existing in a very fine state. Any inorganic adulteration in the fiber certainly results in the same effect. In general, higher viscosity and a clear galette gives the most compact elastic celluloid bearing the highest luster, which is the case when we use wet-beaten pure clean long fiber as the raw material.

II—Concerning manufacturing cost from the standpoint of loss during nitration and washing, and price of raw fibrous materials:

As will be seen from another paper by the author, the yield of the nitro-compound determines the management of the celluloid works. Indeed the output of the celluloid in a celluloid factory is to be calculated as  $(T \times \text{Yield per cent} \times 1.959)$ , where  $T$  is the total amount of fibrous material originally nitrated.

Also loss of fiber in the mixed nitrating acid causes turbidity of the waste acid, which cannot be recovered again as working acid.

As explained in the same paper, the amount of the fiber required for each kg. celluloid is calculated as

$$1/(\text{yield of nitro-compound} \times 1.959).$$

Now suppose the yield and the price of the two different fibers to be  $Y$ ,  $P$  and  $Y'$ ,  $P'$ , respectively, then we have the total cost of 1 kg. of celluloid

$$\frac{P}{Y \times 1.959} \quad \text{or} \quad \frac{P'}{Y' \times 1.959}$$

or their value has the ratio  $PY'/P'Y$ . If this ratio is greater than 1, the first paper or fiber is dearer, while if less the latter is dearer. Tissue costing 45 cents per kg. and of 1.55 yield, is far cheaper than that costing 30 cents but with 0.90 yield. Similarly, when we are required to compare the raw materials for the same purpose, we must calculate this value before our choice, so far as the economical standpoint is concerned.

From the above results, the author values and classifies the raw fibrous materials for celluloid as follows:

- 1st Class—Unbleached mercerized cotton; tissue from white rags and fish nets.
- 2nd Class—Bleached mercerized cotton; tissue from colored rags; tissue from linen fibers.
- 3rd Class—Papers from bast fibers; weavers' waste yarn, scoured and bleached.
- 4th Class—Bamboo tissue as free from adulteration as possible and wet-beaten.
- 5th Class—Chemical wood fiber, and straw, as free from knots as possible.
- 6th Class—Mechanical wood fiber mixed with a little cotton.

The proper mixing of these fibers before making the tissue for the celluloid, is an important and interesting question for both paper mill and celluloid works.

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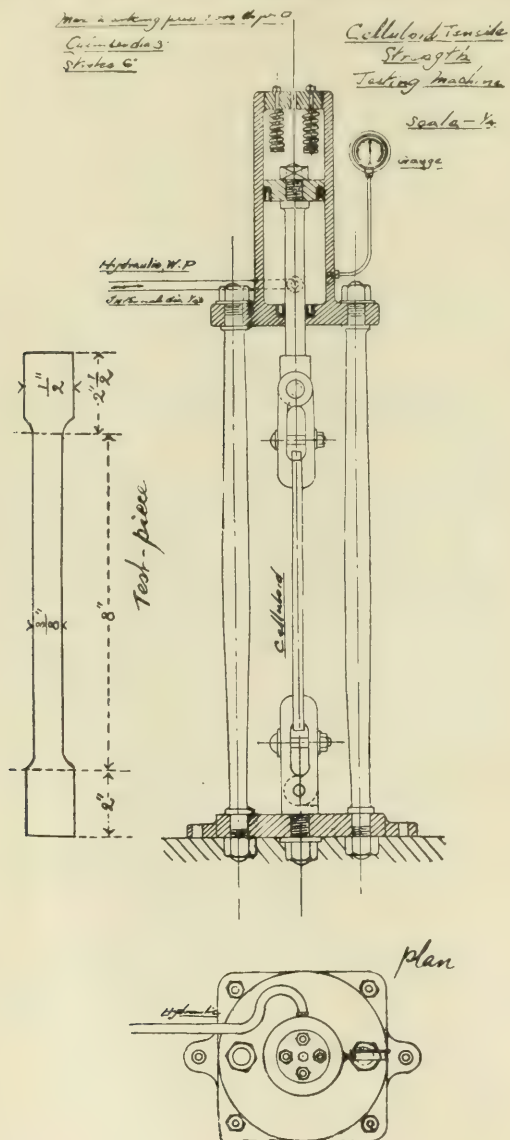


FIG. II

rags has an inclination to make the shade of the galette darker. The bluing of the tissue is certainly undesirable for the celluloid purposes, since it also gives a dark shade. Mechanical wood gives a tobacco-brown nitro-compound and, is therefore, much restricted in its applications.

## SOME SLOW VOLUME CHANGES IN PORTLAND CEMENT

By EDWARD D. CAMPBELL

Received August 3, 1916

Engineers have realized for many years that free lime and magnesia may cause dangerous expansion in Portland cement and have sought by specifications covering chemical composition and physical tests to eliminate trouble from these two sources. Free lime can be readily detected and its deleterious effect prevented by proper ageing of cement before use. Free magnesia, on the other hand, cannot be as readily detected and the expansion due to the presence of free magnesia does not manifest itself to any great extent in the length of time or under the conditions usually employed in testing Portland cement. It is for this latter reason that engineers who consider the safety of structures as the first requisite, usually specify a maximum allowable per cent of magnesia, low enough, so that under no conditions of ordinary practice and manufacture the amount of free magnesia could be large enough to produce serious results. If the total magnesia is kept under 3 per cent no trouble will arise from this cause under any circumstances.

On account of very extensive deposits of limestone too high in magnesia to permit its use in the manufacture of Portland cement if the allowable per cent of magnesia is kept down by specifications to 3 or 4 per cent, efforts have been made to produce from these magnesian limestones Portland cements which would satisfactorily pass all the physical tests to which these cements are usually subjected. Cements containing 7.5 or even 9 per cent magnesia have been prepared which have stood the ordinary physical tests and showed no abnormal expansion after intervals of 6 or even 9 mo. immersion in water. Anyone not familiar with the slow rate of hydration of magnesium oxide would naturally conclude that a cement which gave no abnormal expansion after 9 mo. immersion might be trusted in any work. It is because of this mistake that we are submitting some measurements which have been carried on in continuation of work described by the author in conjunction with Alfred H. White some ten years ago.

In this article, "Some Conditions Influencing Constancy of Volume in Portland Cements,"<sup>1</sup> the preparation and testing of a number of samples of cement of different degrees of basicity, some containing free lime, others free and combined magnesia, was described. The expansion measured by means of a special micrometer on bars 100 mm. in length was expressed in per cent, the measurements being made at increasing intervals of time. The time intervals selected were 7, 14, 21 and 28 days; 2, 3, 4, 6, 9, 12 and 18 mo.; and by intervals of 1 year each after the second year, the longest time recorded being 5 years from the time a given bar was made. The influence of chemical composition and ageing of the cement or clinker on the volume changes was studied and the conclusions in part summarized as follows:

"Free lime in Portland cement will not only not be slaked during the mixing and setting of the cement but will not become

completely hydrated even when the cement is immersed in water, until about 14 days have elapsed. The result of this gradual slaking is to produce abnormal expansion of the cement. Any evil effects due to the presence of free lime in cements kept under water will be manifested within 2 mo. In case free lime is present in cement used in structures above ground or where it is usually dry, the expansion due to hydration of the cement will be more gradual but several times greater in volume than when the material is under water. The expansion due to free lime slaking in the air may become so great after several months as to cause complete disintegration.

"The deleterious effects of free lime may be completely removed by aging the ground cement or storing the clinker to weather until the pat will stand a perfect boiling test. Weathering the clinker for 3 mo. is usually sufficient. It is difficult to state the length of time necessary properly to age ground cement to eliminate free lime. It will not ordinarily be less than one month and may be much longer according to the conditions under which it is stored.

"Cement which passes a perfect boiling test may safely be assumed to contain no free lime. The expansion of a bar of neat cement containing no free lime when kept in cold water for 7 days is usually under 0.040 per cent, but occasionally it may go as high as 0.060 per cent. A cement with 2.8 per cent free lime showed an expansion of 0.220 per cent in the same period.

"The effect of magnesia, like that of lime, depends less upon its total amount than upon the form in which it exists. Combined magnesia like combined lime has no injurious effect in Portland cement. Magnesia combined with silica and alumina forms a hydraulic cement which is safe, but as compared with Portland cement is too weak to be of any commercial value. Free magnesia has no appreciable effect in cement used above ground where it is continuously dry. If the cement is wet for a part or whole of the time, the free magnesia will very slowly hydrate and cause expansion. Even where the cement is continuously immersed in water the expansion due to free magnesia is not appreciable until after 2 mo. and becomes distinctly evident only after a year. The hydration seems to be well under headway only at the end of the first year and expansion continues at an increasingly rapid rate for at least 5 yrs. and probably longer. Ageing does not seem to diminish the deleterious effect of free magnesia in cement. This is to be expected, since the rate of hydration of hard-burned magnesia in air is almost imperceptibly slow.

"The boiling test for 24 hrs. does not detect free magnesia as it does free lime. Cement containing as high as 4 per cent of free magnesia has passed a perfect boiling test, yet the last measurement of this cement at the end of 5 yrs. in cold water showed a total expansion of over 1 per cent, nearly half of which occurred during the fifth year after making.

"This slow hydration of free magnesia with its accompanying expansion seems to be the probable cause of the expansion, frequently accompanied by more or less complete disintegration, so often noted in sidewalks, occurring several years after the walk has been laid.

"One per cent or less of free magnesia in cements kept under water causes little noticeable expansion even in neat cement, probably simply filling up the voids. Increased percentages of free magnesia cause cumulatively greater expansion until with 3 per cent of free magnesia the expansion is too great to be at all safe.

"In the manufacture of cement from raw materials containing magnesium carbonate, some portion of the magnesia will remain in the free state. This amount will increase with coarseness of raw materials, increasing percentage of lime and increasing percentage of magnesia. If the total magnesia does not exceed 3 per cent it is not likely that well-made cement will carry enough of this magnesia in the free form to cause injurious expansion under any conditions of service. If the percentage of total magnesia rises above 3 per cent there will be increasing probability of enough magnesia remaining in the free form to cause injurious expansion."

Since the publication of the work summarized above, measurements of the bars kept in water have been continued, some of the periods being extended up to 13 and 14 years. As the purpose of the present paper is to call attention to the slow volume change, no measurements of expansion for a period of less than one year are given in Table I, in which are shown the long-time measurements of expansion. If the short-time measurements are desired, reference may

<sup>1</sup>J. Am. Chem. Soc., 28 (1906), 1273-1303.



TABLE I. EXPANSION OF BARS OF NEAT CEMENT IN WATER

All measurements represent percentage variation from original volume.																	All measurements represent expansion																
EXPT.	No.	MONTHS							YEARS										REMARKS														
		12	18	2	3	4	5	6	7	8	9	10	11	12	13	14																	
74	A	0.370	0.423	0.447	0.499	0.550	0.582	0.592	0.611	0.625	0.665	0.678	0.688	0.688	0.710	0.720	Free CaO and free MgO																
	D	0.102	0.121	0.164	0.245	0.285	0.307	0.344	0.360	0.372	0.378	0.385	0.391	0.415	0.415	0.415	Aged. Free MgO																
75	A	0.155	0.383	0.390	0.407	0.370	0.432	0.424	0.407	0.388	0.388	0.388	0.388	0.388	0.388	0.388	Free CaO and free MgO																
	D	0.130	0.136	0.152	0.177	0.188	0.185	0.204	0.204	0.204	0.204	0.204	0.204	0.204	0.204	0.204	Aged. Free MgO																
77	A	0.130	0.163	0.158	0.170	0.180	0.190	0.180	0.166	0.188	0.195	0.189	0.189	0.189	0.189	0.189	Good cement used fresh																
	D	0.038	0.032	0.040	0.052	0.056	0.051	0.060	0.063	0.061	0.053	0.053	0.053	0.053	0.053	0.053	After aging																
78	A	0.390	0.414	0.412	0.421	0.441	0.451	0.441	0.428	0.457	0.460	0.458	0.458	0.458	0.458	0.458	Fresh. Free CaO																
79	A	0.160	0.204	0.218	0.250	0.330	0.310	0.310	0.312	0.344	0.380	0.377	0.380	0.376	0.410	0.410	7.2% MgO. Fresh																
	C	0.089	0.104	0.127	0.145	0.177	0.194	0.187	0.211	0.226	0.230	0.233	0.234	0.230	0.251	0.251	7.2% MgO. Aged																
	E	0.095	0.117	0.140	0.180	0.212	0.222	0.247	0.262	0.278	0.279	0.285	0.285	0.300	0.300	0.300	7.2% MgO. Aged																
80	A	0.032	0.057	0.062	0.082	0.100	0.102	0.091	0.072	0.098	0.107	0.102	0.102	0.102	0.102	0.102	All magnesia. Fresh																
82	A	0.010	0.029	0.040	0.059	0.080	0.080	0.088	0.088	0.088	0.088	0.088	0.088	0.088	0.088	0.088	All magnesia. Aged																
81	B	0.077	0.082	0.090	0.099	0.105	0.113	0.107	0.118	0.120	0.121	0.114	0.114	0.114	0.114	0.114	Same as 78, but aged																
	C	0.049	0.051	0.059	0.071	0.070	0.072	0.081	0.085	0.085	0.073	0.073	0.073	0.073	0.073	0.073	Same as 78, but aged																
	E	0.050	0.068	0.062	0.081	0.092	0.092	0.071	0.091	0.100	0.091	0.090	0.090	0.090	0.090	0.090	Same as 78, but aged																
	G	0.089	0.103	0.101	0.115	0.121	0.115	0.104	0.104	0.125	0.122	0.122	0.122	0.122	0.122	0.122	Same as 78, but aged																
83	A	0.100	0.112	0.116	0.132	0.139	0.144	0.140	0.149	0.150	0.155	0.150	0.145	0.143	0.154	0.154	Commercial cement, fresh																
	B	0.095	0.106	0.117	0.134	0.144	0.146	0.146	0.165	0.169	0.170	0.163	0.168	0.160	0.173	0.173	Same + 1% free MgO																
	C	0.113	0.133	0.150	0.170	0.190	0.203	0.200	0.225	0.223	0.232	0.232	0.240	0.232	0.242	0.242	Same + 2% free MgO																
	D	0.127	0.151	0.168	0.197	0.253	0.382	0.525	0.862	1.002	1.072	1.069	1.072	1.067	1.092	1.092	Same + 3% free MgO																
	E	0.158	0.172	0.223	0.290	0.562	1.010	1.390	1.965	2.185	2.280	2.280	2.285	2.281	2.298	2.298	Same + 4% free MgO																
	F	0.093	0.106	0.110	0.119	0.129	0.130	0.122	0.140	0.131	0.140	0.139	0.137	0.133	0.141	0.141	Same + 1% combined MgO																
	G	0.088	0.101	0.107	0.119	0.124	0.130	0.118	0.130	0.132	0.145	0.139	0.130	0.129	0.145	0.145	Same + 2% combined MgO																
	H	0.090	0.101	0.106	0.118	0.130	0.138	0.125	0.148	0.147	0.150	0.149	0.140	0.143	0.160	0.160	Same + 3% combined MgO																
	I	0.096	0.104	0.110	0.120	0.130	0.138	0.125	0.148	0.147	0.150	0.152	0.140	0.147	0.160	0.160	Same + 4% combined MgO																
85	A	0.085	0.089	0.094	0.108	0.110	0.122	0.100	0.108	0.120	0.119	0.121	0.116	0.116	0.130	0.130	Same cement, aged																
	C	0.067	0.074	0.079	0.091	0.100	0.104	0.086	0.099	0.110	0.108	0.095	0.101	0.092	0.110	0.110	Same cement, aged																
	E	0.098	0.106	0.122	0.127	0.150	0.145	0.128	0.142	0.155	0.155	0.150	0.151	0.145	0.166	0.166	Same cement, aged + 1% free MgO																
	G	0.107	0.124	0.135	0.154	0.165	0.185	0.175	0.195	0.215	0.216	0.213	0.214	0.206	0.229	0.229	Same cement, aged + 2% free MgO																
	I	0.115	0.136	0.154	0.185	0.240	0.370	0.474	0.740	0.890	0.894	0.930	0.895	0.891	0.909	0.909	Same cement, aged + 3% free MgO																
	K	0.141	0.175	0.199	0.282	0.615	0.944	1.311	5.222	5.753	5.81	1.580	1.578	1.601	1.601	1.601	Same cement, aged + 4% free MgO																
	M	0.082	0.093	0.096	0.109	0.115	0.119	0.106	0.120	0.130	0.135	0.125	0.120	0.117	0.083	0.083	Same cement, aged + 1% combined MgO																
	O	0.074	0.083	0.087	0.104	0.107	0.115	0.103	0.115	0.125	0.127	0.117	0.122	0.115	0.135	0.135	Same cement, aged + 2% combined MgO																
	Q	0.070	0.080	0.087	0.108	0.099	0.109	0.101	0.118	0.130	0.131	0.125	0.128	0.120	0.169	0.169	Same cement, aged + 3% combined MgO																
	S	0.052	0.062	0.069	0.081	0.084	0.095	0.089	0.109	0.119	0.124	0.115	0.122	0.112	0.139	0.139	Same cement, aged + 4% combined MgO																

be made to the above-mentioned paper. A study of the figures given in the accompanying table seems to sustain fully the conclusions drawn from the results published 10 yrs. ago. The continued expansion due to free magnesia long after 5 years is very clearly brought out, as well as the fact that if magnesium oxide is in the combined form it will produce little or no volume change.

In view of the fact that efforts are being made to utilize, as a source of raw material for Portland cement, limestones too high in magnesia to enable the production of a cement low enough in this constituent to be safe under any conditions of manufacture, attention should be called to the results of the long-time measurements on Expts. 74 and 79. Both of these cements contain about 7 per cent total magnesia, but Expt. 74 contains 0.53 per cent less silica and 0.67 per cent more calcium oxide than Expt. 79. The CaO ratio of Expt. 74 is 280.2 while that of Expt. 79 is 270.7 to 100 molecules of  $\text{SiO}_2$ . In addition to the difference in basicity the raw material used in Expt. 74 was not quite as finely divided as that used in Expt. 79. Although in Expt. 79 by keeping the basic ratio low and having the material very finely ground, a cement was produced with a total magnesium oxide per cent of 7.2, and which would pass all the ordinary tests to which cements would be subjected and which even after 13 or 14 yrs. immersion had not expanded to any extent which would probably be dangerous, yet a relatively slight increase in the basic ratio and coarseness of raw material has shown in Expt. 74 very nearly double the amount of expansion taking place after the first year, this increased expansion being due to the increased proportion of free magnesia. It is this liability of having a dangerous amount of free magnesia in cements made from raw materials much higher in magnesia than is usually considered permissible for the best quality that should make manufacturers very cautious about adopting high magnesia raw material and if they do employ such

material they should realize that much greater care in manufacturing will be required to produce a reliable cement than if the purer raw material were used.

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### THE EFFECT OF TEMPERATURE AND THE TIME FACTOR IN THE FORMATION OF GASOLINE IN THE GAS PHASE AT CONSTANT PRESSURE

By GUSTAV EGLOFF, THOMAS J. TWOMEY AND ROBERT J. MOORE

Received September 6, 1916

In a recent communication<sup>1</sup> the formation of gasoline from catalysis in the gas, liquid and solid phase system was studied. The present paper deals with the production of gasoline by the gas phase system at constant pressure and varying temperatures and rates of oil flow or time factor.<sup>2</sup>

#### SCOPE OF THE INVESTIGATION

In the present investigation a series of experiments were conducted with a view to ascertaining the value of a Pennsylvania crude petroleum oil, after removal of the gasoline present in the oil, for cracking purposes in the production of "cracked gasoline," this cracking to take place without the removal of waxes, gas, fuel and lubricating oil or other constituents of a like value, present in the residue from the crude oil; in short, to convert the residue into gasoline at constant pressure of 150 lbs., temperatures of 600, 650 and 700° C., and rates of oil flow of 17, 23, 30, 36, 45 and 65 gal. per hr.

#### EXPERIMENTAL PROCEDURE

The experimental work was carried on in an 8-in. diameter steel tube, gas-heated, and the temperature control maintained by means of a base metal thermocouple. The pressure in the system was built up to 150 lbs. by means of an air compressor with natural

<sup>1</sup> Egloff and Moore, *Met. and Chem. Eng.*, **15** (1916), 67.

<sup>2</sup> Egloff and Twomey, "The Time Factor in the Formation of Aromatic Hydrocarbons from a Paraffin Base Oil," *Ibid.*, **15** (1916), 245.

gas. A carefully selected oil meter was used which was calibrated before each test. The oil was pumped by means of a triplex pump. All precautions used and details of the mechanism have been described elsewhere.<sup>1</sup> The analysis<sup>2</sup> was conducted by means of a Hempel distilling head and a 300 cc. round bottom flask. A 200 cc. sample was distilled and the cut to 150° C. was taken as representing the gasoline fraction. The specific gravities of the oils were taken with a Westphal balance at 15.5° C. The olefin content of the gasoline cut was determined by means of a Babcock milk tester bottle and centrifuge. The details of the method have been given in an earlier paper.<sup>3</sup> A discussion of the rate of oil flow and the time factor relationship has been given by a number of investigators.<sup>4</sup>

#### THE OIL USED FOR GASOLINE PRODUCTION

The Pennsylvania crude petroleum was analyzed before removal of gasoline fraction, 0° to 150° C. (Table I). By distillation the gasoline fraction was removed and the residue analyzed with the results given in Table I.

TABLE I—DISTILLATION ANALYSIS OF ORIGINAL OIL AND RESIDUE AFTER REMOVAL OF GASOLINE CUT (0 TO 150° C.)

Temperatures ° C.	ORIGINAL OIL		RESIDUE	
	Per cent by Vol.	Sp. gr. 15.5° C.	Per cent by Vol.	Sp. gr. 15.5° C.
0 to 150.....	24.5	0.727	0.8	...
150 to 200.....	14.7	0.769	20.9	0.771
200 to 250.....	8.0	0.783	11.9	0.780
250 to 300.....	18.5	0.807	33.4	0.813
Residue.....	33.8	...	32.0	...
Loss.....	0.5	...	1.0	...
Sp. Gr. Original.....	...	0.815	...	0.826

This residue was then subjected to cracking conditions of three temperatures and varying rates of oil flow, 20 gals. being used in each experiment.

#### EXPERIMENTAL DATA

The experimental data are presented in Table II and appear graphically in Figs. I to VI.

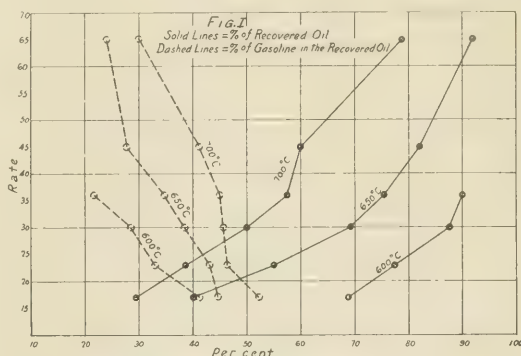
RECOVERED OIL (Fig. I)—In the thermal decomposition<sup>5</sup> of petroleum oils a progressive rise in temperature increases the decomposition of the starting oil.

TABLE II—THE EFFECT OF TEMPERATURE AND THE TIME FACTOR ON OIL RECOVERED AND GASOLINE CUTS WHEN "CRACKING" OILS UNDER CONSTANT PRESSURE

Gals. per Hr.	Percentages: 600° 650° 700°	OIL RECOVERED—		Gasoline in		Gasoline CUT		PERCENTAGES OF ORIGINAL OIL	
		Specific Gravities:	600° 650° 700°	600° 650° 700°	Specific Gravities:	% Olefins in:	600° 650° 700°	Gasoline	Olefins
17	68.8 40.0 29.4	0.828 0.907 0.936	41.1 43.3 51.8	0.757 0.819	0.834	28.0 27.0 26.0	28.3 17.3 15.1	7.9 4.7 3.9	31.2 60.0 70.6
23	77.5 55.0 38.8	0.825 0.862 0.920	33.0 43.1 46.3	0.756 0.784	0.825	26.0 24.0 29.0	25.6 23.7 17.9	6.7 5.7 5.2	22.5 43.0 61.2
30	87.5 69.1 50.0	0.824 0.836 0.882	28.6 38.5 45.3	0.750 0.762	0.785	24.0 28.0 28.0	25.0 26.3 22.7	6.0 7.6 6.3	12.5 30.9 50.0
36	90.0 75.5 57.5	0.820 0.827 0.848	21.7 34.8 45.0	0.745 0.759	0.783	23.0 26.0 28.0	19.5 27.3 25.9	4.5 6.8 7.3	10.0 24.5 42.5
45	82.0 60.0	0.824 0.843	28.1 41.2	0.758	0.779	25.0 27.0	23.0 24.7	5.7 6.7	18.0 40.0
65	92.0 78.8	0.820 0.832	23.9 30.0	0.749	0.769	22.0 25.0	22.1 23.6	4.9 5.9	8.0 21.2

As the decomposition increases, the conversion of the high boiling point aliphatic hydrocarbons to low boiling paraffin and ethylene series compounds increases to a maximum, with coincident formation of small amounts of cyclic substances. The aromatic hydrocarbons increase at the expense of the low boiling point paraffins and olefins and perhaps acetylenes (no clearcut experimental information is at hand as to the presence of acetylene or its derivatives) which were

first formed. The per cent of recovered oil is an excellent criterion as to the formation of low boiling paraffin hydrocarbons, for a recovery of less than 75 per cent indicates that the reaction has gone well toward the formation of aromatic compounds. Although the low boiling aromatic compounds are excellent hydrocarbons for motor fuel the reaction has gone beyond the point of economy of conversion due to the formation of considerable amounts of gas and carbon. The latter at present has not been utilized, although of lampblack consistency. The per cent of recovered oil increased with increase of the rate



of oil flow<sup>1</sup> which indicates less conversion toward the aromatic hydrocarbons and more toward the aliphatic substances. Within the range of the above experiments the effect of temperature was greater than the rate of oil flow or time factor.

GASOLINE IN THE RECOVERED OIL (Fig. I)—The constituents boiling below 150° C. have been taken as representing the gasoline cut. In refinery practice the cut may run above this temperature. As the temperature increased the per cent boiling below 150° C. increased, while with increase of rate of oil flow the per cent of the gasoline cut decreased.

#### SPECIFIC GRAVITY OF THE RECOVERED OIL (FIG. II)—

The specific gravity of the recovered oil increased with increase of temperature. This is in accord with previous investigations upon the thermal decomposition of hydrocarbon oils for low boiling point aliphatic or aromatic formation.<sup>1</sup> In plant control the physical constant of specific gravity is the most rapid method for controlling the type conversion desired. The higher the specific gravity of the recovered oil the greater the aromatic formation in the recovered oil. For a given oil, after a series of analyses of the recovered oil under varying conditions of temperature and rates of oil flow have been made, a graph can readily be constructed from which the per cents

<sup>1</sup> Met. and Chem. Eng., 15 (1916), 245.

<sup>2</sup> Rittman, Twomey and Egloff, *Ibid.*, 13 (1915), 682.

<sup>3</sup> Egloff and Twomey, *Ibid.*, 14 (1916), 247.

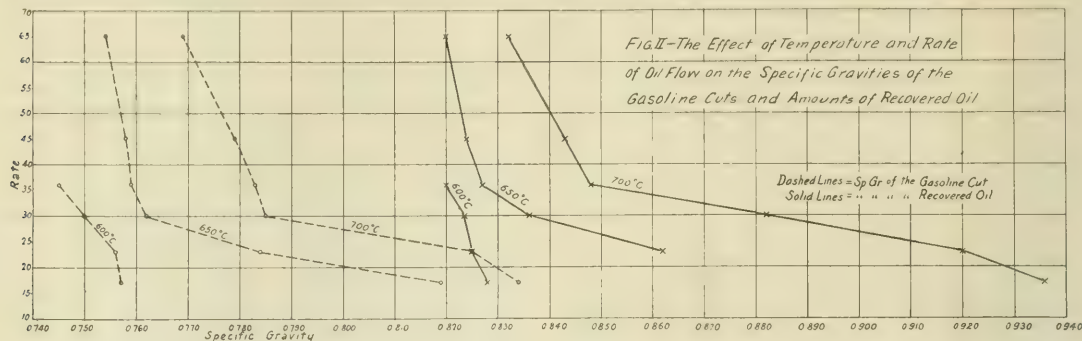
<sup>4</sup> Hempel, J. Gasbel., 53 (1910), 77, 101, 137 and 155; Tocher, J. Soc. Chem. Ind., 13 (1894), 231; Jones, Am. Gaslight J., 99 (1913), 273; Whitaker and Alexander, This Journal, 7 (1915), 484; Egloff and Twomey, Met. and Chem. Eng., 15 (1916), 245.

<sup>5</sup> Egloff and Twomey, J. Phys. Chem., 20 (1916), 121.

<sup>1</sup> Egloff and Twomey, Met. and Chem. Eng., 15 (1916), 245.



of constituents plotted against the specific gravity would give a rapid method for control of the products desired. This method must be employed for each particular oil utilized for gasoline or aromatic production. In all thermal, pressure or catalytic reactions among hydrocarbons of the aliphatic type, aromatic hydrocarbons apparently form, to some extent.



The specific gravity of the recovered oil decreased as the rate of oil flow increased, or as the time factor decreased.

**SPECIFIC GRAVITY OF THE GASOLINE CUT (FIG. II).—**The specific gravity of a "cracked gasoline" is always higher than that of a gasoline derived by simple distillation at atmospheric pressure, from a petroleum crude oil. This increase in specific gravity is due to aromatic hydrocarbons being present, the specific gravity of these being much higher than of the paraffins. The specific gravity of the gasoline cut increased with increase of temperature and decreased as the rate of oil flow increased.

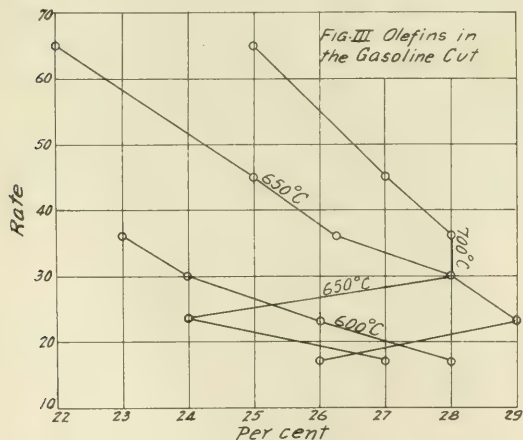
**OLEFINS IN THE GASOLINE CUT (FIG. III).—**The olefin content of the gasoline cuts did not vary much, al-

per hour the olefin content changed from 28 to 23 per cent. No marked differences were to be noted in the olefin content of the various gasoline cuts. The gasoline cut after treatment with sulfuric acid gave a water white oil without appreciable odor and after standing a week no resinous material precipitated out of solution which seems to have occurred in a

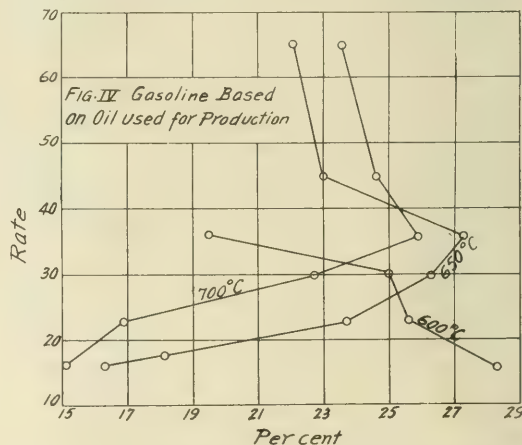
number of cases, and was probably due to insufficient washing with sulfuric acid. In cracking reactions unsaturated compounds form coincidentally with the formation of saturated hydrocarbons of the paraffin series in the cracked gasoline, but usually in much lower per cent than the paraffin hydrocarbons. They may be removed from the gasoline cut by the following methods:

- 1—Sulfuric acid treatment
- 2—Chlorination of the gasoline cut converting the unsaturated compounds to chlor-derivatives and utilizing as solvents
- 3—Esterification, formation of acetates, .....
- 4—Hydrogenation

Another disposition of the unsaturated compounds, if really objectionable in gasoline, which is more than questionable, is to blend with "natural gasoline,"



though the conditions of the experiments varied widely. Within the temperature range of the experiments the olefin content increased as the temperature increased with the exception of the experiment at 17 gal. an hr. and temperature from 600 to 700° C. under which condition the per cent of olefins decreased. As the rate of oil flow changed from 17 to 36 gal.

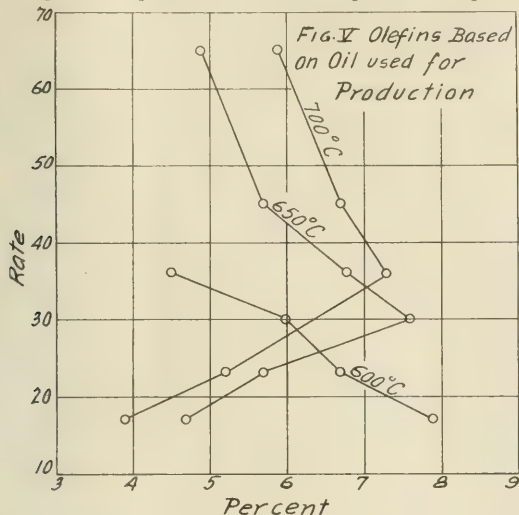


or the cut may be used directly as motor fuel with the unsaturated compounds present.

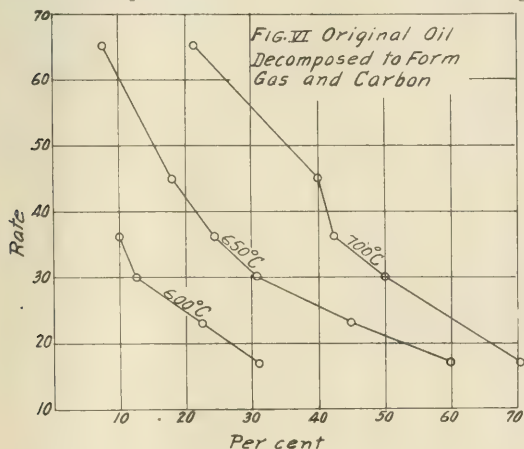
**GASOLINE ON THE BASIS OF OIL USED (FIG. IV).—**Industrially the valuable results are those which express the per cent of gasoline formation on the basis of oil used for production. The maximum yield of gasoline was found to be 28.3 per cent. Increase of rate at

600° C. decreased the per cent of gasoline formation from 28.3 to 19.5. At 650° C. the maximum formation of 27.3 per cent occurred at 36 gal. per hr. A change of temperature to 700° C. gave a maximum at 36 gal. per hr. of 25.9 per cent.

The best conditions of operation for this type oil for gasoline production with respect to capacity



factor of gallons per hour and the per cent of oil left over for the purpose of re-cracking after cracked gasoline removal, was found to be at a temperature of 650° C. 150 lbs. pressure and 65 gal. per hr. The latter conditions gave a per cent of 22.1 on basis of oil used for production. Maxima are shown in Fig.



IV of gasoline formation which is a result of the two factors of per cent of recovered oil and the per cent of gasoline in the recovered oil.

**OLEFINS ON THE BASIS OF OIL USED**—In Fig. V maxima are to be noted in the formation of olefins on the basis of oil used at 30 gal. per hr. of 7.6 per cent at 650° C. Increasing the temperature to 700° C. at 36 gal. per hr. the per cent of olefins was 7.3 while no peak is shown in the olefin formation at 600° C.

#### THE EFFECT OF TEMPERATURE AND RATE OF OIL FLOW ON THE PER CENT OF ORIGINAL OIL DECOMPOSED TO FORM GAS AND CARBON

Increase of temperature increased the decomposition of the starting oil which seems to be the invariable rule in all hydrocarbon oils which have been subjected to pressure and temperature treatment. When the rate of oil flow is increased the per cent of recovered oil increased, hence decreasing the decomposition of the starting oil used. This is in direct accord with theoretical considerations.<sup>1</sup> The differences between the per cent of recovered oil and 100 gives the per cent of starting oil going to carbon and gas. The gas formed is usually scrubbed for its constituents which are soluble in the scrubbing oil, leaving a gas which is usually utilized for heating the cracking tubes. The carbon formed is a small per cent of the original oil and is, in characteristics, similar to ordinary lampblack.

#### SUMMARY

I—The residue of a Pennsylvania crude oil after the gasoline had been removed was subjected to temperatures of 600, 650 and 700° C. at constant pressure of 150 lbs. and varying rates of oil flow of 17, 23, 30, 36, 45 and 65 gal. per hr., for the purpose of gasoline formation from the residue.

II—The per cent of the recovered oil decreased with increase of temperature and increased with increase of the rate of oil flow. The specific gravity of the recovered oil increased with increase of temperature but decreased with increase of the rate of oil flow.

III—Upon the basis of 100 gal. of oil used the maximum of 28.3 per cent of gasoline for every 100 used under conditions of 600° C. and 17 gal. per hr. was found. The best working conditions with this oil gave 22.1 per cent gasoline at 65 gal. per hr. and 650° C.

IV—The minimum specific gravity of the gasoline formed was found to be 0.745 at 36 gal. per hr. and temperature of 600° C., under which conditions 19.5 per cent gasoline was formed.

V—The olefin formation in the gasoline cut ranged between 22 and 29 per cent in the recovered oil. Upon the basis of 100 gal. of oil used the minimum formation of 3.9 per cent and maximum of 7.9 per cent of olefins were recorded.

VI—The per cent of oil going to gas and carbon with the oil used gave a minimum of 10 per cent and maximum of 70.6 per cent.

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#### THE ESTERS OF OLEIC ACID AND THEIR HYDROGENATED PRODUCTS

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The hydrogenation of the glycerides of various unsaturated fatty acids in the presence of finely divided nickel has claimed the attention of numerous investigators. This problem, so important commercially,

<sup>1</sup> Egloff and Twomey, *Met. and Chem. Eng.*, **15** (1916), 245.



has been thoroughly studied from both the technical and scientific standpoint. Very little work was done on the hydrogenation of esters of oleic acid other than the glycerine esters.

In 1906 Bedford<sup>1</sup> studied the esterification of linolic and linolenic acid and the hydrogenation of these esters in the presence of finely divided nickel. The ethyl and methyl esters of these acids were prepared by him as follows: The free fatty acid was boiled under reflux with an excess of the alcohol in the presence of a small amount of sulfuric acid. The product was then treated with an excess of sodium bicarbonate solution. The oil that separated out was decanted off and dissolved in ether. The ether solution was washed with water, dried with anhydrous sodium sulfate and then distilled to remove the ether. The oil left behind was purified by vacuum distillation. The ethyl esters of linolic and linolenic acid were hydrogenated in the presence of finely divided nickel at about 180° C. Ethyl stearate was obtained in both cases.

The work done on the esterification of oleic and stearic acid is more extensive. Berthelot prepared the mono-glycerides by heating the fatty acid with an excess of glycerine in a sealed tube. This method generally gave a product contaminated with the di-glyceride.<sup>2</sup> Other methods for the preparation of the glycerides of fatty acids involve the use of halogen substituted glycerides and sodium salts of fatty acids.<sup>3</sup> Mixtures of mono- and di-glycerides of the higher fatty acids may be prepared by heating their tri-glycerides with an excess of glycerine to 200 to 250° C. in the presence of such catalytic bodies as finely divided aluminum oxide, thorium oxide or titanium oxide.<sup>4</sup>

Di-glycerides are prepared similarly to the mono-glycerides with only the modification that a larger proportion of fatty acid is employed, or that the di-halogen substituted glycerides are employed instead of the mono as in the case of mono-glycerides. According to Grün<sup>5</sup> pure di-glycerides may be prepared by treating 3 hrs. at 70° C. a solution of 1 part fatty acid in 1½ parts sulfuric acid (78.3 per cent acid strength) with glycerol-di-sulfuric acid prepared from 4 parts sulfuric acid (98.3 per cent strength) and 1 part glycerine. On heating 1 part of  $\alpha$ -mono-stearin with three parts of stearic acid to 280° C. for 3 hrs. Berthelot obtained  $\alpha,\alpha$ -distearin. Another method employed by him for the preparation of this substance was to heat stearin with an excess of glycerine to 220° C. or to heat equal parts of stearic acid and glycerine to 160° C. for 14 hrs. It was also prepared by Guth by heating 1 molecule  $\alpha,\alpha$ -dichlorhydrin with 2 molecules of sodium stearate in a sealed tube at 140 to 150° C. for 6 to 8 hrs. The  $\alpha,\beta$ -isomer was prepared from  $\alpha,\beta$ -dibromohydrin and sodium stearate.  $\alpha,\alpha$ -Diolein was prepared by Berthelot on heating 1

part of  $\alpha$ -mono-olein with 5 parts oleic acid to 250° C. for several hours, or on heating olein with glycerol to 200° C. for 22 hrs. Guth prepared the  $\alpha,\alpha$ -diolein from  $\alpha,\alpha$ -dichlorhydrin and sodium oleate.  $\alpha,\beta$ -Diolein was prepared from  $\alpha,\beta$ -dichlorhydrin and sodium oleate.

Berthelot prepared pure triglycerides by heating glycerine and fatty acids.<sup>1</sup> Scheij<sup>2</sup> heated glycerol with an excess of fatty acid in a slow current of air with the object of obtaining complete esterification by removing the water as it was formed. Tri-stearin can also be prepared by heating mono-stearin or distearin with an excess of stearic acid or tri-hydrin with sodium stearate. The method of preparation of tri-olein is similar in all respects to the preparation of tri-stearin.

Esters of fatty acids other than glycerides are prepared by dissolving the fatty acid in methyl, ethyl, amyl, etc., alcohols, then passing a current of hydrochloric acid through the solution and washing the product with water.<sup>3</sup> Ethyl stearate was prepared with a yield of 80 per cent by heating stearic acid in a 3 per cent solution of dry hydrochloric acid in ethyl alcohol.<sup>4</sup> Pottevin<sup>5</sup> prepared esters of oleic acid by adding to the mixture of the fatty acid and alcohol 1 per cent of finely divided hog's pancreas which had been exhausted with ether and alcohol.<sup>6</sup>

#### EXPERIMENTAL

In an investigation pertaining to the hydrogenation of oils which has been in progress in this laboratory for some time, information was desired on the behavior of various esters of the fatty acids in the hydrogenation process and in connection with this work the oleic esters of methyl, ethyl, propyl, butyl, amyl and benzyl alcohols were prepared, also the glycerides of oleic acid. These products in turn were hydrogenated and the behavior of each during the hydrogenation operation was noted.

The following data briefly indicate some of the results obtained during the investigation.

#### METHYL OLEATE

U. S. P. oleic acid (56.4 g.) was dissolved in 25.6 g. acetone-free methyl alcohol. The solution was treated with 0.7 g. sulfuric acid and then boiled for 5½ hrs. The product, which separated into two layers on standing, was washed a number of times with distilled water until free from sulfuric acid. The emulsion that was obtained was broken by heating for a short while on a hot water bath. The oily layer was carefully decanted from the aqueous layer and dried. The oil did not possess any characteristic odor. It was homogeneous and almost colorless. It had an acid number of 17.6.

The oil was treated with a 10 per cent aqueous solution of sodium hydroxide in the cold. After intimate mixing the caustic soda was drawn off and

<sup>1</sup> "Über die Ungesättigten Säuren des Leinöls," Dissertation, Erlangen, 1906; *Ber.*, **42** (1909), 1324.

<sup>2</sup> "Chimie organique fondée sur la synthèse, Paris," 1860, Vol. 11; *Ann. de chim. et de phys.*, [3] **41** (1854), 420.

<sup>3</sup> Kraft, *Ber.*, **36** (1903), 4343; Guth, *Zeit. f. Biolog.*, **44** (1903), 78; Romburg, *Rec. d. trav. chim. Pays-Bas*, **1882**, 186.

<sup>4</sup> *Seifen. Ztg.*, **1914**, 1092. German patent 277,641, 1914, to Naamlooze Vennootschap Ant. Jurgens Vereenigde Fabrieken.

<sup>5</sup> *Ber.*, **38** (1905), 2284.

<sup>1</sup> *Ann. de chim. et de phys.*, [3] **41** (1854), 420.

<sup>2</sup> *Rec. d. trav. chim. Pays-Bas*, **18**, 169.

<sup>3</sup> Lewkowitsch, "Oils, Fats and Waxes," **1** (1913), 148.

<sup>4</sup> Holzman, *Arch. der Pharm.*, **236** (1898), 409; *Chem. Cent.*, **II**, **69** (1898), 755.

<sup>5</sup> *Compt. rend.*, **138** (1904), 378; *Chem. Cent.*, **I**, **75** (1904), 787.

<sup>6</sup> Lewkowitsch, "Oils, Fats and Waxes," **1** (1913), 6-37.

the oil was washed with a saturated solution of sodium chloride until the wash waters ceased to react alkaline. This treatment removed all of the free caustic soda leaving the oil and the saponified oleic acid intimately mixed with one another. The mixture of soap and methyl oleate was shaken with 15 to 20 times its volume of water and allowed to stand until the emulsion separated into two layers. The lower turbid layer, containing most of the soap in solution, was drawn off and the operation repeated until the wash waters were free from turbidity. The dried ester was a liquid and was milky in appearance. On standing for several hours the turbidity disappeared from the upper portion of the ester. The acid number of the oil fell to 1.3. The iodine number was found to be 87.0. The theoretical iodine number of methyl oleate is 85.8. The experiment was repeated with the object of preparing methyl oleate free from turbidity and gave the same results as obtained above.

**HYDROGENATION OF METHYL OLEATE**—A portion of methyl oleate containing 1 per cent of finely divided metallic nickel (reduced for 15 to 20 min. in a stream of hydrogen at 320 to 350° C.) was treated for about 2 hrs. at about 180 to 200° C. with hydrogen which was simply allowed to bubble through the liquid as a brisk stream, thereby maintaining the catalyzer in suspension. The mixture of oil and catalyzer was filtered in the hot oven. The filtered solid product obtained was white and crystalline. It had an iodine number of 0.4 and melted at 37° C.

The melting point of this product as well as the melting point of the esters described below were determined as follows: A glass capillary about 2 in. long and open at both ends was filled about  $\frac{1}{6}$ th full with molten oil. After the oil had solidified the capillary was attached in the usual way to a thermometer and immersed in a water bath having the upper part of the capillary above the surface of the liquid. The melting point noted was that temperature at which the oil became sufficiently molten to be moved upwardly in the capillary by the pressure of the water.

#### ETHYL OLEATE

Oleic acid (50 g.), 50 g. of ethyl alcohol (sp. gr. 0.816 at 15° C.) and 1 g. concentrated sulfuric acid were boiled for  $4\frac{1}{2}$  hrs. The product on standing separated out a heavy oil. Separation of oil in this manner was also observed in the other esterification experiments. The product was washed with distilled water until it was free from alcohol and sulfuric acid. The emulsion of water and oil was treated in the same way as the emulsion obtained in the case of methyl oleate. The dried oil had a straw-yellow color and possessed an agreeable odor. The acid number was 19.8.

The free oleic acid was removed with 10 per cent aqueous sodium hydroxide according to the method described under methyl oleate. The acid number of the ethyl oleate was reduced by this treatment from 19.8 to 0.6. Its iodine number was 83.3. The iodine number of pure ethyl oleate is 81.9.

**HYDROGENATION OF ETHYL OLEATE**—A portion of the ethyl oleate containing 1 per cent of metallic nickel

(reduced for 15 min. in a stream of hydrogen at 320 to 350° C.) was exposed to a rapid current of hydrogen for about 2 hrs. The oil was filtered through an ordinary filter paper in the hot oven. The product melted at 31° C. Its iodine number was 5.3.

#### PROPYL OLEATE

Oleic acid (56.4 g.), 24 g. propyl alcohol (Kahlbaum) and 0.4 g. concentrated sulfuric acid were boiled for  $4\frac{1}{2}$  hrs. The mixture was washed free from sulfuric acid and alcohol and the oil was dried in the usual way. The acid number of the product was 11.2. It was then treated with alkali according to the method described above. The acid number was reduced by this treatment to 0.5. The product was practically colorless and without odor. Like methyl oleate it possessed a marked turbidity, but on standing the upper portion of the product became clear. The iodine value of the product was found to be 77.9. The iodine value of pure propyl oleate is 78.4.

**HYDROGENATION OF PROPYL OLEATE**—The hydrogenation in this case was carried out under conditions practically identical to those employed in the hydrogenation of methyl and ethyl oleate. The hardened oil had an iodine number of 1.3. It melted at 27° C.

#### ISO-BUTYL OLEATE

The amounts of material employed in the preparation of butyl oleate were 56.4 g. oleic acid, 29.6 g. iso-butyl alcohol (C. P.) and 0.5 g. concentrated sulfuric acid. The mixture was boiled for  $5\frac{1}{4}$  hrs. and then washed free from sulfuric acid and steam-distilled until the distillate came over odorless. The oil had an acid number of 9.3. Treatment with alkali reduced the acid number to 0.4. The ester was of a straw-yellow color and practically odorless. It had an iodine number of 75.7. The iodine number of pure iso-butyl oleate is 75.1.

**HYDROGENATION OF ISO-BUTYL OLEATE**—The ester was hydrogenated for about 2 hrs. in the presence of 1 per cent metallic nickel (reduced for 15 min. at 320 to 350° C.). The temperature of hydrogenation was 180 to 200° C. The hydrogenated product was soft and translucent and distinctly crystalline. It somewhat resembles crude paraffin. It had an iodine value of 0.2 and melted at 25° C.

#### AMYL OLEATE

Amyl oleate was prepared as follows: 56.4 g. oleic acid, 33.2 g. amyl alcohol (B. P. 130–132) and 0.9 g. concentrated sulfuric acid were boiled under a reflux condenser for  $5\frac{1}{4}$  hrs. The product was washed free from acid and steam-distilled until the distillate came over odorless. The dried ester had an acid number of 4.5. After treatment with alkali solution the acid number fell to 0.7. The ester was brownish yellow in color and possessed an odor characteristic of fats and oils. Its iodine value was 71.3. The iodine value of pure amyl oleate is 72.1.

**HYDROGENATION OF AMYL OLEATE**—The product was hydrogenated in the usual manner under conditions similar to those employed in the previous experiments. The hydrogenated product was soft and non-homo-



geneous, consisting of a liquid oil and a crystalline body. It resembled crude paraffin. It had an iodine value of 1.7 and melted at 22° C.

#### GLYCERINE OLEATE

Oleic acid (56.4 g.) and 18.4 g. glycerine were heated for 5 hrs. at 240° C. with continuous stirring. The oily product was washed several times with warm water and dried. Its acid number was 0.6. It was dark in color, very viscous and not uniform in appearance. In cool weather a crystalline body formed which rendered the ester opaque. The iodine number of the product was 69.4. Pure glycerol mono-oleate has an iodine number of 71.3.

**HYDROGENATION OF GLYCERYL OLEATE**—The ester was hydrogenated in the usual way. Treatment with hydrogen for about 2 hrs. at 180 to 200° C. gave a product which melted at 59° C. and possessing an iodine number of 6.5. The hydrogenated product was similar in appearance to a good grade of hardened cottonseed oil, except that it was somewhat darker in color.

#### BENZYL OLEATE

Oleic acid (56 g.), 49 g. benzyl alcohol and 1 g. concentrated sulfuric acid were boiled under reflux for 6 hrs. The product was steam-distilled until the distillate came over odorless. The oil was then treated with alkali to remove the free oleic acid, dried and distilled at 25 to 40 mm. pressure. The oil came over largely at 275 to 285° C. It was light yellow in color and practically odorless. Its acid value was 0.7, and the iodine value was 62.3. The iodine value of pure benzyl oleate is 68.2. In another case, the same amounts of benzyl alcohol and oleic acid were used but the amount of sulfuric acid was reduced to 0.5 g. The mixture was heated for 5¼ hrs. at 145 to 150° C. The product was steam-distilled, washed free from acid and dried. It had an acid number of 8.7. Treatment with sodium hydroxide solution reduced the acid number to 0.4. The ester was of a dark brown color, almost odorless and had an iodine value of 54.5.

**HYDROGENATION OF BENZYL OLEATE**—Hydrogenation in the presence of finely divided reduced nickel gave a product which had an iodine value of 6.3 and a melting point of 28° C.

#### BEHAVIOR OF OLEIC ACID WITH PHENOL, RESORCIN AND BETA-NAPHTHOL

Oleic acid (28.2 g.) and 37.6 g. phenol were boiled for 4 hrs. under reflux. The product was then washed with boiling water until it was free from phenol. The acid number of the dried oil was 201. Oleic acid (28 g.) and 22 g. resorcin were treated for 4 hrs. at 180 to 200° C. A considerable amount of the resorcin was lost by sublimation. The product darkened considerably. It was purified by washing with hot water and drying. Its acid value was 197. Beta-naphthol when heated with oleic acid for several hours to 200° C. failed to combine with it.

#### OLEIC ACID AND ANILINE

Aniline (24.4 g.) and 37 g. oleic acid were heated under a reflux condenser for 4 hrs. at 170 to 190° C.

The mixture darkened considerably. It was steam-distilled until the distillate was free from aniline. The acid number of the steam-distilled product was 30.5. It became solid on standing. The substance was treated with a solution of sodium hydroxide and washed free from alkali and sodium oleate. The acid number of the product was reduced to 3.6. The product melted at 34° C. It was dark brown in color and had a greasy feel.

**HYDROGENATION OF THE PRODUCT**—The material was hydrogenated for 2 hrs. at 190 to 200° C. in the presence of 1 per cent finely divided reduced metallic nickel. The hydrogenated product was filtered in the hot oven. It had an iodine number of 30.5. The iodine value of the unhydrogenated substance was 69.5. The iodine value of oleic anilide is 71.6. The product melted at 76° C. and was very hard and brittle. This and other allied bodies are being made the subject of further investigation in this laboratory.

#### SUMMARY

I—The esters of oleic acid with methyl, ethyl, propyl, iso-butyl, amyl and benzyl alcohols and also glycerine were prepared. These bodies were of oily consistency and liquid at room temperature.

II—These esters were hydrogenated in a liquid state in the presence of finely divided reduced nickel and products were obtained that were practically saturated.

III—The nature of the alcohol did not seem to affect to any great extent the rate or degree of hydrogenation of the oil.

IV—A product derived by heating oleic acid and aniline was found to hydrogenate readily to form relatively a very hard product.

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#### WATER ABSORPTION BY VULCANIZED FIBER

By ROLLIN G. MYERS

Received August 3, 1916

The writer conceived the idea of using vulcanized fiber for a golf ball covering, *i. e.*, as a substitute for the more expensive gutta percha or rubber. The

TABLE I

Expt. No.	Color and Texture	Size in Inches	Time Immersed Hours	GRAMS WEIGHT Original	After Im-mersion	Per cent Water Absorbed
1.....	Hard Red	1 X 1 X 1/32	4	0.591	0.866	46.53
2.....				0.599	0.890	48.58
3.....				0.558	0.810	46.16
4.....				0.569	0.846	48.66
5.....				6.700	9.490	41.64
6.....	Flexible	1 X 1 X 1/16	4	1.222	1.704	39.44
7.....				1.254	1.751	39.63
8.....				1.275	1.742	36.62
9.....				1.285	1.766	37.46
10.....				1.341	1.785	33.10
11.....	Hard gray	2 X 2 X 1/32	4	1.208	1.610	33.27
12.....				1.327	1.764	32.93
13.....				1.300	1.725	36.69
14.....				7.360	9.790	33.08
15.....				6.995	...	51.06
16.....	Hard gray	1 X 1 X 1/16	4	1.721	2.371	37.76
17.....				1.254	1.772	41.30
18.....				1.829	2.599	42.09
19.....				1.546	2.178	40.87

#### AVERAGE ABSORPTION (PERCENTAGES) FOR 4 HOURS IMMERSION

Dimensions	Hard Red	Flexible Red	Hard Gray
1 X 1 X 1/32 in.	47.98	..	51.06
1 X 1 X 1/16 in.	38.25	33.74	40.50

undeniable toughness of this substance, combined with its sufficiently high resiliency, were properties entirely in its favor. Considerable water is absorbed, however, when it is placed in this liquid for any length of time. This property is decidedly objectionable, since the fiber shows a marked decrease in its resiliency and toughness. In order to measure the actual quantity of water absorbed, the following experiments were made with materials furnished by the American Vulcanized Fiber Co. These are summed up in Table I. Three other experiments made on rate of absorption are summarized in Table II.

TABLE II

Expt. No.	Color and Texture	Size	Weight taken Grams	PERCENTAGE INCREASE					Total
				1st hr.	2nd hr.	3rd hr.	4th hr.		
1.....	Hard Gray	2 × 2 × 1/32	4.235	25.92	17.24	6.42	3.52	53.10	
2.....			4.082	11.14	10.20	6.53	3.23	31.13	
3.....	Hard Red	2 × 2 × 1/16	6.901	17.40	7.13	7.37	5.83	37.73	

The results indicate that the greatest part of the water absorbed is during the first hour. From then on there appears to be a steady decrease until the experiment was finished. The absorption is completed in 7 to 8 hours, possibly. The total increase in absorption agrees quite well with that observed in Table I, excepting the value obtained in Expt. 3; no reason can be given for this divergence.

The writer decided to treat the fiber with various substances to see if he could not reduce the degree of water absorption, and by so doing annul the effect of this property to such an extent as to make this

TABLE III

(A) Saturated with 5 per cent alum solution, then in 8 to 9 per cent ammonia solution, finally in water and then dried.

(C) First saturated with water, then placed in boiled linseed oil, which is heated slowly from the ordinary temperature to 135-140° C. for an hour or two. The fiber was then taken out and allowed to dry.

(D) The fiber was placed in a nearly boiling saturated agar-agar solution for 2 or 3 hrs., then taken out and dried.

(E) Saturated with 15 per cent NaOH solution for 2 or 3 hrs., then exposed to the action of carbon disulfide vapor in a tight jar for about 48 hrs.; finally washed with dilute hydrochloric acid and dried.

(F) Placed in about 70 per cent sulfuric acid, then washed and dried.

(G) Saturated with a strong solution of zinc sulfate solution, then placed in 8-9 per cent ammonia water, washed a little and dried.

(H) Saturated with a mixture of blood albumen, borax, magnesium sulfate and glycerine, then exposed to the action of steam and dried.

(I) Saturated with a hot 15 per cent gelatin solution, then exposed to the action of hot formaline vapor and dried.

(J) The wet fiber was placed in hot molten paraffin, then heated to 115-120° C. for 1 or 2 hours, then removed and allowed to cool.

(K) The moist fiber placed in a mixture of Burgundy pitch, paraffin and linseed oil, which is heated to 105-110° C. for 1 or 2 hrs., then taken out and cooled.

Expt. No.	Method of Treatment	Color and Texture	Size in inches	Per cent of Water Absorbed	Time of immersion	REMARKS
1	A	Hard Red	1 8 X 1 25 dia. hemisphere shell	16.44	5.5	No change
2	B	Hard Gray	2.5 X 2 X 1/16	41.07	6.0	No change
3	C	Piece from Ex. 2 Retreated		38.47	4.0	No change
4	C	Hard Red	2 X 2 X 1/16	43.05	...	No change
5	D	Hard Gray	2 X 2 X 1/32	9.76	4.0	Brittle
6	D	Hard Gray	2 X 2 X 1/32	17.80	...	No change
7	E	Hard Red	2 X 2 X 1/16	5.50	...	No change
8	E	Hard Gray	2 X 2 X 1/16	45.45	...	No change
9	F			41.40	4.0	A slight increase in flexibility apparent
10	F			44.45	6.0	
11	G			50.08	4.0	
12	H	Hard Red	1 1/16 Irreg. in shape	35.84	...	
13	I	Hard Gray		35.53	...	
14	I			37.73	...	Brittle
15	J			8.66	...	No change
16	K	Piece from 13 Retreated		10.88	...	Brittle
17	K	Piece from 15 Retreated		21.32	...	Brittle
18	K	Piece from 16 Retreated		16.36	...	Brittle
19	K	Hard Red 2 X 2 X 1/16		17.86	...	No change

material of value for a golf ball cover. Table III is a summary of the results of these later experiments.

These preliminary experiments indicate that the objectionable property of absorbing relatively large quantities of water can be done away with to a large extent, perhaps completely. The final mechanical difficulty of covering the elastic rubber core with the treated fiber in such a way as to eliminate any tendency of cracking or of the tearing away of the latter from the core, would require further experimentation to be overcome.

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## A BOILING METHOD FOR THE DETERMINATION OF WATER-SOLUBLE ARSENIC IN LEAD ARSENATE

By GEORGE P. GRAY AND A. W. CHRISTIE

Received July 18, 1916

### INTRODUCTION

Some 3000 tons of arsenic trioxide have been annually produced in the United States during recent years as a by-product in smelters of the western states and an equal amount is also imported under normal conditions.<sup>1</sup> Probably the largest use of this "white arsenic" is in the preparation of lead arsenate used solely in the control of leaf-eating insects. This commodity is usually supplied to the consumer in the form of a paste containing 40 to 50 per cent water, 12 to 16 per cent arsenic pentoxide, and 30 to 40 per cent lead oxide. Of recent years, however, the dried powder is coming into favor to some extent.

The acid and basic salts of lead and arsenic acid, and possibly the neutral salt, are believed to comprise the various brands on the market. Most commercial lead arsenates are probably mixtures rather than any pure salt.

In order to compound an arsenical which may be safely applied to growing plants without fear of defoliation and yet will poison the insects, many factors must be taken into consideration. The most important thing to be considered is that the arsenical must be as free from water-soluble arsenic as can be economically produced on a commercial scale. The grower has a right to demand this protection for his orchards and crops for the reason that arsenic in *water-soluble form* is one of the most violent plant-poisons known. It has been shown that certain pure salts of lead and arsenic acid are exceedingly insoluble in water.<sup>2,3,4</sup> Commercial lead arsenates, however, usually contain a small amount of water-soluble arsenic as an impurity which has not been washed out during the process of manufacture. The majority of lead arsenates which are being offered for sale in California at the present time are reasonably free from impurities. Occasionally, however, a sample is received by the Insecticide and Fungicide Laboratory of the University of California

<sup>1</sup> F. L. Hess, "The Production of Antimony, Arsenic, Bismuth, and Selenium in 1912," 1913, "The Mineral Resources of the United States," U. S. Geological Survey.

<sup>2</sup> R. H. Robinson and H. V. Tartar, "The Valuation of Commercial Arsenate of Lead," THIS JOURNAL, 7 (1915), 499;

<sup>3</sup> "The Arsenates of Lead," Ore. Agr. Exp. Sta., Bull. 128 (1915);

<sup>4</sup> H. V. Tartar and R. H. Robinson, "The Arsenates of Lead," J. Am. Chem. Soc., 36 (1914), 1843.



which is found to contain sufficient water-soluble arsenic to be a menace to foliage. The Federal Insecticide Act of 1910 and the state insecticide laws are quite uniform in restricting the amount of water-soluble arsenic in lead arsenate to 0.75 per cent. An accurate method is, therefore, necessary to determine this solubility. An ideal method should be rapid in order to be adaptable to factory control and at the same time should be adequate for the examination of specimens to determine their suitability as insecticides and establish their legal status.

Neither of the two provisional methods of the Association of Official Agricultural Chemists<sup>1,2</sup> nor other published methods seem to meet these requirements in all respects.

#### PROVISIONAL METHODS OF THE A. O. A. C.

Haywood's method for the determination of water-soluble arsenic in commercial lead arsenates was made a provisional method of the Association of Official Agricultural Chemists in 1907<sup>3</sup> and still remains as such.<sup>4</sup> It is given below in full in order that other methods may be more readily compared with it.

The paste is prepared for analysis by drying at from 80 to 100° C., and grinding to a powder. Two grams of the powder are placed in a flask with 200 cc. of CO<sub>2</sub>-free water and allowed to stand 10 days, shaking eight times a day at hourly intervals. A 200 to 400 cc. aliquot of the filtrate from the above digestion is used for the determination of water-soluble arsenic oxide as follows: "Add 0.5 cc. of sulfuric acid and evaporate it to a syrupy consistency; then heat on the hot plate to appearance of white fumes. Add a very small amount of water and filter off lead through the very smallest filter paper, using as little wash water as possible. Place this filtrate in an Erlenmeyer flask, and determine arsenic as described under total arsenic oxide, using the same amount of reagents and the same dilutions." [The method for the determination of "total arsenic oxide" referred to in the above quotation is a modification of the Gooch and Browning method,<sup>5</sup> the accuracy of which is not under discussion in this paper.]

McDonnell, A. O. A. C. Referee on Insecticides for 1910,<sup>6</sup> conducted some experiments to determine the time necessary to dissolve the water-soluble arsenic from lead arsenate and concluded that the digestion need not exceed 2 to 4 days. The following year several chemists cooperated in making a comparison of the results obtained by a 1-day extraction and a 10-day extraction. The data reported, however, were rather conflicting.<sup>7</sup>

The investigation was continued by Averitt, Referee for 1912.<sup>8</sup> The 10-day method was severely criticized in the Referee's report. Methods which were thought to correspond more closely to field conditions were proposed for trial by cooperating chemists. Two grams of the paste were placed in a bottle with 200 cc. of CO<sub>2</sub>-free water and shaken in a mechanical shaker for 3 hrs. In comparison with the above method of extraction, the same quantity of sample and water were placed in a bottle

and shaken every half-hour during a working day. Only three chemists cooperated in this study, so that the results obtained were not very conclusive. The temperature of digestion was also studied.

Very little work was done on this problem by the A. O. A. C. during the following year, but the opinion of the Referee is expressed in his report as follows:<sup>1</sup>

"It is to be noted that the methods of analysis are not in question at all. The time of digestion is pretty well established and a few degrees in temperature is not very material in view of the fact that both time of digestion and temperature are entirely arbitrary. The Referee is well aware and has pointed out the fact that what we are determining and calling soluble arsenic is largely soluble lead arsenate, but as both time and temperature of digestion are not absolute factors, it is probably a matter of small moment."

Upon the recommendation of Averitt another provisional method was adopted by the A. O. A. C. at its 30th annual convention.<sup>1</sup> The recommendation to drop the existing 10-day provisional method was not adopted. The more recent method differs from the 10-day method in the following points: (1) The paste is used for extraction instead of the air-dry sample. (2) The proportion of sample to water is increased. (3) The time of digestion is reduced to 24 hrs. (4) The temperature of digestion is specified at 32° C.

No further work has been done by the Association in this investigation.

#### THE COLBY METHOD

A method proposed by Colby<sup>2</sup> for the determination of water-soluble arsenic in Paris green has been used to a considerable extent in the California Insecticide Laboratory for a similar purpose in the examination of lead arsenate. Colby weighed out a 0.5 g. sample of the air-dry powder and placed it in a flask with 100 cc. of carbon-dioxide-free water, set in a warm place, and shook the flask every hour during the working day. After standing over night, the water was poured off and a fresh 100 cc. added and treated as before on the second and third day. The 300 cc. of leachings were combined, carefully filtered, and arsenic determined as in the provisional 10-day method of the A. O. A. C., except that sulfuric acid was not added for the removal of the lead unless the same could be detected by a preliminary qualitative test.

#### PROPOSED SHORT METHOD OF CURRY AND SMITH

Curry and Smith<sup>3</sup> were the first to propose the weighing of the paste for analysis without previous drying. This was done with the idea that the sample in this condition would come to equilibrium with the water more quickly. Digestion was made by continuously stirring the sample with water by means of a hot air engine in a thermostat at a temperature of 20° C. for 18 hrs. These investigators found that higher results were obtained for water-soluble arsenic if the quantity of water per unit of sample were increased. They attributed this to the solubility of lead arsenate itself and proposed a solubility factor to be applied as a correction according to the proportion of sample to water.

#### THE OREGON STATION METHOD

Robinson and Tartar<sup>4</sup> appear to have been the first to propose the use of hot water for the extraction of the soluble impurities in lead arsenate. The method of these investigators, known as the "Oregon Station Method," is in brief as follows:

<sup>1</sup> Association of Official Agricultural Chemists, Proceedings of Annual Convention, 30th, Jour. A. O. A. C., Vol. 1, Nos. 1 and 2 (1913).

<sup>2</sup> G. E. Colby, "Arsenic Insecticides," Cal. Agr. Exp. Sta., Bull. 151 (1903).

<sup>3</sup> B. E. Curry and T. O. Smith, "A Short Method for the Determination of Soluble Arsenic in Commercial Lead Arsenates," THIS JOURNAL, 4 (1912), 198.

<sup>4</sup> Loc cit.

<sup>1</sup> Association of Official Agricultural Chemists, Proceedings of Annual Convention, 25th, U. S. Dept. Agr., Bur. Chem., Bull. 122 (1908).

<sup>2</sup> Association of Official Agricultural Chemists, Proceedings of Annual Convention, 31st, Jour. A. O. A. C., Vol. 1, No. 3, and 1, No. 4, Part I (1914).

<sup>3</sup> Association of Official Agricultural Chemists, Proceedings of Annual Convention, 24th, U. S. Dept. Agr., Bur. Chem., Bull. 116 (1907).

<sup>4</sup> Association of Official Agricultural Chemists, "Official and Provisional Methods of Analysis," U. S. Dept. Agr., Bur. Chem., Bull. 107 (revised), (1909).

<sup>5</sup> Ibid.

<sup>6</sup> Association of Official Agricultural Chemists, Proceedings of Annual Convention, 27th, U. S. Dept. Agr., Bur. Chem., Bull. 137 (1910).

<sup>7</sup> Association of Official Agricultural Chemists, Proceedings of Annual Convention, 28th, U. S. Dept. Agr., Bur. Chem., Bull. 152 (1911).

<sup>8</sup> Association of Official Agricultural Chemists, Proceedings of Annual Convention, 29th, U. S. Dept. Agr., Bur. Chem., Bull. 162 (1912).

Four to six g. of the sample are washed on a filter paper with hot water until the washings amount to 1000 cc. Arsenic is determined in an aliquot of the washings in the same manner as in the provisional methods of the A. O. A. C., except that the treatment with sulfuric acid and evaporation for the removal of lead is omitted, for no water-soluble lead was found in any of the samples. Attention was called to the necessity of the use of water free from carbon dioxide and ammonia, they being the first to emphasize that the water used for extraction must be ammonia-free.

#### DISCUSSION OF THE PRESENT METHODS

As the matter now stands, there are two provisional methods for the determination of water-soluble arsenic in lead arsenate, which are recognized by the Association of Official Agricultural Chemists. The original 10-day method is time-consuming and for this reason is impracticable for factory control. The evidence produced by Robinson and Tartar<sup>1</sup> and confirmed by the writers, very strongly indicates that the extraction of lead arsenate by cold water does not remove all the soluble matter even if continued for a period of ten days. It has been shown by the results of chemists who have cooperated in the investigations of the A. O. A. C. that the time of digestion can be shortened without materially affecting the results. The more recent provisional method of the A. O. A. C. specifies the use of the paste for digestion, shortens the time of digestion to 24 hrs., and involves the use of a thermostat to control the temperature at 32° C. Here again the question arises concerning the complete extraction of the soluble matters by means of tepid water. The shaking of the sample at hourly intervals is not a serious objection, but the experience of the writers is that this detail is apt to be forgotten during attention to other duties.

Colby's method is an improvement over the 10-day method and the results obtained are practically the same by either.

Curry and Smith's method requires the use of a stirring device which is not always available. The solution of the soluble matters doubtless would be hastened if the original paste were not dried before analysis, as proposed by their method and subsequently written into the later method of the A. O. A. C. The views of Curry and Smith concerning the correction of the results obtained by subtracting a solubility factor for lead arsenate have not been corroborated by other investigators as will be shown in a later section.

Robinson and Tartar observe that the results obtained by the Oregon Station method are always higher than those obtained by the 10-day provisional method of the A. O. A. C. It is maintained by them, however, that this is not due to any hydrolysis of the lead arsenate nor to the solubility of lead arsenate in hot water; that the results obtained by their method are not too high, but that the results by the 10-day method are too low. In support of this, they point out the following facts: In cases where only a trace of soluble arsenic is obtained in the sample, the results are the same by either method; no soluble lead is found in the pure samples made in their laboratory nor in commercial samples; the amount of soluble impurities is always greater by their method than by the 10-day method, indicating that the latter does not extract all of the impurities. The main points given above of Robinson and Tartar's argument have been amply confirmed by independent investigations of this laboratory.

#### CONCERNING THE SOLUBILITY OF LEAD ARSENATE

Certain results obtained by Curry and Smith<sup>1</sup> seem to indicate that lead arsenate itself is sufficiently soluble in water to give different results when different volumes of water are used in making the extraction of soluble arsenic. So far as known to the writers, these results have not been corroborated by other investigators. The mass of evidence is to the contrary as will be shown by the following considerations:

If pure lead arsenate is appreciably soluble in water, lead will be found in the water extract thereof in molecular proportion to arsenic present. The ratio of  $\text{As}_2\text{O}_5$  to  $\text{PbO}$  in  $\text{PbHAsO}_4$  is 1 to 1.9; the ratio is about 1 to 3 in a basic lead arsenate; therefore, if measurable quantities of arsenic were found in the water extract from a pure lead arsenate, two or three times this quantity of lead would also be found. This has not been the experience of analysts as evidenced by their published results, some of which will be reviewed below.

A sample of lead arsenate was prepared by the A. O. A. C. Referee on Insecticides and sent to 7 cooperating chemists for analysis. In the reports of these chemists, presented before the 26th annual convention of the Association in 1909,<sup>1</sup> it is noted that 5 report no lead present in the water extract obtained by the 10-day provisional method of the Association, one reports 0.04 per cent, and one does not report on lead.

Robinson and Tartar<sup>2</sup> report no lead found in the examination of 6 samples of commercial lead arsenate. They prepared specimens of both acid and basic lead arsenates and determined their solubility in water by the 10-day method. Both types failed to yield sufficient soluble arsenic from 800 cc. of the water extract to be quantitatively estimated by making the final titration with  $N/50$  iodine solution.

Many samples of commercial lead arsenate have been examined in this laboratory in which neither water-soluble lead nor arsenic could be found, except possibly in the merest traces. Only in rare instances is water-soluble lead detected in any of the samples.

From a consideration of these data, it seems apparent that the solubility of lead arsenate itself is not a factor to be taken into account in the determination of soluble arsenic in lead arsenate.

#### REMOVAL OF LEAD FROM WATER EXTRACT BEFORE TITRATION OF ARSENIC

It appears that a considerable amount of water-soluble lead was a common impurity in commercial lead arsenates before the passage of the Insecticide Act of 1910. Analyses of 50 samples were published in 1910 by Haywood and McDonnell<sup>3</sup> in which this impurity is reported in amounts ranging from 0.06 per cent to 1.61 per cent. The removal of lead from the water extract before the titration of arsenic was doubtless a necessary procedure in the earlier years of lead arsenate manufacture.

Very great improvements, however, have been made during the last few years in the processes for its commercial manufacture. Many manufacturers are now using lead oxide and arsenic acid as the raw materials with a small amount of acetic acid as a catalyzer. The insecticide compounded in this manner is remarkably free from by-products and needs little or no washing to be salable. Even the manufacturers using the older process of double decomposition of lead acetate (or nitrate) and sodium arsenate are very careful to

<sup>1</sup> Association of Official Agricultural Chemists, Proceedings of Annual Convention, 26th, U. S. Dept. Agr., Bur. of Chem., *Bull.* 132 (1909).

<sup>2</sup> *Loc. cit.*

<sup>3</sup> J. K. Haywood and C. C. McDonnell, "Lead Arsenate," U. S. Dept. Agr., Bur. of Chem., *Bull.* 131 (1910).

<sup>1</sup> *Loc. cit.*



wash out any excess of the arsenical salt and soluble by-products in order to comply with the National and state insecticide laws. By either process, it is customary to use the arsenical ingredient in excess. It is, therefore, quite improbable that more than a trace of water-soluble lead will be found in any lead arsenate of modern manufacture. As evidences of these improvements, the following may be cited:

In 1912, Holland and Reed<sup>1</sup> determined water-soluble lead in five samples with the following results: none, 0.01 per cent, none, 0.14 per cent, and 0.06 per cent. As previously noted, Robinson and Tartar failed to detect lead in the water extract from six samples. Curry and Smith<sup>2</sup> considered it unnecessary to remove the small amount of lead in the water extract from certain samples which were being studied. This laboratory frequently makes a qualitative test for water-soluble lead, but very seldom is any found.

Both provisional methods of the A. O. A. C. provide for the removal of lead from the water extract before the reduction and titration of the arsenic therein. This procedure may be sometimes desirable, but in the opinion of the writers may be usually omitted in the examination of a product of modern manufacture.

#### THE PROPOSED METHOD

The senior writer became engaged in the work of the Insecticide and Fungicide Laboratory a number of years ago and was very soon impressed with the desirability of developing a more satisfactory method for the determination of water-soluble arsenic in lead arsenate. A critical study was made of the published methods and from time to time, as opportunity afforded, practically all of them were tried. None seemed to be entirely satisfactory, so new methods were given a trial. It soon became evident that neither the acid nor the basic type of lead arsenate is appreciably soluble in boiling water, nor is either type decomposed by prolonged boiling. It also seemed entirely feasible to extract completely the soluble matters by boiling in water from 5 to 10 min. Digestion on the steam bath also seemed permissible after the manner of digestion of a barium sulfate precipitate in order to clear up the liquid and facilitate filtration. This preliminary work was so encouraging that the writers felt warranted in making a thorough test of a tentative method which had been outlined. It is especially gratifying to note that independent investigations of Robinson and Tartar<sup>2</sup> have produced a method that is based upon the same principle as the one proposed by the writers; namely, the insolubility of lead arsenate in hot water.

The detail of the method finally decided upon is as follows:

**PROCEDURE**—Weigh 0.5 g. of the dry powder and place in a 500 cc. Erlenmeyer flask. Add 200 cc. of distilled water and boil briskly for 10 min. (If the liquid is cloudy or the sample does not settle readily, digest on the steam bath an hour or two, or until the supernatant liquid is clear.) Filter through

No. 590 S. & S. filter paper; wash with a small quantity of hot water, receiving the filtrate in a 500 cc. Erlenmeyer flask. Add 1 g. of potassium iodide and 4 cc. of concentrated sulfuric acid and boil until the volume is reduced to about 40 cc. Dilute to about 200 cc. and discolor any free iodine remaining by means of approximately *N*/20 sodium thiosulfate. Add methyl orange and nearly neutralize with a concentrated solution of sodium hydroxide. Add sodium bicarbonate until alkaline and then an excess. Titrate with *N*/20 iodine solution, using starch paste as indicator.

#### DISCUSSION OF THE PROPOSED METHOD

The air-dry sample is preferred to the paste for analysis as it is thought that the dry salt more nearly represents the condition of the insecticide after application to foliage and exposure to weather.

It does not seem necessary that the extractive water be free from carbon dioxide for the reason that arsenic acid is more highly ionized in aqueous solution than carbonic acid and the latter would not be expected to liberate free arsenic acid from an arsenate. Haywood and McDonnell<sup>1</sup> concluded that lead arsenate is *slightly* less soluble in distilled water *saturated* with carbon dioxide than in distilled water free from carbon dioxide. No difference in the results was observed by the writers whether boiled or unboiled distilled water was used for making the extraction. The influence of ammonia if present in the extraction water was not investigated by the writers. Robinson and Tartar,<sup>1</sup> however, make the statement that: "It is imperative that no carbon dioxide nor ammonia be present in the water as they may react with the lead arsenate, liberating arsenic in soluble form." It is a well known fact that the acid type and most commercial lead arsenates are partially soluble in ammonia. It, therefore, seems reasonable to conclude that the extractive water should be ammonia-free. The writers are not convinced, however, that the absence of carbon dioxide therefrom is essential. Both of these points need further study.

Experiments by this laboratory have shown that the soluble matters of lead arsenate are completely extracted from lead arsenate by boiling in water 5 or 10 min., while a complete extraction of soluble matters is almost impossible by digesting in cold or tepid water. Moreover, as previously pointed out, there appears to be no solution or hydrolysis of lead arsenate even by prolonged boiling or by digestion on the steam bath for several hours.

If the sample settles out clear after boiling, filtration may be made at once. Many samples, however, have a tendency to remain in suspension. Boiling and digestion on the steam bath will clear up most samples which are difficult to filter otherwise. Samples containing soap or other organic matter are occasionally encountered which are still obstinate after the above treatment, but a clear filtrate is usually obtained by running through the filter several times. In all cases the filtration is greatly facilitated by boiling and digestion.

<sup>1</sup> E. B. Holland and J. C. Reed, "The Chemistry of Arsenical Insecticides," Mass. Agr. Exp. Sta., 24th Annual Report (1912).

<sup>2</sup> *Loc. cit.*

<sup>1</sup> *Loc. cit.*

The omission of the procedure for the removal of lead in the water extract has been discussed in a previous section. It is found that this step is not usually necessary in the examination of lead arsenates of modern manufacture. The evaporation of 200 cc. of the filtrate in the presence of 0.5 cc. of sulfuric acid to a syrupy consistency is a time-consuming operation; the heating of this small quantity of "syrup" to the appearance of white fumes of sulfuric acid is not without danger of volatilizing some of the arsenic, especially since the syrupy residue is distributed over the surface of a large evaporating dish. If there is any doubt about the advisability of omitting this part of the customary procedure, a qualitative test for lead can be easily made of the filtrate and the step omitted or not according to the test.

The remainder of the procedure is sufficiently familiar not to require discussion.

#### EXPERIMENTAL DATA

Ten samples were selected representing the products of several manufacturers and showing a wide range in composition, including both acid and basic types. Some contained only traces of water-soluble arsenic and others had considerably more than the limit fixed by law. Some contained organic matter. It is thought that practically all types of lead arsenate which are on sale were represented in the samples analyzed.

It did not seem worth while to make a comparison of all of the methods which have been proposed, but water-soluble arsenic was determined by the 10-day provisional method of the A. O. A. C.<sup>1</sup> and by the proposed boiling method. The results are given in Table I.

TABLE I—PER CENT OF WATER-SOLUBLE ARSENIC CALCULATED AS  $As_2O_3$  ON 50 PER CENT WATER BASIS

The samples analyzed contained various amounts of water ranging from 21 to 57 per cent. The maximum amount permitted by Federal and state laws is 50 per cent. In order to make the results comparable and to show more readily the legal status of the samples by both methods, the results were calculated to a 50 per cent water basis.

Sample	A. O. A. C. 10-day Method (Duplicates)	Proposed Boiling Method (Duplicates)	Remarks
A.....	0.25 0.25	0.36 0.39	Acid type
B.....	1.26 1.26	2.17 2.14	Acid type (contains much organic matter)
C.....	0.29 0.29	0.46 0.44	Acid type
D.....	0.07 0.07	0.06 0.06	Acid type
E.....	0.36 0.40	0.45 0.45	Acid type
F.....	0.07 0.07	0.03 0.03	Basic type
G.....	0.18 0.15	0.19 0.16	Acid type
H.....	0.08 0.08	0.09 0.08	Acid type
I.....	0.95 0.91	1.15 1.12	Acid type
J.....	0.07 0.07	0.01 0.01	Basic type

#### DISCUSSION OF RESULTS

The results obtained by the proposed method are higher than those obtained by the 10-day method except where there is no soluble arsenic present or only a trace. It is admitted that the boiling method is a severe test. All the samples listed in Table I, however, which do not pass by the boiling method do not pass by the 10-day provisional method. Examination of some 30 samples, the products of different manufacturers, collected by the inspectors of this laboratory revealed the fact that only 3 samples would not pass inspection even by the more severe treatment of the method under discussion. The manufacturers are able to and do produce lead arsenate which will stand this test; if not, carelessness in the manufacturing process is indicated.

<sup>1</sup> Loc. cit.

Some of the advantages claimed for the method are:

(1) *Rapidity and accuracy*: This should appeal to the factory man as a quick means of laboratory control for his product. Assuming the proof to be sufficient that lead arsenate is not appreciably dissolved by boiling water, the extraction of the soluble matter by the proposed method is logical and is the most rapid manner of complete extraction.

(2) A clear filtrate is readily obtained from most samples.

(3) The procedure for the removal of lead may usually be omitted, thus avoiding the possibility of volatilizing some of the arsenic and saving several hours time.

#### SUMMARY

It is highly desirable that the methods in use by the officials of control laboratories should be suitable for factory control. Accuracy is the prime essential in the first case; both accuracy and rapidity are desirable in the latter. This desideratum is not fully realized in either of the two provisional methods of the Association of Official Agricultural Chemists, nor in other published methods for the determination of water-soluble arsenic in commercial lead arsenate.

It is shown that the solubility of lead arsenate itself is not a factor to be taken into account in the determination of water-soluble arsenic.

The procedure for the removal of lead from the water extract before the titration of soluble arsenic may be usually omitted.

The soluble matters are completely extracted from commercial lead arsenates by boiling in water 5 or 10 min., while a complete extraction is almost impossible by digesting in cold or tepid water. There appears to be no appreciable solution or hydrolysis of lead arsenate even by prolonged boiling or by digestion on the steam bath for several hours.

A method for the determination of water-soluble arsenic in commercial lead arsenates is submitted by the writers for criticism. The method is the result of the conclusions which have been stated above. The test is admitted to be a severe one, but the manufacturers are producing lead arsenates which are easily able to stand the test.

The results obtained by the boiling method are higher than those obtained by the 10-day provisional method of the A. O. A. C., but are thought to be more nearly correct than the latter.

Samples which are shown by the boiling method to contain too much water-soluble arsenic to be legally salable will very seldom pass inspection by either method.

The procedure, as outlined, is shorter than any heretofore published, consuming not more than 3 to 4 hours' time after the sample is sufficiently dried to powder readily. It yields accurate results and does not require the use of expensive apparatus. It should, therefore, be adequate to the needs of both the official chemist and to the factory chemist.



# AN OXALATE-IODIDE PROCESS FOR PARIS GREEN ANALYSIS<sup>1</sup>

By C. A. PETERS AND L. E. FIELDING

Received August 17, 1916

One of us<sup>2</sup> has shown that copper may be precipitated quantitatively as the oxalate, provided 40 mg. or more of copper salt are present in 50 cc. of liquid and that copper may be separated quantitatively from arsenic by this method.

In view of this fact it would seem simple to adapt the method to the determination of copper and arsenic in Paris green by precipitating the copper as the oxalate and determining the arsenic in the filtrate by oxidation with iodine. This paper outlines such a process.

In this precipitation of copper by oxalic acid, Peters<sup>3</sup> separated copper oxalate in the presence of 10 per cent nitric acid, finding that copper oxalate precipitated from neutral and faintly acidic solutions too fine to be retained on the filter. It was deemed wise to avoid the use of nitric acid in this process because of the possible oxidation of arsenic acid and, consequently, sulfuric acid was used to decompose Paris green. In order to determine how little sulfuric acid would be necessary to decompose the Paris green, 0.25 g. of various samples of the latter were weighed out and treated with varying amounts of dilute sulfuric acid. To determine how completely the copper in these acid solutions could be precipitated by oxalic acid, the crystallized acid was added to the boiling hot liquid at the rate of 2 g. to each 50 cc. and the filtrates after standing various lengths of time were tested for copper by potassium ferrocyanide in acetic acid solution. The data are presented in Table I.

TABLE I

Sulfuric acid (1 : 10) Cc. used	VOLUME Cc.	C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> ·2H <sub>2</sub> O Grams	TEST WITH FERROCYANIDE After 1 hour	After 18 hours
5	100	4	Strong	Faint
3	100	4	Strong	Faint
1	100	4	Strong	Very faint
0.7	100	4	Strong	Negligible

It is evident from Table I that even 0.7 cc. of 1 : 10 sulfuric acid is sufficient to decompose the Paris green. Tests showed copper to be present in all cases after standing 1 hour. When, however, the material stood over night, the tests for copper when only 0.7 cc. 1 : 10 sulfuric acid was present were so faint as to be quantitatively negligible. These facts then outline the conditions under which Paris green is decomposed and the copper may be quantitatively precipitated.

In most of these experiments a slight precipitate was noticeable in the decomposed Paris green solution, the quantity varying with the different samples used. This was proved to be silica by filtering off a precipitate on paper, burning the paper and treating with hydrofluoric and sulfuric acids. Upon igniting and weighing the precipitate it lost two-thirds its weight, 0.0124 g., showing the presence of silica in the precipitate. There being a possibility that the precipitate might hold some arsenic, the siliceous residue

after digestion with acid was collected on asbestos and washed until the filtrates no longer acted on litmus. Then the precipitate was washed with a few drops of 30 per cent caustic soda. The caustic filtrate was neutralized with hydrochloric acid and again made alkaline with bicarbonate and treated with iodine. Only one drop was necessary to give permanent color, showing that no iodine was held by the silica.

To determine if the arsenic in the filtrate could be measured by iodine after neutralizing the oxalic acid present, a measured amount of the standard arsenite solution was drawn off, 2 g. of oxalic acid added, and the solution neutralized with dry sodium bicarbonate and titrated with iodine. The addition of oxalic acid caused no change in the standard so that it may be assumed that the arsenic could be determined quantitatively in the filtrate from the copper oxalate precipitation.

The method as outlined is as follows: Weigh out about 0.25 g. of Paris green in a small beaker, add less than 1 cc. of 1 : 10 sulfuric acid and boil at a volume 50 cc. for two minutes. While hot add cautiously and slowly 2 g. of oxalic acid crystals, heat again to boiling and allow to stand over night. Filter off the precipitated copper oxalate onto an asbestos filter, wash the precipitate with a little water to carry all the arsenic into the filtrate, and replace the crucible, asbestos and precipitate in the original beaker. Add a convenient amount of water, 5 or 10 cc. of 1 : 1 sulfuric acid, heat nearly to boiling and titrate with standard permanganate. From the amount of permanganate used the copper can be calculated.

Neutralize the oxalic acid and the sulfuric acid in the filtrate by adding dry sodium bicarbonate and, after an excess of bicarbonate has been added, run in standard iodine solution to color. From the iodine solution used the arsenic can be calculated.

The results of an analysis of the Paris green solution by the proposed method and by standard methods are given in Table II. For standard methods that described by Avery and Beans<sup>1</sup> was used for arsenic, and the thiosulfate process as outlined by Gooch and Heath<sup>2</sup> was applied for the copper determination.

TABLE II—PARIS GREEN ANALYSIS

	Total Per cent As <sub>2</sub> O <sub>3</sub>	Total Per cent CuO
Standard methods.....	57.39	29.82
	57.46	29.86
New method.....	57.33	29.78
	57.42	29.78

It is evident that the process possesses the same degree of accuracy as the one commonly used.

**PRECAUTIONS**—In adding the dry oxalic acid to the 50 cc. of solution from Paris green it is well to add the first few crystals slowly, as the solution is very apt to be in a superheated condition and will boil over if the whole mass of crystals is added at one time.

The end-point in the titration of the copper oxalate by the permanganate is naturally slow, depending upon the speed with which the oxalic acid is liberated. This depends in turn upon the concentration of the

<sup>1</sup> From a thesis of L. E. Fielding, optionally presented for the degree of B.Sc. at the Massachusetts Agricultural College at Amherst.

<sup>2</sup> *Am. Jour. Sci.*, [4] 10, 359; also Gooch, "Methods in Chemical Analysis," p. 131.

<sup>3</sup> *Loc. cit.*

<sup>1</sup> *J. Am. Chem. Soc.*, 23 (1901), 485.

<sup>2</sup> *Am. Jour. Sci.*, [4] 24, 67; also Gooch, "Methods in Analysis," p. 121.

sulfuric acid and the temperature of the system. The end-point, however, is definite and cannot be overstepped. The presence of the asbestos is no objection.

#### SUMMARY

A method for the analysis of Paris green is proposed by which the copper is precipitated as the oxalate and the oxalic acid combined is titrated with permanganate, the arsenic being oxidized in the filtrate by iodine after being made alkaline. The procedure is accurate and, with the exception of the fact that the copper oxalate must stand over night, rapid.

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### THE DETERMINATION OF SULFUR IN IRON AND STEEL

By H. B. PULSIFER

Received July 17, 1916

In 1904, Hendrixson announced<sup>1</sup> that iron dissolves easily in chloric acid, going quantitatively to the ferric condition. At that time the author was studying the methods for the determination of sulfur in iron and steel and at once recognized the possibility of using chloric acid as the solvent in the analysis.

Chloric acid is a highly satisfactory solvent for the usual finely granular material used for analysis; the action takes place rapidly and with far less gas evolution than when nitric acid is the solvent. In attempting quantitative data on samples of known

prints and through the microscope the actual condition is far more truthfully revealed than from the reports of the analyst who may rely on one single result or unwittingly fail to indicate the diversity of his check determinations.

The statistical method of studying the distribution of results would be highly illuminating but is hardly practical because of the material, time and labor required. In no case on the samples here studied were less than duplicate results obtained; often 3 and in several cases 6 or 7 determinations were run for the sake of establishing a mean value of the sulfur content.

#### PREPARATION OF SAMPLE

We suppose that sulfur occurs in our materials as sulfide of iron, sulfide of manganese, or indeed as a double sulfide of the two. These sulfides are probably quite insoluble in the more common  $\alpha$ - and  $\beta$ -modifications of ferrite for we have no difficulty in discovering the particles with the microscope when only a few hundredths of one per cent of sulfur are present in the metal. This discrete occurrence of sulfur in the metal, and in particular its segregation in that portion of an ingot which solidifies last is perfectly well known to metallurgists and metallographers. The bearing of this on the results obtained by the analyst is highly significant. Even more imperative is its dictum regarding the preparation of the sample.

In a 5-g. sample of metal it requires about 0.0005

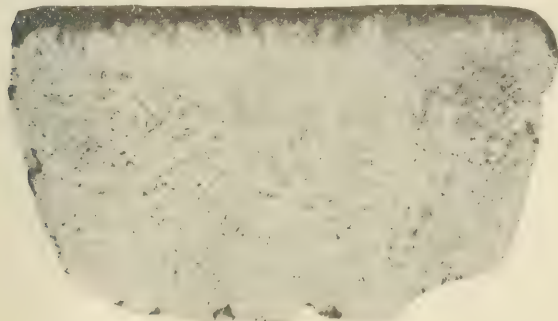


FIG. I—SULFUR PRINT OF CAST IRON INGOT

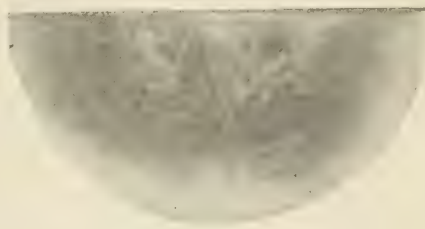


FIG. II—SULFUR PRINT OF STEEL SHAFTING

sulfur content the work developed largely into a study of the uniformity of samples, the nitric acid and fusion methods, the precision of results and the work of others.

A limited number of analyses by the new method indicate the difficulties and possibilities of its use.

From the analytical point of view the segregation of sulfur in the ferrous materials was first mentioned by Eggertz in 1868;<sup>2</sup> our Bureau of Standards has frequently related its difficulties along the same line, while Bauer and Deiss<sup>3</sup> take particular pains to expound the difficulty and indicate how the analyst shall avoid falling into serious error.

This segregation of sulfur is a well known condition to the metallurgist and metallographer; with sulfur

<sup>1</sup> *J. Am. Chem. Soc.*, **26** (1904), 747.

<sup>2</sup> *Chem. News*, **18** (1868), 15.

<sup>3</sup> "Sampling and Chemical Analysis of Iron and Steel," translated by Hall and Williams, 1916.

g. of sulfur or 0.00014 g. FeS or MnS to influence the analysis by 0.001 per cent. This is represented by a cube of the substance 0.3 mm. on a side; such a particle will barely pass a 50-mesh screen. For some degree of safety, then, the material should pass an 80-mesh screen and be thoroughly mixed; this material would be uniform to about 0.001 per cent, in 5-g. lots. The actual loss of sulfur by such treatment awaits investigation. Variations due to analytical conditions might still cause deviations.

Figs. I to IV visualize this common characteristic of materials. Fig. I is a full-size sulfur print made by photographic paper on a small ingot of cast iron. It shows the spots of sulfide throughout the entire section and, in particular, the layer at the top which is extremely high in sulfur. The accurate sampling of such an ingot is obviously quite a task.

Analyses of crushed millings gave the following results:



Original Crushed Millings	PERCENTAGES OF SULFUR AFTER GRINDING	
	20 to 100 mesh	Through 100 mesh
0.171	0.171	0.164
0.176	0.171	0.165
0.176	0.171	0.167
0.182	0.174	...
0.182	0.174	...
0.184	0.175	...
0.184	0.177	...
0.194	0.177	...
0.197	...	...
0.201	...	...

Some of the material which persisted coarsely granular even after the twenty passes through the disc grinder was probably high in sulfur although small in amount.

Fig. II is another sulfur print of a section of shafting showing high sulfur spots. Figs. III and IV are photomicrographs of this material at 200 diameters, suitably etched. The two prints were of spots a bare half-inch apart on the metal surface. Fig. III shows fine, practically sulfur-free metal; Fig. IV shows typical sulfides. Each cube the size of the dark spot would put 0.001 per cent of sulfur in a 5-g. sample. Remembering that the entire area of Fig. IV represents an actual surface of only 0.16 sq. mm. and is just a trifle too large to pass a 50-mesh screen we are naturally not surprised that the results of analyses on coarse turnings varied from 0.06 to 0.09 per cent sulfur.

For real precision the analyst can best determine the limits of the sulfur range on the weight of sample and fineness selected. The average result is, of course, the best value available. The fallacy of any selection which sorts out one size of particle is plain; nothing could be more untechnical than to pound the material and screen out a portion for analysis. The great objective is how to reduce a lot to the desired size; at the present moment there is no light on the difficulty.

#### METHODS OF ANALYSIS

A perusal of the accompanying bibliography in the original allows one to classify the methods for sulfur determination according to the following scheme:

- I—Direct combustion in oxygen.
- II—Volatilization as  $\text{SCl}_2$  in chlorine at red heat.
- III—Volatilization with  $\text{H}_2$  and  $\text{CO}_2$  at red heat as  $\text{H}_2\text{S}$ .
- IV—Fusion of powdered sample with oxidizing alkaline salts; sintering of powder with  $\text{MgO}$  and  $\text{NaOH}$ .
- V—Oxidizing both iron and sulfur with acid solution (or halogen); precipitation of sulfur direct or after various manipulations.
  - A—Bromine.
  - B—Concentrated  $\text{HNO}_3$ .
  - C— $\text{KClO}_3$  and  $\text{HCl}$ .
  - D—Aqua regia.
  - E—Bromine and  $\text{HCl}$ .
  - F— $\text{HNO}_3$  and  $\text{KClO}_3$  and  $\text{KBr}$ .
  - G—Chloric acid.
- VI—Nitric acid solution and fusion of the evaporated mass.
- VII—Solution of iron leaving sulfur and sulfides ready to filter off and oxidize by acids or fusion.
  - A—Ferric chloride solution.
  - B—Copper-alkali ( $\text{Na}$ ,  $\text{K}$ , or  $\text{NH}_4$ )-chloride solution.
- VIII—Sulfur evolved as  $\text{H}_2\text{S}$  with  $\text{H}_2\text{SO}_4$ , or  $\text{HCl}$ , or both.
  - A— $\text{H}_2\text{S}$  oxidized to  $\text{H}_2\text{SO}_4$  direct or after precipitation of a metal, weighing as  $\text{BaSO}_4$ . Oxidation by:
    - 1—Bromine.
    - 2—Chlorine.
    - 3—Permanganate.

- 4—Hydrogen peroxide.
- 5—Sodium peroxide.
- 6—Lead peroxide.
- 7—Hydrogen flame and permanganate.

B— $\text{H}_2\text{S}$  determined volumetrically.

- 1—Iodine titer directly.
  - 2—Iodine in excess and back with thio-sulfate.
  - 3—Iodine liberated by  $\text{KMnO}_4$ , back with thio-sulfate.
  - 4—Direct titer with  $\text{KMnO}_4$ .
- (Absorbents for these 4 are  $\text{NaOH}$ ,  $\text{KOH}$ , salts of  $\text{Pb}$ ,  $\text{Cd}$  and  $\text{Zn}$ )
- 5— $\text{FeCl}_3$  is reduced to  $\text{FeCl}_2$  and run back with  $\text{K}_2\text{Cr}_2\text{O}_7$ .
  - 6— $\text{ZnS}$  reduces  $\text{Fe}^{++}$  to  $\text{Fe}^+$  and back with  $\text{KMnO}_4$ .
  - 7—Absorb in  $\text{NaOH}$  and titrate with  $\text{Pb}(\text{NO}_3)_2$ .
  - 8—Absorb in standard arsenite and back with iodine.
  - 9—Absorb in  $\text{AgNO}_3$  to  $\text{AgS}$  and  $\text{KSCN}$  titer.

C— $\text{H}_2\text{S}$  determined gravimetrically, weigh as  $\text{CuO}$ ,  $\text{AgS}$ ,  $\text{Ag}$ ,  $\text{As}_2\text{O}_3$  or  $\text{BaSO}_4$ .

D—Colorimetric determination of  $\text{H}_2\text{S}$ .

- 1—Use a  $\text{Pb}$  salt.
- 2— $\text{Cd}$  salt gives  $\text{CdS}$ .
- 3—Absorb in  $\text{As}_2\text{O}_3$  solution.
- 4—Formation of methylene blue.
- 5—Gives color to metal foil.

E— $\text{H}_2\text{S}$  precipitates  $\text{PbS}$ , to be read in graduated tube after whirling.

Concerning these methods of analysis a few explanatory remarks will indicate their relative importance and certain conditions of use.

Method I has been abandoned, after trial, except for particular ferro-alloys.

Method II is justly dismissed without comment.

Method III has some figures to substantiate it, but has too many inherent difficulties.

Method IV has been supported by considerable evidence of accuracy and by several workers. The material is best very finely powdered, a serious objection. Manipulation may also be objected to. Extremely slight practical use apparently attaches to the method.

Method V is widely used in one or another form, especially for more precise work. Nitric acid used as solvent must be replaced by hydrochloric and the silica is best rendered insoluble by baking. The ferric chloride may be separated by ether or the iron may be precipitated with ammonia and either the sulfuric acid washed out of the hydroxide or the hydroxide dissolved out of the already precipitated barium sulfate. Ferric iron may be reduced to ferrous by a variety of reagents or the same prevented from entering the barium sulfate precipitate by using organic substances to form complex ions unaffected by the precipitation. Residues remaining after the acid treatment of the original sample may get special attention and the sulfur recovered added to the main portion.

This method has been abundantly disparaged and can, of course, be proven inadequate by uncritical operators. On the other hand, the method has been substantiated by abundance of the best work and nothing less than fresh evidence can shake it. The precipitation of the barium sulfate in the ferric chloride solution has been checked as accurate by workers of

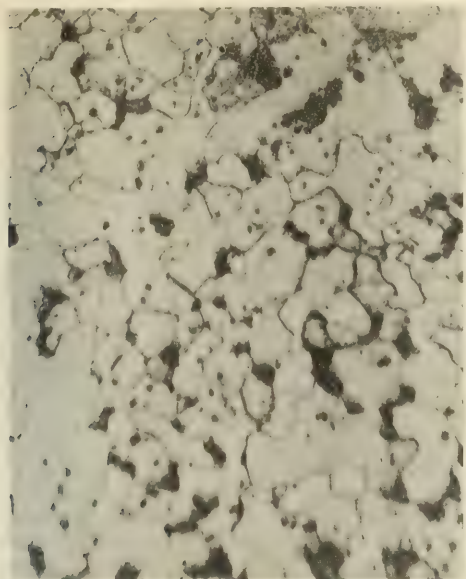


FIG. III  $\times 200$ —SECTION OF STEEL SHAFTING  
FINE, PRACTICALLY SULFUR-FREE METAL

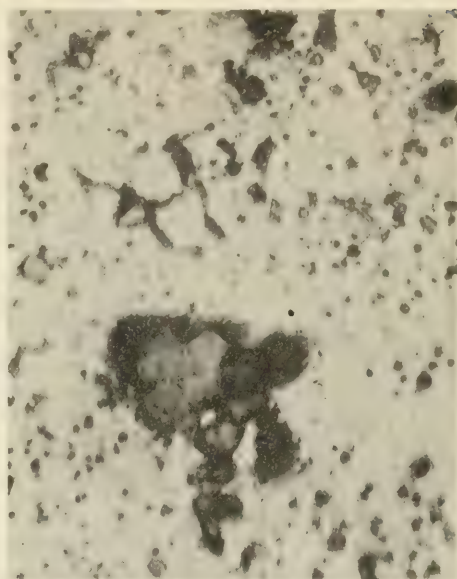


FIG. IV  $\times 200$ —SECTION HALF INCH DISTANT FROM FIG. III  
STEEL ROTTEN WITH SULFIDES

six nations. A table covering this point is offered in this paper as bearing directly and unequivocally on this point.

Method VI is generally considered an excellent control method.

Method VII is both old and new and theoretically excellent; the slowness of solution is always against it.

Method VIII has received by far the most attention from earliest to latest times, as the history of sulfur determination ranges. Samples may be annealed before dissolving, without or with admixed reagents. The evolution may be effected by acid alone or in the presence of hydrogen or carbon dioxide, or both. The gases may be passed through a red hot tube. The residue may be oxidized wet or by fusion or treated with hydrogen and hydrochloric acid at a red heat, any recovery being added to the main portion. The cumulative evidence is that quick evolution with concentrated hydrochloric acid gives a close approximation if not the exact sulfur content. Only in unusual cases will sulfur persist in the residue.

The author has experimented considerably with this method but delays results for a later communication.

A complete review and digest of the whole subject is needed but requires far more space than the importance of the subject would warrant.

As other workers have established the accuracy of the nitric acid method by attempting to measure or recover barium sulfate from the filtrate, a procedure always liable to renewed error through impurities and the environment, the author ran a series of 28 lots simply to establish the actual recovery on a measured amount of sodium sulfate. Every condi-

tion closely approached that of an actual analysis.

The ferric chloride solution was made by dissolving 560 g. of the pure solid salt in 2 liters of water, filtering and using 50 cc. in each case.

The sodium sulfate solution was made by dissolving 1.220 g. of the pure fused salt in 1 liter of water: 10 cc. were taken in each instance with a pipette delivering 9.996 cc., temperature corrected. All determinations were made at the same time with a

TABLE II—DETERMINATIONS TO SHOW THE INFLUENCE OF HYDROCHLORIC ACID ON THE SOLUBILITY OF BARIUM SULFATE IN FERRIC CHLORIDE SOLUTION

No.	FeCl <sub>3</sub> Grams	Na <sub>2</sub> SO <sub>4</sub> Grams	HCl (1.19) Cc.	Weight BaSO <sub>4</sub> Gram
1.....	None	None	0.02	No ppt.
2.....	None	None	0.02	No ppt.
3.....	None	0.0122	0.02	0.0205
4.....	None	0.0122	0.02	0.0204
5.....	14	None	1.00	0.0001
6.....	14	None	1.00	0.0004
7.....	14	0.0122	0.20	Fe pptd.
8.....	14	0.0122	0.40	Fe pptd.
9.....	14	0.0122	0.60	Fe pptd.
10.....	14	0.0122	0.80	Fe pptd.
11.....	14	0.0122	1.00	0.0221 (red)
12.....	14	0.0122	1.20	0.0206 (red)
13.....	14	0.0122	1.40	0.0207 (pink)
14.....	14	0.0122	1.60	0.0204 (gray)
15.....	14	0.0122	1.80	0.0204
16.....	14	0.0122	2.00	0.0210
17.....	14	0.0122	2.20	0.0200
18.....	14	0.0122	2.50	0.0205
19.....	14	0.0122	2.80	0.0209
20.....	14	0.0122	3.10	0.0203
21.....	14	0.0122	3.50	0.0204
22.....	14	0.0122	4.00	0.0210
23.....	14	0.0122	4.50	0.0207
24.....	14	0.0122	5.00	0.0209
25.....	14	0.0122	5.50	0.0203
26.....	14	0.0122	6.00	0.0207
27.....	14	0.0122	6.50	0.0208
28.....	14	0.0122	7.00	0.0207
Average of last 17.....				0.0206
Average deviation.....				0.0002

volume of 120 cc.; precipitations were made hot; solutions stood at the boiling point for an hour, then over night before filtering. Precipitates were washed 3 times with hot dilute hydrochloric acid (10 cc.



1.10 acid in 750 cc. water) and 10 times with hot water.

The barium sulfate equivalent of 0.0122 g.  $\text{Na}_2\text{SO}_4$  is 0.0000 g.  $\text{BaSO}_4$ .

The conclusion seems inevitable that moderate amounts of hydrochloric acid do not appreciably increase the solubility of the barium sulfate in the ferric chloride solution.

The details of the nitric acid and Bamber's method are well known and do not need repetition here. Ordinary directions for the nitric acid method say to add a little sodium salt to hold the  $\text{SO}_3$ . What direct evidence this is based upon, the author has not been able to find; the measurements available indicate that ferric sulfate begins to decompose somewhat above  $300^\circ\text{C}$ .;  $200^\circ\text{C}$ . was the temperature of the laboratory hot plate. No sodium salt was added in any of the analyses.

Bamber's method was carried out with the aid of a vacuum desiccator, an electric muffle and an electric hot plate for evaporating the water extractions of the fusions. During evaporation in the desiccator the temperature was about  $95^\circ\text{C}$ ., the gauge at from 10 to 15 in. and a current of air was let in through cotton. In the electric muffle the mass dried in a platinum dish was exposed to a temperature of  $900^\circ\text{C}$ . until red hot throughout, which required from 1 to 3 min.

None of the reagents used contained measurable amounts of sulfur in the amount used for analysis.

Blanks run on Bamber's method indicated that check analyses carried through in every detail exactly like a complete determination would average 0.006 per cent sulfur. It is to be noted that such a blank does not determine any impurity in the reagents but rather what has strayed in by accident. The comparatively long evaporations and numerous handlings make the process highly liable to positive error; as already noted, dust bearing 0.00005 g. sulfur would increase results by 0.001 per cent. The laboratory was far from free of dust and fume, as a beam of light will demonstrate in even a reasonably clean place, and during the three days of an analysis it is no wonder that most of the samples ran high by this amount. It is more surprising that some of them checked the nitric acid method almost exactly. As this throws an element of uncertainty on both the analyses and the blanks the only conclusion is that for strictly reliable results the process must be carried out in a place absolutely dust- and fume-free and where the blanks systematically give zero correction. This type of a blank does not register a uniform positive correction but a fortuitous error. Others have usually found that the method gives high results. The conclusion is that Bamber's method, except under the most rigid control, is not as reliable as the nitric acid method.

**DETAILS OF CHLORIC ACID METHOD:** 5 g. of the well-mixed sample were weighed out into a 400 cc. beaker and the cover-glass placed. The sample was moistened with 2 cc. water and the grains shaken over the bottom so that they would not clump when the acid was added; 40 cc. chloric acid (sp. gr. 1.20) were poured in; solu-

tion took place at once. Enough hydrofluoric acid was added to dissolve the separated silica and immediately the solution was digested with 10 cc. conc. hydrochloric for 2 or 3 min. over a flame. The mixture was then filtered through a 7 cm. paper with suction, and 10 cc. conc. hydrochloric acid were added to the filtrate which was evaporated to small bulk.

The residue on the paper was placed on a little sodium peroxide and sodium carbonate mixture in a nickel or silver crucible, some of the mixture placed above for a cover, and with the crucible cover held down with the tongs the crucible heated in a bare flame. After the flash the melt may be swirled to complete fusion and then poured on metal. If the chloric acid is barium-free the melt may be dissolved in dilute hydrochloric acid and added to the main portion. If the chloric acid contained barium the melt is to be dissolved in water, filtered, acidified, and then added to the main portion.

The united solutions should now contain about the right amount of free acid and if clear may be brought to 100 cc. volume for precipitation of the sulfur as barium sulfate. If the solutions have separated silica they must be filtered before making up to standard volume. To the hot solution 10 cc. of 10 per cent barium chloride solution are added, the beaker is placed to keep just below boiling for an hour, then set aside to cool and filtered the next morning. The barium sulfate is filtered, ignited and weighed as usual.

Sodium fluosilicate may separate on mixing the two solutions or later. This is one of the most insoluble sodium salts and if it appears must be washed out with hot water. On this account as little hydrofluoric acid and sodium salts as possible should be used. The crystals are large and transparent and easily noted if present.

Sulfur present in the chloric acid must be corrected for on the final result.

#### PRECISION OF RESULTS

A little familiarity with this type of analytical work brings out clearly those sources of error which make up the inequality of the results as recorded in Table III.

TABLE III—AVERAGE RESULTS BY THE THREE METHODS

METHOD: Sample	Lots	NITRIC ACID			Lots	BAMBER'S			Lots	CHLORIC ACID		
		% S	Av. Probable	Error		% S	Av. Probable	Error		% S	Av. Probable	Error
1 Iron...	4	0.008	0.001	3	0.016	0.002	2	0.014	0.002	2	0.014	0.002
2 Iron...	4	0.009	0.001	4	0.018	0.001	3	0.014	0.003	3	0.014	0.003
3 Steel...	3	0.009	0.002	3	0.021	0.001	2	0.023	0.001	2	0.023	0.001
4 Iron...	5	0.013	0.001	3	0.020	0.001	2	0.016	0.001	2	0.016	0.001
5 Steel...	3	0.018	0.002	5	0.030	0.002	2	0.030	0.002	2	0.030	0.002
6 Iron...	7	0.025	0.001	6	0.034	0.002	2	0.038	0.002	2	0.038	0.002
7 Iron...	6	0.028	0.002	8	0.041	0.001	4	0.030	0.005	4	0.030	0.005
8 Iron...	2	0.030	0.000	5	0.035	0.004	3	0.039	0.004	3	0.039	0.004
9 Steel...	4	0.032	0.001	3	0.030	0.002	2	0.030	0.003	2	0.030	0.003
10 Iron...	6	0.032	0.002	3	0.042	0.001	3	0.038	0.002	3	0.038	0.002
11 Iron...	3	0.038	0.003	3	0.039	0.005	5	0.049	0.002	5	0.049	0.002
12 Iron...	4	0.039	0.001	3	0.045	0.002	2	0.043	0.004	2	0.043	0.004
13 Iron...	5	0.050	0.003	6	0.059	0.002	3	0.052	0.002	3	0.052	0.002
14 Iron...	2	0.061	0.001	5	0.066	0.003	2	0.065	0.002	2	0.065	0.002
15 Iron...	6	0.064	0.002	5	0.071	0.003	4	0.063	0.003	4	0.063	0.003
16 Iron...	8	0.069	0.003	6	0.076	0.003	2	0.069	0.002	2	0.069	0.002
17 Iron...	3	0.077	0.002	2	0.084	0.001	2	0.074	0.002	2	0.074	0.002
18 Iron...	5	0.081	0.002	3	0.092	0.002	2	0.080	0.001	2	0.080	0.001
19 Iron...	4	0.101	0.002	3	0.103	0.000	2	0.098	0.001	2	0.098	0.001
20 Iron...	4	0.117	0.003	3	0.136	0.004	3	0.131	0.003	3	0.131	0.003
21 Iron...	7	0.179	0.004	4	0.198	0.004	2	0.186	0.014	2	0.186	0.014
22 Iron...	4	0.259	0.004	3	0.267	0.002	2	0.261	0.013	2	0.261	0.013

(1) There are slight variations due to the deviations inherent in working with barium sulfate: precipitating in the acid ferric chloride solution, filtering,

washing and igniting. This degree of uncertainty is best indicated in Table II; depending on the total amount of the sulfate weighed the percentage error is greater or less but evidently means a per cent sulfur variation of from 0.001 per cent to 0.002 per cent above or below the true value.

(2) There appear in most of the samples wider fluctuations due to the inhomogeneity of the material; superimposed upon the digressions inherent in the method this often causes a result to deviate several times the average deviation. This difficulty has been continually recorded in the literature and could be further discussed from the preceding results if space allowed. It demands that for any really accurate determination of sulfur enough lots be run to establish the range on the sample at hand. If it were possible to grind so that the entire sample will pass an 80-mesh screen this entire difficulty should vanish.

(3) A source of error comes unexpectedly from laboratory conditions or the liabilities of the somewhat difficult determination that sulfur is. An unnoticed cloud of dust might make a constant error in an entire batch of determinations, for common laboratory dust reeks with sulfur and a quite imperceptible drift of sodium sulfate particles would damage everything exposed. Another source of this type of error lies in holding all the sulfur on solution in nitric acid. Even with great care sulfur may be lost in the fumes. In fact, every method yet proposed for the minutely occurring sulfur in iron or steel has plenty of sources of this sort of error. Bamber's method with its tediousness and many transferals is especially liable; the chloric acid method has the same introduced through the use of hydrofluoric acid and the fusion of the residue. All oxidation check results recorded in the literature bear witness to the correctness of this conclusion.

Composite samples of the barium sulfate precipitates were well mixed and analyzed as follows:

TABLE IV—PERCENTAGES OF IMPURITIES IN BARIUM SULFATE PRECIPITATES

	Chlorine	Ferric Oxide	Silica
Bamber's Method.....	0.14	0.35	0.81
Nitric-Hydrochloric Method.....	0.21	0.79	0.49
Chloric Acid Method.....	0.11	1.64	1.23

Of course the residues from high sulfur samples predominate in such a composite and it gives no indication of individual goodness or badness; the table is interesting as showing the greatest purity for the Bamber residues, as might be expected, but the almost equal purity of the nitric acid precipitates.

#### SUMMARY

I—A bibliography covering 285 original articles relating to the determination of sulfur in ferrous materials has been compiled and appears below.

II—The methods of sulfur determination have been classified and very briefly discussed.

III—The character of the sample as regards sulfur segregation has been emphasized and illustrated. The fineness of the sample wholly to correct segregation on the material actually used for the analysis should be such that it will pass an 80-mesh screen.

For coarse material precise results can be obtained

only by running a series of analyses which will indicate the limits of the variations.

IV—Bamber's, the Nitric-Hydrochloric and the Chloric Acid methods were tried on some 22 samples ranging from 0.008 to 0.25 per cent sulfur and comprising 238 results.

V—A series to test directly the reliability and precision of the nitric acid method as affected by the solubility of barium sulfate in ferric chloride solution of varying hydrochloric acid content fully substantiates the wide-spread confidence in the method.

VI—Bamber's method is seen to be especially liable to high results due to its length and liability to contamination. Blank check results indicate that if carried out under the best of conditions in a special laboratory the results would almost exactly agree with those by the nitric acid method.

VII—The Chloric Acid method is found to give results usually between those of the first two methods mentioned. The advantage of the method lies in the almost instant and gentle solution of the material and in wholly avoiding the use of nitric acid. The difficulty of the method lies in the accompanying use of hydrofluoric acid which attacks the beakers and may bring a separation of sodium fluosilicate to be dissolved away from the final barium sulfate precipitate. Dehydration of the chlorate solution does not seem to give as good results and lengthens the process. By this method it is possible to have the barium sulfate precipitated in about 20 minutes after the sample is weighed out.

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- 1888—J. Leutscher. *Iron Age*, Vol. 41, page 325. "The Use of Centrifugal Machines in the Iron and Steel Laboratory." Measures the  $\text{PbS}$  ppt.
- 1888—C. Meinecke. *Z. angew. Chem.*, Vol. 1, page 376. "Ueber die Bestimmung des Schwefels im Eisen." 7 samples show weakness of evolution method; then 7 by his old copper-sodium chloride method give correct results.
- 1888—J. J. Morgan. *Chem. News*, Vol. 58, page 49. Call Arnold and Hardy's new method only modification of Parry's.
- 1888—J. J. Morgan. *Chem. News*, Vol. 58, page 63. "On the Determination of Sulfur in Iron and Steel." General review and discussion of all methods.
- 1888—Prost. *Bull. acad. roy. belg.*, Vol. 16, page 216. "Étude de l'action de l'acide chlorhydrique sur la fonte." Organic sulfur compounds are evolved and in residue.
- 1888—W. Körber. *Z. angew. Chem.*, Vol. 1, page 487. "Ueber einen verbesserten Zersetzungs- und Absorptions-Apparat." Cuts and details.
- 1888—B. W. Winder. *Chem. News*, Vol. 58, page 95. "Estimation of Sulfur in Iron and Steel." Says Morgan's methods are all old and well known.
- 1889—Jannasch and Richards. *J. prakt. Chem.*, N. S., Vol. 39, page 321. "Ueber die Bestimmung des Schwefels, ure bei Gegenwart von Eisen." Works with salts; finds only fusion method accurate.
- 1889—Marsh. *J. Anal. Appl. Chem.*, Vol. 3, page 164. "The Reduction of Barium Sulfate to Barium Sulfide on Ignition with Filter-Paper." Reduction is found in the 30 samples investigated.
- 1889—B. Platz. *Stahl u. Eisen*, Vol. 9, page 405. "Zur Bestimmung des Schwefels in Eisen." Finds no  $\text{H}_2\text{S}$  lost when diss. in  $\text{HNO}_3$ ; results on 5 samples.
- 1889—M. A. von Reis. *Stahl u. Eisen*, Vol. 8, page 827. "Zur Bestimmung des Phosphors und Schwefels im Eisen." Sinters fine metal with magnesia and soda; results on 18 samples.
- 1889—M. A. von Reis. *Stahl u. Eisen*, Vol. 9, page 497. "Zur Bestimmung des Schwefels im Eisen." Questions accuracy of dissolving in  $\text{HNO}_3$ .
- 1889—E. F. Smith. *J. Franklin Inst.*, Vol. 127, page 313. "Oxidation by Means of the Electric Current." Electrical oxidation of sulfur to  $\text{Na}_2\text{SO}_3$  in alk. fusion.
- 1889—A. Vosmaer. *Chem. Ztg.*, Vol. 13, page 695. "Ueber die Wiborgh'sche colorimetrische Schwefelbestimmungsmethode." Presents certain refinements.
- 1890—L. Archbutt. *J. Soc. Chem. Ind.*, Vol. 9, page 25. "The

Determination of Sulfur in Iron and Steel." Oxidation method; tests solubility of  $\text{BaSO}_4$ .

1890—L. Blum. *Z. anal. Chem.*, Vol. 29, page 138. "Zur Bestimmung des Schwefels im Eisen." *Fears solubility of  $\text{BaSO}_4$  in  $\text{HBr}$ .*

1890—J. B. Cohn. *J. Soc. Chem. Ind.*, Vol. 9, page 16. "Wiborg's Method for the Analysis of Sulfur in Iron and Steel." *Describes the method.*

1890—C. Reinhardt. *Stahl u. Eisen*, Vol. 10, page 430. "Schnelle gewichtsanalytische Schwefelbestimmung in Stahl und Roheisen." *Evolution  $\text{Br}$ -oxidation method with known sulfur in the solution to filter small amounts easier.*

1890—W. Thörner. *Chem. Ztg.*, Vol. 14, page 1655. "Mittheilungen aus der Laboratoriumspraxis." *Refinements of evolution process.*

1891—J. M. Camp. *J. Anal. Appl. Chem.*, Vol. 5, page 409. "Absorption Apparatus for Sulfur Determination." *Tube filled with beads and bromine water.*

1891—G. Hattensauer. *Chem. Ztg.*, Vol. 15, page 521. "Zur Schwefelbestimmung in Eisen und Stahl." *Evolution method and solution in cupric chloride give same results; 7 samples compared.*

1891—Reis and Wigert. *Stahl u. Eisen*, Vol. 11, page 480. "Zur Bestimmung von Schwefel im Eisen." *Evolution method with oxidation of  $\text{H}_2\text{S}$  and precipitation with barium nitrate given as a quick method.*

1891—A. J. Rossi. *Stahl u. Eisen*, Vol. 11, page 927. "Bestimmung von Schwefel." *Combination of evolution and  $\text{Br}$ -oxidation methods.*

1891—F. P. Treadwell. *Ber.*, Vol. 24, page 1937. "Beitrag zur quantitativen Bestimmung des Schwefels." *Changes sulfur to  $\text{FeS}$  and uses evolution method.*

1891—J. M. Wilson. *J. Anal. Appl. Chem.*, Vol. 5, page 439. "A Method of Standardizing Iodine Solution for the Determination of Sulfur in Steel and Pig Iron." *Standardizes against sample of known sulfur content.*

1892—H. C. Babbitt. *J. Anal. Appl. Chem.*, Vol. 6, page 301. "Wiborg's Colorimetric Sulfur Determination." *Describes the process.*

1892—L. Blum. *Z. anal. Chem.*, Vol. 31, page 290. "Absorptions-apparat zur Bestimmung des Schwefels im Eisen." *Improved apparatus.*

1892—Lee S. Clymer. *J. Anal. Appl. Chem.*, Vol. 6, page 318. "Sulfur Determinations by Different Methods." *Startling results by inter-natal analysis and by different methods.*

1892—A. T. Eastwick. *J. Anal. Appl. Chem.*, Vol. 6, page 246. "The Determination of Sulfur in Iron and Steel." *Concerns iodine-evolution method.*

1892—J. van Leeuwen. *Chem. Centr.*, Vol. 63 [2], page 757. From R. P. B., Vol. 11, page 103. "Einfluss des Schwefels des Steinkohlengases auf die Bestimmung des Schwefels durch Schmelzung." *Uses a spirit flame.*

1892—J. van Leeuwen. *Rec. trav. chim.*, Vol. 11, page 103. "L'influence du soufre du gaz de houille sur le dosage du soufre par fusion." *Use alcohol or benzene flame.*

1892—H. L. Payne. *J. Anal. Appl. Chem.*, Vol. 6, page 481. "Standard Iodine Solution: A Method for Its Preparation." *Iodine freed by permanganate.*

1892—M. Ripper. *Z. anorg. Chem.*, Vol. 2, page 36. "Beiträge zur Gewichtsanalyse der Schwefelsäure." *A critical paper on  $\text{BaSO}_4$ , with some results.*

1892—A. Schneider. *Z. physik. Chem.*, Vol. 10, page 423. "Ueber einen Fall der festen Lösung." *Finds a rather constant per cent of iron in  $\text{BaSO}_4$  ppt.*

1892—F. P. Treadwell. *Ber.*, Vol. 25, page 2377. "Beitrag zur Schwefelbestimmung II." *As above and uses  $\text{H}_2\text{O}_2$  or iodine titer.*

1892—F. H. Williams. *Eng. Soc. West. Penn.*, Vol. 8, page 328. "Note on the Use of Hot Acid in the Evolution of Sulfur as  $\text{H}_2\text{S}$  from Pig-Iron." *A few results on hot, cold, concentrated and dilute acid.*

1892—F. L. Crobaugh. *J. Anal. Appl. Chem.*, Vol. 7, page 280. "Cadmium Chloride as an Absorbent of Hydrogen Sulfid." *States minimum quantity necessary.*

1893—H. A. Hooper. *Chem. News*, Vol. 68, page 191. "A New Method for the Rapid Estimation of Sulfur in Steels, Pig-Irons, Etc." *Evolution method, titrates with standard lead solution.*

1893—E. M. Stahl. *Stahl u. Eisen*, Vol. 13, page 686. "Zur Schwefelbestimmung." *Special apparatus for evolution method.*

1893—J. K. Mackenzie. *J. Anal. Appl. Chem.*, Vol. 7, page 134. "Absorption Bulb for Sulfur Determinations." *Convenient form with stopcock.*

1893—Parry and Morgan. *Chem. News*, Vol. 67, page 247. From "Industries." "The Analysis of Iron and Steel." *Aqua regia oxidation method.*

1893—W. Schindler. *Z. angew. Chem.*, Vol. 6, page 111. "Beitrag zur Schwefelbestimmung im Eisen nach der Schwefelwasserstoffmethode." *Concentrated  $\text{HCl}$  gives all sulfur by either  $\text{Br}$  or  $\text{H}_2\text{O}_2$  oxidation to  $\text{H}_2\text{SO}_4$ .*

1893—L. Schneider. *Oesterr. Z. Berg. Huttenw.*, Vol. 41, page 365. "Beiträge zur Chemischen Untersuchung des Stahles." *Evolution method with absorption in  $\text{MnO}_2$ .*

1894—H. K. Bamber. *J. Iron Steel Inst.*, Vol. 45 [1], page 319. "On the Analysis of Steel." *States the fusion method in detail with results on 6 samples.*

1894—T. S. Gladding. *J. Am. Chem. Soc.*, Vol. 16, page 398. "On the Estimation of Sulfur in Pyrites." *Small, precisest reagent.*

1894—E. Johnson. *Chem. News*, Vol. 70, page 212. "The Estimation of Sulfur in Pyrites." *Adds  $\text{H}_2\text{NaPO}_4$  to reduce iron and rid of nitrates.*

1894—M. A. von Reis. *Stahl u. Eisen*, Vol. 14, page 963. "Zur Bestimmung von Schwefel im Eisen." *Details for accuracy in evolution method; oxidizes with  $\text{H}_2\text{O}_2$ .*

1894—J. E. Sleeper. *Chem. News*, Vol. 69, page 63. "On the Precipitation of Barium Sulfate in the Presence of Silica, and the Decomposing Action of Hydrofluoric Acid on the Former." *Interesting results with analytical figures.*

1894—Spüller and Kahlmann. *Chem. Ztg.*, Vol. 18, page 2040. "Bestimmung des Schwefels in Stahl und Eisen." *Evolution method absorbing in  $\text{NaOH}$ ; uses current of  $\text{N}_2$ ; weighs as  $\text{BaSO}_4$ .*

1895—J. O. Arnold's Book: "Steel Works Analysis." Pub. by Whit-taker & Co., London. *Pages 96 to 110 on sulfur determination.*

1895—L. Campredon. *Compt. rend.*, Vol. 120, page 1051. "Dosage du soufre dans les fontes, les aciers et les fers." *Iodine evolution method using  $\text{CH}_3\text{I}$  and  $\text{H}_2$ .*

1895—A. Carnot. *Rev. Univ. Mines*, Vol. 8, page 357. "Methodes d'analyse des fontes, des fers et les aciers." *A lengthy review.*

1895—A. Carnot's Book: "Methodes d'Analyse des Fontes, des Fers & des Aciers." Pub. by Dunod & Vicq., Paris. *Pages 82 to 96 on sulfur.*

1895—A. Forestier. *Bull. soc. chim. Paris*, Vol. 13, page 586. "Essai des aciers, fer et fontes par l'analyse chimique." *Brief review.*

1895—H. F. J. von Jorstorff's Book: "Fortschritte im Eisenhütten-Laboratorium." Pub. by A. Felix, Leipzig. *Pages 115 to 142 about sulfur.*

1895—L. D. LeKoninck. *Chem. Ztg.*, Vol. 19, page 502. "Vorschlag zur Bestimmung von Schwefel in Eisensorten." *Evolution method using  $\text{SnCl}_4$ .*

1895—G. Lunge. *J. Am. Chem. Soc.*, Vol. 17, page 181. "On the Estimation of Sulfur in Pyrites." *Refutes Gladding's variations with several analyses according to his method.*

1895—G. Lunge. *Z. angew. Chem.*, Vol. 8, page 69. "Ueber die Bestimmung des Schwefels im Schwefelkies." *Same as in *J. Am. Chem. Soc.**

1895—F. C. Phillips. *J. Am. Chem. Soc.*, Vol. 17, page 891. "The Evolution Method for the Determination of Sulfur in White Cast-Iron." *Critical study of evolution method; finds organic sulfur compounds. Many results given, an important contribution.*

1895—E. J. Read. *Chem. News*, Vol. 72, page 299. "Apparatus for Estimation of Sulfur in Iron."

1895—Richards and Parker. *Z. anorg. Chem.*, Vol. 8, page 413. "Ueber die Einschliessung von Baryumchlorid durch Baryumsulfat." *Study of  $\text{BaSO}_4$  pptn.*

1896—George Auchy. *J. Am. Chem. Soc.*, Vol. 18, page 406. "Drown's Method of Determining Sulfur in Pig Iron." *Evolution with absorption in  $\text{KMnO}_4$ ; mainly study of effect of oxalic acid on  $\text{BaSO}_4$ .*

1896—G. G. Boucher. *Chem. News*, Vol. 74, page 76. "Estimation of Sulfur in Cast-Iron or Steel." *Recommends copper ammonium chloride method for accuracy; essentially Meisner's method.*

1896—C. W. Fouk. *J. Am. Chem. Soc.*, Vol. 18, page 793. "The Effect of an Excess of Reagent in the Precipitation of Barium Sulfate." *An excellent study with the now well-known conclusions.*

1896—Presenius and Hintz. *Z. anal. Chem.*, Vol. 35, page 170. "Ueber eigenthümliche Löslichkeitsverhältnisse des schwefelsauren Baryts." *13 pages on the solubility of  $\text{BaSO}_4$  in water and salt solutions.*

1896—T. S. Gladding. *J. Am. Chem. Soc.*, Vol. 18, page 446. "On the Estimation of Sulfur in Pyrites." *Holds for slow addition of precipitant.*

1896—M. Lucas. *Bull. soc. chim. Paris*, Vol. 17, page 144. "Les Methodes de dosage du Phosphore et du soufre, dans le fer, l'acier et la fonte." *Evolution method with red-hot tube. Table of results—mostly as published by others.*

1896—M. Lucas. *Bull. soc. chim. Paris*, Vol. 17, page 150. "Application de la méthode de dosage colorimétrique du plomb au dosage du soufre dans le fer, l'acier et la fonte." *Absorbs  $\text{H}_2\text{S}$  in alkaline lead sol. and makes precise color estimation by purifications.*

1896—F. A. Matthewman. *J. West. Scot. Iron Steel Inst.*, Vol. 3, page 1. From *J. Iron Steel Inst.*, Vol. 49 [1], page 537. *Reported of some importance; original article not available.*

1896—J. J. Morgan. *Chem. News*, Vol. 72, page 257. "Estimation of Sulfur in Cast-Iron or Steel." *Discusses Boucher's method and refers it to C. Meinecke, 1888.*

1896—F. C. Phillips. *J. Am. Chem. Soc.*, Vol. 18, page 1079. "The Determination of Sulfur in Cast Iron." *Direct oxidation method; nitrate and heat.*

1896—Wilhelm Schulte. *Stahl u. Eisen*, Vol. 16, page 865. "Eine Neue Methode zur Bestimmung des Schwefels im Eisen." *Develops the evolution method, using  $\text{Cd}(\text{C}_2\text{H}_3\text{O}_2)_2$ ,  $\text{CuSO}_4$ ,  $\text{CuS}$  and weighing as  $\text{CaO}$ .*

1896—H. Wedding's Book: "Handbuch der Eisenhüttenkunde." Pub. by F. Vieweg & Sohn, Braunschweig. *Gives 10 methods.*

1897—A. A. Blair. *J. Am. Chem. Soc.*, Vol. 19, page 114. "The Determination of Sulfur in Pig Iron." *Review Bamber's method in detail; refers to work of Phillips.*

1897—G. G. Boucher. *Chem. News*, Vol. 75, page 121. "Volumetric Estimation of Sulfur in Iron, Steel and Sulphides of Iron." *Evolution-titration method, using  $\text{FeCl}_3$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ ; 8 results.*

1897—Louis Campredon. *Stahl u. Eisen*, Vol. 17, page 486. "Bestimmung des Schwefels im Eisen." *Confirms necessity of heating gases in evolution method; 1 table.*

1897—Carnot and Goutal. *Compt. rend.*, Vol. 125, page 75. "Sur l'emploi des sels cuivreux pour préparer le dosage de divers éléments dans les fontes et les aciers." *Dissolves in  $\text{Cu-K}$ -chloride solution and oxidizes residue with bromine.*

1897—Carnot and Goutal. *Ann. chim. anal.*, Vol. 2, page 301. "Sur l'emploi des sels cuivreux pour préparer le dosage de divers éléments dans les fontes et les aciers." *See above; credits Berzelius with origin of dissolving iron in cupric chloride.*

1897—C. B. Dwyer. *J. Am. Chem. Soc.*, Vol. 19, page 93. "Some Present Possibilities in the Analysis of Iron and Steel." *Review. Evolution method hazardous, oxidation method slow. Rate of output stated.*

1897—O. Herting. *Chem. Ztg.*, Vol. 21, page 87. "Beitrag zur Bestimmung des Schwefels in Eisensorten." *Evolution-iodine method; results on 4 samples.*

1897—E. S. Johnson. *J. Am. Chem. Soc.*, Vol. 19, page 288. "Some Apparatus for the Technical Analytical Laboratory." *Stand with burners to hold flasks and absorption tubes for evolution method, using hydrogen.*

1897—E. K. Landis. *J. Am. Chem. Soc.*, Vol. 19, page 261. "Standard Iodine Solution for Sulfur Determinations." *Reactions and calculations.*

1897—F. Marboutin. *Mon. sci.*, Vol. 50, page 644. "Sur le dosage de l'acide sulfurique. Méthode en poids et méthodes volumétriques." *Mainly titration methods for water analysis.*

1897—R. K. Meade. *J. Am. Chem. Soc.*, Vol. 19, page 581. "A New Apparatus for Sulfur Determinations in Iron and Steel and a Useful Form of Wash-Bottle." *Stand to hold evolution flask and separatory funnels for absorption.*

1897—Wilhelm Schulte. *Stahl u. Eisen*, Vol. 17, page 489. "Bestimmung des Schwefels im Eisen." *Confirms necessity of passing evolution gases through hot tube; 2 tables of results.*

1898—Eng. Soc. West. Penn. Book: "Methods for the Analysis of Ores, Pig Iron and Steel of the Pittsburgh Region." *Chem. Pub. Co., Easton, Pa. Yields company methods; uncritical.*

1898—E. Franke. *Stahl u. Eisen*, Vol. 18, page 326. "Zur Bestimmung des Schwefels in Eisen." *A study of modifications of evolution method. 27 samples are run by 5 different methods; remarkable uniformity. Schulte's method best of all.*

1898—J. T. Stahl. *Chem. News*, Vol. 78, page 294. "Blank Tests." *Gets blank by deducting weight of larger from twice weight of half sample.*

1899—Aulich. *Stahl u. Eisen*, Vol. 19, page 878. "Schwefel in Eisenerzen und Eisenhüttenenergieen." *Review of oxidation methods.*

1899—F. L. Crobaugh. *Iron Trade Review*, Vol. 32, No. 27, page 12. "Methods for the Iron Laboratory—IV, Sulfur." *Evolution method; starts with cold dilute acid;  $\text{CaCl}_2$  and iodine titration.*

1899—O. Herting. *Chem. Ztg.*, Vol. 23, page 768. "Die brauchbaren Methoden zur Bestimmung des Schwefels im Eisen." *A rather brief review.*

1899—Kuster and Thiel. *Z. anorg. Chem.*, Vol. 19, page 97, 1900: Vol. 25, page 319. "Ueber die Bestimmung der Schwefelsäure bei Gegenwart von Eisen." *Figures show that oxalic and tartaric acids keep iron from  $\text{BaSO}_4$ .*

1899—C. Meinecke. *Z. anal. Chem.*, Vol. 38, page 209. "Ueber die Bestimmung der Schwefelsäure, mit besonderer Berücksichtigung der Bestimmung des Schwefels in Eisenerzen und Eisenhüttenprodukten." *Oxidation method; reduces  $\text{Fe}^{3+}$  with zinc and gets results identical with  $\text{H}_2\text{O}_2$ .*



- 1899—M. J. Moore. *J. Am. Chem. Soc.*, Vol. 21, page 972. "Notes on the Determination of Sulfur in Pig-Iron." Results depend on cooling of metal.
- 1900—J. Thull. *Z. anal. Chem.*, Vol. 38, page 342. "Die massanalytische Bestimmung des Schwefels in Kohleisen, Stahl u. s. w. durch arsenige Säure." Evolution method with arsenic-iodine titration.
- 1900—B. Mount. *Analyst*, Vol. 25, page 131. "The Determination of Carbon and Sulfur in Steel." Not possible by direct combustion.
- 1900—O. N. Heidenreich. *Z. anorg. Chem.*, Vol. 20, page 233. "Ueber die Bestimmung des Schwefels in Kies bei Gegenwart von Eisen." Reduces before precipitating with  $\text{BaCl}_2$ ; results on 1 sample.
- 1900—A. Ledebur's Book: "Leitfaden für Eisenhütten Laboratorien." 5th edition. F. Vieweg & Sohn, Braunschweig.
- 1900—Adolf Riemer. *Stahl u. Eisen*, Vol. 19, page 1064. "Bestimmung des Schwefels in Roh- und Flusseisen." Disparages Wiborg's and exponents iodine method.
- 1901—U. Antony. *Gazz. chim. ital.*, Vol. 31 [iii], page 274. "Determinazione dello zolfo e del fosforo nei prodotti siderurgici." Alkaline fusion of the fine powder.
- 1901—George Auchy. *J. Am. Chem. Soc.*, Vol. 23, page 147. "Determination of Sulfur in Wrought Iron and Steel." Evolution method with constant positive correction; 60 results.
- 1901—Blair and Shimer. *Trans. Am. Inst. Mining Eng.*, Vol. 31, page 748. "A Crystalline Sulfide in Pig-Iron." Finds an insoluble  $\text{C-Fe-Ti-S}$  compd.
- 1901—A. Classen's Book: "Ausgewählte Methoden der Analytischen Chemie." Pub. by F. Vieweg & Sohn, Braunschweig. 10 pages on sulfur determination.
- 1901—W. G. Lindsay. *School Mines Quart.*, Vol. 23, page 24. "On a Colorimetric Method for the Estimation of Sulfur in Pig-Iron." Forms methylene blue; results on 3 samples.
- 1901—N. W. Lord. *J. Am. Chem. Soc.*, Vol. 23, page 675. "The Determination of Sulfur in Iron and Steel." Recommends bromine or nitric acid-chlorate-bromide solution with pptn. of iron before adding  $\text{BaCl}_2$ . Results on 7 samples; suggest constant correction.
- 1902—Felix Bischoff. "Beiträge zu der Analyse des Eisens." *Stahl u. Eisen*, Vol. 22, page 719. States allowable deviations in individual results. Ignores unequal distribution.
- 1902—Felix Bischoff. *Stahl u. Eisen*, Vol. 22, page 754. "Beiträge zu der Analyse des Eisens." Claims  $\text{CuS}$  unaffected by evolution method; discusses method and modifications.
- 1902—Felix Bischoff. *Stahl u. Eisen*, Vol. 22, page 1136. "Beiträge zu der Analyse des Eisens." Refutes *ad hoc* results on 9 samples.
- 1902—Brentley and Ibbotson's Book: "The Analysis of Steel-Works Materials." Longmans, Green & Co. Excellent chapter and essay on sulfur. Summarizes important contributions. 150 references in bibliography, mostly from "Chem. News" and "J. Iron and Steel Inst." Nothing new but advice.
- 1902—Geo. T. Dougherty. *Iron Age*, Vol. 69, page 14. "Notes on Iron Analysis." Improved annealing; results on 6 samples.
- 1902—T. Naske. *Stahl u. Eisen*, Vol. 22, page 333. "Colorimetrische Methode zur Bestimmung des Schwefels im Roheisen." Enlarges on errors of color and evolution methods.
- 1902—T. Naske. *Stahl u. Eisen*, Vol. 22, page 1134. "Beiträge zu der Analyse des Eisens." Asserts hydrides of As, P and Si spoil Bischoff's evolution method.
- 1902—J. V. R. Stehman. *J. Am. Chem. Soc.*, Vol. 24, page 644. "The Application of Eschka's Method to Pig Irons." Good results with finely ground sample.
- 1902—Walters and Miller. *Eng. Soc. West. Penn.*, Vol. 18, page 83. "An Accurate Estimation of Sulfur in Iron by the Evolution Method." Anneals samples before evolution method; results on 19 samples.
- 1902—A. Wencelius's Book: "Methodes d'Analyse des Laboratoires d'Acieries Thomas." Beranger, Paris. Schulle's method on page 48.
- 1903—E. Jackson. *Iron Trade Review*, Vol. 36, page 61. "Loss of Sulfur in Boregas of Cast Iron." Results on 7 samples; steel no loss.
- 1903—H. E. Field. *J. Am. Foundrymen's Assoc.*, Vol. 11, page 129. "Standard Methods for Analyzing Iron." States numerous minute details for both evolution and oxidation processes.
- 1903—W. G. Ireland. *Iron Trade Review*, Vol. 36, No. 49, page 69. "Cast Iron Sulfur." Claims evolution sulfur less as sample size.
- 1903—A. Klein. *Chem. Ztg.*, Vol. 27, page 729. "Neuerungen im analytischen Arbeiten." Improved apparatus for evolution method.
- 1903—N. W. Lord's Book: "Notes on Metallurgical Analysis." 2nd Ed. Ohio State University. 15 pages on sulfur determination.
- 1903—E. Prost's Book: "Manuel d'Analyse Chimique." Beranger, Paris. Pages 199-204 on sulfur determination.
- 1903—C. A. Seylor. *Analyst*, Vol. 28, page 97. "Note on the Estimation of Sulfur in Pig-Iron." Anneals at  $750^\circ$  for 15 min. and uses conc.  $\text{HCl}$ .
- 1904—F. L. Crobaugh's Book: "Methods of Chemical Analysis and Foundry Control." On page 59 confirms Dickson and Ireland that evolution sulfur is lower as sample size.
- 1904—G. T. Dougherty. *Iron Age*, Vol. 73, No. 13, page 3. "The Total Sulfur and Different Forms of Sulfur in Pig and Cast Iron." Residual sulfur not evolved from some irons until annealed; results on 8 samples.
- 1904—Ford and Willey. *J. Am. Chem. Soc.*, Vol. 26, page 81. "The Determination of Sulfur in Iron." Review; criticizes Noyes and Helmar; recommends Bamber's method; precautions.
- 1904—L. Fricke. *Stahl u. Eisen*, Vol. 24 [2], page 890. "Schwefelbestimmung im Roheisen und Stahl durch Titration mit Jod- und Thio-sulfat-lösung." Follows Klein and Lunge.
- 1904—S. S. S. S. *Stahl u. Eisen*, Vol. 24, page 487. "A Rapid Method for the Determination of Total Sulfur in Iron by Evolution." Anneals in iron dust; no figures.
- 1904—J. C. Olsen's Book: "Quantitative Chemical Analysis." D. Van Nostrand, N. Y. Pages 351 to 356 on sulfur.
- 1905—C. Friedheim's Book: "Leitfaden für die quantitative chemische Analyse." C. Habel, Berlin. Page 327 gives evolution and colorimetric methods.
- 1905—H. Van F. Furman's Book: "A Manual of Practical Assaying." Wiley, New York, 5th Ed. Chap. II, p. 88. Compilation of methods.
- 1905—C. Krug. *Stahl u. Eisen*, Vol. 25, page 887. "Eine Kritik der Schwefelbestimmung im Eisen." The silver oxide and ether oxidation methods.
- 1905—C. R. McCabe. *J. Am. Chem. Soc.*, Vol. 27, page 1203. "Note on the Gravimetric Determination of Sulfur in Iron and Steel." For the oxidation method dissolves sample in reflux flask.
- 1905—Jacopo Petroni. *Iron-Conferece Annaler*, Vol. 60, page 187. "Om bestämning af svavel uti järn." A massive article of 47 pages. Reviews methods critically with fresh material. Many references and tables. Finds concentrated  $\text{HCl}$  gives correct evolution results.
- 1905—H. B. Pulsifer. *Chem. News*, Vol. 90, page 230. "A Radically New Method for the Determination of Sulfur in Irons and Steels." Chloric acid method, weighing as barium sulfate.
- 1906—McParlane and Gregory. *Chem. News*, Vol. 93, page 201. "A Modified Evolution Method for the Determination of Sulfur in Pig-Iron." Anneals with cream of tartar; *huc check results*.
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## A MODIFICATION OF PRICE'S METHOD FOR THE SEPARATION OF THE SEVEN PERMITTED COAL-TAR DYES TO INCLUDE TARTRAZINE<sup>1</sup>

By CLARENCE ESTES

Received July 31, 1916

*Food Inspection Decisions* 76, 117 and 129 of the United States Department of Agriculture have been amended by *Food Inspection Decision* 164, so that hereafter, the following 8 coal-tar dyes may be used to color food products, subject to the provision of *Food Inspection Decisions* 76, 117 and 129: 107—Amaranth, 56—Ponceau 3R, 517—Erythrosin, 85—Orange I, 4—Naphthol Yellow S, 435—Light Green S F Yellowish, 692—Indigo Disulfonic Acid, and 94—Tartrazine.

A method for the separation of the first seven coal-tar dyes, when occurring in mixtures, has been worked out by Price, which depends upon the solubility or insolubility of the dyes in various solvents, but so far as the writer is aware, there has not been published a method for the separation of the eight permitted coal-tar dyes. I wish, therefore, to give a modification of Price's scheme to include the new permitted coal-tar dye Tartrazine.

THE REAGENTS are the same as those given by Price with the addition of glacial acetic acid and concentrated hydrochloric acid.

PROCEDURE—Assuming that the dyes occur together in a food product and it is desired to separate and identify them, it is first necessary to separate the dyes from the food products by slightly acidifying an aqueous solution of the material with hydrochloric acid; then add a piece of white woolen cloth, which has been freed from grease, and boil until most of the color has been removed. Remove the dyed cloth and rinse thoroughly in boiling water to remove any foreign material which may be adhering to the fiber. The dyes are stripped from the cloth by immersing in a very dilute solution of ammonia and boiling. When stripping of the dye from the cloth is complete, acidify and repeat the dyeing process with a new piece of cloth if fruit colors are present; remove the cloth after the second stripping and evaporate to dryness on a water bath. This leaves the dyes in a pure dry condition ready for the separation.

Rub a small quantity of the dyes in an evaporating dish with about 25 cc. of supersaturated solution of ammonium sulfate, filter, and wash the residue with small portions of the supersaturated solution of ammonium sulfate until the washings are no longer colored red. The filtrate and washings will contain *Amaranth*, *Tartrazine* and a small quantity of *Naphthol Yellow S*. The *Naphthol Yellow S* is separated from *Amaranth* and *Tartrazine* by extracting several times with ethyl acetate until it is no longer colored yellow. The ethyl acetate extract containing the *Naphthol Yellow S* is discarded, as it will be separated in a pure state later. *Amaranth* and *Tartrazine* are separated from the ammonium sulfate by extracting with acetone. The acetone solution is diluted with water and evaporated on a steam bath until the acetone has been expelled.

<sup>1</sup> U. S. Department of Agriculture, Bureau of Animal Industry, *Bull.* 180.



SCHEME FOR THE SEPARATION OF THE EIGHT PERMITTED COAL-TAR DYES  
 Amaranth, Tartrazine, Erythrosin, Naphthol Yellow S, Light Green  
 S F Yellowish, Orange I, Indigo Disulfonic Acid and Ponceau 3 R

Rub a small quantity of the mixed dyes in an evaporating dish with supersaturated solution of  $(\text{NH}_4)_2\text{SO}_4$ , filter and wash with the supersaturated solution of  $(\text{NH}_4)_2\text{SO}_4$  until the washings are no longer red

FILTRATE contains Amaranth, Tartrazine and a small quantity of Naphthol Yellow S. Shake with acetic ether. Acetic ether removes Naphthol Yellow S. This solution is discarded

$(\text{NH}_4)_2\text{SO}_4$  SOLUTION contains Amaranth and Tartrazine, which are removed by shaking with acetone. Dilute the acetone solution with  $\text{H}_2\text{O}$  and drive off the acetone. Supersaturate the aqueous solution containing Amaranth and Tartrazine with NaCl, filter, and wash with supersaturated NaCl solution until filtrate is no longer yellow

FILTRATE contains Tartrazine. Add excess of conc. HCl or glacial acetic acid and shake with acetone. Dilute the acetone solution with  $\text{H}_2\text{O}$ . Drive off the acetone and Tartrazine remains

RESIDUE contains Erythrosin, Naphthol Yellow S, Light Green, S F Yellowish, Orange I, Ponceau 3 R and Indigo disulfonic acid. They are separated according to Price's scheme as given in *Circ. 180*, Bureau of Animal Industry, U. S. Dept. Agr.

The aqueous solution containing Amaranth and Tartrazine is supersaturated with sodium chloride, filtered, and residue and filter paper washed with the supersaturated solution of sodium chloride until washings are no longer colored yellow. The filtrate and washings contain Tartrazine, while the undissolved portion contains Amaranth. Tartrazine<sup>1</sup> is separated in the pure state from the sodium chloride solution by adding an excess of either glacial acetic acid or concentrated hydrochloric acid and extracting with acetone. The acetone is evaporated off on a steam bath, which leaves the Tartrazine<sup>2</sup> in a pure condition. Amaranth is obtained in a pure state by adding to the residue an excess of either glacial acetic acid or concentrated hydrochloric acid and extracting with acetone. The acetone is evaporated off on a steam bath, which leaves the Amaranth in a pure condition.

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### SWEET WINES OF HIGH ALCOHOL CONTENT WITHOUT FORTIFICATION<sup>3</sup>

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 Received June 30, 1916

Port wine, as made in California, normally contains over 20 per cent alcohol by volume and California sherry over 18 per cent. Under ordinary conditions, the must, or crushed grapes, is allowed to ferment until 6 to 10 per cent alcohol is formed and the alcohol content is then increased to the desired point by the addition of 180 proof (90 per cent) grape brandy. Until the past season, a tax of 3 cents per proof gallon was paid on this fortifying brandy. Owing to the necessity for increased revenue, the U. S. Government in 1915 increased the tax from 3 cents per proof gallon to 55 cents per proof gallon.

If the fortified sweet wines were to be made in the usual way under this heavy tax, the cost of production would be prohibitive. Two methods were used by

California wine makers last season to avoid the tax entirely or to decrease the amount of brandy used in fortification. By one method, grapes of high sugar content were used. By employing selected pure yeast, potassium metabisulfite to eliminate wild yeasts or bacteria, and by keeping the temperature of the fermenting must down by artificial cooling to the optimum for fermentation, wines of approximately 15 per cent alcohol were produced. Where so much alcohol is formed by fermentation, only a small amount need be added in the form of fortifying brandy to produce wines of the required alcohol content. Where the wine is to be fortified, it must not contain more than 15 per cent alcohol by volume before fortification to comply with the U. S. Revenue Regulations.

By a second method, sweet wines of high alcohol content were made without fortification. The method consists in adding grape syrup to the must during fermentation. It is claimed that wines of over 18 per cent alcohol were produced in this way. To obtain data on this process, the following four experiments were carried out (tables omitted).

EXPERIMENT 1789—SWEET WINE, SHERRY TYPE, NOT FORTIFIED, SYRUP ADDED DURING FERMENTATION—Very ripe Semillon grapes of 27.3 Balling or Brix degree were used. The juice was allowed to settle 24 hrs. to clear partially and it was then inoculated with pure Burgundy wine yeast; 75 mg. of  $\text{SO}_2$  per liter were used before settling of the juice to check growth of wild yeasts during this period. The fermentation was carried out at a room temperature of 21–25° C. in a 5-gal. keg. Grape syrup of 60 per cent Balling was added near the end of fermentation. The wine was racked after fermentation and stored in glass demijohns.

EXPERIMENT 1821—SWEET WINE, PORT TYPE, WITHOUT FORTIFICATION, SYRUP ADDED DURING FERMENTATION—This lot was made in the laboratory in a 5-gal. barrel. Red grape juice from experimental juice made at Davis in 1914 was used. A syrup made by boiling down a mixture of red juice and raisin juice to 65 per cent Balling was added during fermentation. The wine was roughly filtered after fermentation and stored in a well filled and corked demijohn.

EXPERIMENT 1966b—SWEET WINE, SHERRY TYPE, NOT FORTIFIED, RAISINS ADDED DURING FERMENTATION—This experiment was carried out at the University Farm at Davis. Ripe Semillon grapes were crushed and pressed. The juice was given 75 mg.  $\text{SO}_2$  per liter and allowed to settle 24 hrs. It was racked and inoculated with pure yeast: 100 lbs. Semillon grapes were sun-dried to 63 lbs., crushed, and added to the fermenting must near the end of the fermentation. The mixture was later pressed and fermentation allowed to proceed at room temperature for a time and the final fermentation was carried out in a room kept at 25° C. The wine was stored several weeks at this temperature to subject it to extreme conditions favorable to spoilage.

EXPERIMENT 1973—SWEET WINE WITHOUT FORTIFICATION, PORT TYPE, SYRUP ADDED DURING FERMENTATION—This wine was made in practically the same way as Wine 1821. Grape syrup from Burger grapes and made by vacuum evaporation on a commercial scale was used to add during fermentation. Only one addition of syrup was made. The wine was racked clear after fermentation and stored in a well-filled 5-gal. demijohn.

The results reported below demonstrate that a sound sweet wine of over 18 per cent alcohol can be made by the addition of syrup during fermentation, provided the wine is filtered or racked clear after fermentation and stored in clean, well-filled containers.

<sup>1</sup> An extraction of about 98 per cent has been made.

<sup>2</sup> For the reactions which are used to identify the separated colors, see Allen's "Commercial Organic Analysis," Vol. V, 4th Ed.

<sup>3</sup> This interesting treatise is given in full with the exception of much of the tabulated matter which to our regret could not be included on account of lack of space. The comment on this tabulated matter makes the article sufficiently clear in itself. [EDITOR'S NOTE.]

ANALYSES OF EXPERIMENTAL SWEET WINES: After Storage the Wines were Analyzed and Tasted with the Following Results

Wine	Alcohol	Volatile Acid	Total Acid	Sugar	OBSERVATIONS
1789(a)	18.20	0.030	0.80	7.5	Excellent "sherry" flavor
1966b	19.9	0.406	1.20	2.7	"Tourne" bacteria. Spoiled
1821	18.40	0.076	1.10	11.40	Condition and flavor excellent
1973	18.30	0.060	1.00	14.40	Good "port" flavor

(a) At one time during fermentation Wine 1789 reached 20.1 per cent alcohol but the addition of syrup later reduced this somewhat.

Experiment 1966b shows that raisins may be used instead of grape syrup to increase the sugar in the fermenting must and to invigorate the yeast. It also indicates the danger of spoilage of such wine unless precautions are taken to get it clear after fermentation and store it in full containers. In spite of its alcohol content of 19.9 per cent, this wine was completely spoiled by the growth of "tourne" bacteria (*Bacterium mannitoaecum*). It is a well-known fact that fortified wines of 19 per cent alcohol or over are not readily attacked by this organism although it is found living in wines of over 20 per cent alcohol. It is possible that alcohol formed by fermentation in the wine is less toxic than that distilled and added to the wine; that is to say, perhaps aldehydes or other compounds formed during distillation may increase the toxicity of the alcohol to the organisms of wine. Experiments made in 1915 on this point bear out the above statement.

The authors also have results of experiments showing the effect of a number of additions of syrup during fermentation: (a) one addition of syrup; (b) three additions of syrup; (c) four additions (tables omitted). These tests and data obtained from a number of similar experiments indicate that the number of additions of syrup does not materially affect the result if the additions are made before the yeast has become weakened.

#### MAXIMUM ALCOHOL FORMED BY BURGUNDY WINE YEAST BY NORMAL FERMENTATIONS

In the following experiment, musts varying from 28.3 Balling to 43.9 Balling were made up by the addition of grape syrup to grape must. The different lots were inoculated and kept at room temperature until fermentation ceased. They were then analyzed for alcohol content.

#### RESULTS IN BALLING DEGREES

MUST	I	II	III	IV
Jan. 14.....	31.0	35.7	39.8	43.9
Jan. 17.....	11.0	35.5	38.5	41.6
Jan. 18.....	5.4	35.5	...	41.6
Jan. 19.....	4.0	34.5	37.5	41.6
Jan. 20.....	1.8	34.5	26.7	...
Jan. 24.....	...	25.5	26.7	...
Jan. 29.....	...	15.6	...	...
Jan. 31.....	...	...	...	...
Feb. 1.....	...	13.7	24.0	29.6
Feb. 9.....	...	13.0	22.8	27.4
Mar. 8.....	...	...	...	...
Apr. 5.....	...	13.0	...	...

#### ANALYSIS OF WINES I IV, APRIL 5, 1916

WINE	I	II	III	IV
Alcohol (per cent) .....	17.2	15.2	11.4	11.3

From these results, it may be seen that musts of 35 Balling and above are not fermented to give very high yields of alcohol (see II, III and IV). The alcohol yield in I is remarkable and is about 0.6 per cent higher than is usually obtained with this yeast as a maximum by the usual "straight" fermentation of sweet must. It is probable that high concentrations,

e. g., 35 per cent Balling or over, interfere seriously with the growth of the yeast, giving a smaller crop of yeast or a weaker yeast than normally develops in musts of lower sugar concentration. The formation of 17.2 per cent alcohol by a single straight fermentation of must of 31 Balling has little practical value for unfortified sweet wine because the addition of syrup will be necessary after fermentation and would reduce the alcohol content so that the wine would be liable to spoilage. Therefore, the syruing method of fermentation is better because it gives high alcohol yields and also gives a wine with sufficient sugar for a sweet wine of Port or sherry type.

#### USE OF SAKÉ YEAST

Saké yeast is used in Japan for the fermentation of rice mash in the manufacture of Japanese saké beer. It is accredited with the ability to form 22 per cent alcohol in rice mash. Wine yeast is described in the literature as being able to form in must not more than 16.5 per cent alcohol by volume.

The saké yeast was grown in grape must several generations to accustom it more or less to the new medium. Straight fermentation and fermentations to which syrup was added were tried with this yeast but 15.2 per cent alcohol was the maximum formed.

#### SAKÉ YEAST ALCOHOL YIELDS

	Per cent
Alcohol by "straight" fermentation.....	13.3
Alcohol by "syrued" fermentation, one addition of syrup.....	15.2
Alcohol by "syrued" fermentation, two additions of syrup.....	14.6

Apparently the saké yeast does not become easily acclimated to grape must.

#### TESTS TO DETERMINE NATURE OF THE SUBSTANCE IN GRAPE SYRUP WHICH STIMULATES YEAST TO HIGH ALCOHOL FORMATION

Invert sugar syrup, made by hydrolyzing cane sugar with HCl and neutralizing with KOH, was added to must during fermentation but gave no increased alcohol yield. Ammonium salts gave no definite effect. The dealcoholized extract from fermented must did not give the desired result. Evidently growth of yeast and fermentation use up the invigorating substance. The ash of must gave no definite result. Phosphates seemed to increase the alcohol yield, but not markedly so. The experiments on this point are so far more or less negative and indefinite.

#### SUMMARY AND CONCLUSIONS

I—In four small scale fermentations representing five or more gallons each, wines of over 18 per cent alcohol were made by fermentation of grape must by "Burgundy" wine yeast and the addition of grape syrup during fermentation. One of these wines reached 19.9 per cent alcohol.

II—The maximum alcohol obtained by a "straight" fermentation with the same yeast was 17.2 per cent; in most cases, the maximum was 16.6 per cent or less by this method. The fact that the syruing method in practically all cases gave wines of 18 per cent alcohol or over shows that the exceptionally high yields are due to the addition of the syrup.

III—Tests made to throw light on the character of the invigorating compound of the syrup showed



that it was not the sugar of the syrup, but did not give any definite evidence as to what the compounds causing the increased activity of the yeast might be.

IV—Partially dried grapes may be used instead of syrup during fermentation to increase the sugar content and invigorate the yeast. Therefore, no expensive evaporating system is necessary in the application of the new method.

V—Where the wine made by the new method was not filtered and carefully handled, it was spoiled by the growth of "tourne" bacteria. Where it was racked clear or filtered after fermentation and kept in well-filled packages, it kept well and developed an agreeable "rancio" or "sherry" flavor.

Whether the method will become important commercially remains to be seen. It was applied on a large scale during the past season by several large companies in California, but the results of this work are not available for publication.

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### • TOTAL CARBON IN SOIL BY WET COMBUSTION

By C. J. SCHOLLENBERGER

Received August 23, 1916

The determination of total carbon in soil is necessary in certain soil investigations. Of the several methods used, that of combustion in a furnace, absorption and weighing of the carbon dioxide obtained is probably the most accurate, provided the necessary precautions are observed. The latter include not only the complicated purifying and drying train common to all gravimetric carbon determinations, but a second combustion tube with copper oxide or some similar arrangement to insure complete oxidation of volatile carbon compounds which may be distilled off before a temperature sufficiently high for complete combustion has been attained. A further precaution necessary in the case of soils high in carbonate carbon is a determination of carbonate in the residue after the ignition.

In this connection it may be well to call attention to the fact that the wet combustion-volumetric method described by Ames and Gaither<sup>1</sup> is capable, with slight changes, of affording results which compare very favorably with those obtained from a furnace combustion and gravimetric determination. The changes referred to consist in the use of a mixture of phosphoric and sulfuric acids, instead of sulfuric acid alone, with chromic anhydride as the oxidizing agent, in the substitution of barium hydroxide for sodium hydroxide as the alkaline absorbent for carbon dioxide, and in the replacement of the modified Camp absorption tube described in the original article by Meyer's absorption apparatus or Truog's bead tower,<sup>2</sup> together with changes in procedure made necessary by the changes in reagents employed.

The apparatus used and the method of operation are practically the same as those described in the article first cited, with the changes as noted; the absorption apparatus being filled with the alkaline absorbent, a gentle suction is turned on to facilitate the

addition of the reagents. To the sample (1 to 3 g.) in the boiling flask is added 10 cc. of the oxidizing mixture made as follows: chromic anhydride 85 g. dissolved in 100 cc. water and diluted to 250 cc. with 85 per cent phosphoric acid. The 10 cc. portion of oxidizing mixture is followed by 25 cc. 85 per cent phosphoric acid and by 25 cc. concentrated sulfuric acid. The mixture is heated rapidly at first, but with a lower flame when the reaction is well started; after the chromic acid is largely decomposed, a more intense heat may be used, but very hard boiling is unnecessary; the heating should be continued about 30 min. after boiling begins. A current of purified air is aspirated through the apparatus in volume just sufficient to prevent the hot acid mixture being forced up the stem of the separatory funnel for addition of reagents. The apparatus should be so arranged that the condensed water will run down the outside of the stem of this funnel and not drop directly into the hot acid; this simple precaution will prevent much trouble and breakage of apparatus.

The partial substitution of phosphoric for sulfuric acid reduces to a negligible quantity the fuming noticed when sulfuric acid alone is used; heavy fumes of sulfuric acid are objectionable, not only for the reason that they cause a consumption of the alkaline absorbent, but because they prevent complete absorption of carbon dioxide. Phosphoric acid alone was tried, but invariably gave results too low; a certain amount of sulfuric acid is absolutely necessary to insure complete oxidation. The determination is completed by titrating the barium carbonate as described by Cain<sup>3</sup> or by titrating the excess of barium hydroxide as described by Truog.<sup>2</sup>

The latter method, while not absolutely accurate under all conditions, as was pointed out in a former article<sup>3</sup> is sufficiently so for most purposes and is very much more rapid and convenient; with either method, the solutions used should be standardized against a sample of known carbon content. Blanks should be run for carbon in reagents, etc.

PER CENT TOTAL CARBON IN SOIL BY SEVERAL METHODS

Sample	1	2	3	4	5
Furnace combustion, Gravimetric.....	0.94	2.69	1.13	0.88	2.95
New wet combustion, Volumetric,					
Ba(OH) <sub>2</sub> .....	0.94	2.66	1.13	0.87	2.84
Old wet combustion, Volumetric,					
NaOH.....	0.90	2.62	1.10	0.80	2.72
Parr method.....	0.83	2.66	1.10	0.97	..

In the table are presented results obtained on five samples of soil by the gravimetric method (combustion with copper oxide in combustion tube, absorption and weighing of carbon dioxide), by the wet combustion-volumetric method as modified, titrating excess barium hydroxide without removal of carbonate, by the wet combustion-volumetric method as originally described, and by the Parr method of combustion in bomb with sodium peroxide and measurement of carbon dioxide in gas burette. The results tabulated are from the averages of at least two closely agreeing determinations.

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<sup>1</sup> THIS JOURNAL, 6 (1914), 465.

<sup>2</sup> *Ibid.*, 7 (1915), 1045.

<sup>3</sup> *Ibid.*, 8 (1916), 427.

<sup>1</sup> THIS JOURNAL, 6 (1914), 561.

<sup>2</sup> *Ibid.*, 7 (1915), 1045.

## SOME COMPARISONS OF METHODS FOR DETERMINING NITROGEN IN SOILS

By W. L. LATSHAW

Received August 14, 1916

Since determinations of nitrogen in soils have been made by the Kjeldahl method or some of its various modifications, considerable trouble has been experienced with the flasks bumping while distilling the ammonia from the digest. In some cases the bumping is so violent that flasks are thrown off the still. This is very annoying, especially when using glass flasks.

Various means have been proposed to meet the trouble as: (1) Distilling with steam; (2) Transferring digest to a copper flask and allowing it to bump, the danger of the flask breaking being eliminated. These methods answer the purpose, but ignore the real issue—the cause of the bumping. Furthermore, they are both laborious and consume considerably more time than would a satisfactory method by which the distillation could be made in the same flasks as the digestion.

To perfect a method of this nature, we had to know the cause of the bumping. In our regular work in which we diluted our digest to 600 cc. before distilling, using 800 cc. flasks and the same amount of zinc as when we diluted to 400 cc. before distilling, we noticed that very little bumping took place, while those diluted to the less extent bumped considerably. Thus it would seem to be a problem of diluting the heavy alkaline digest<sup>1</sup> which consists of sand and a heavy voluminous precipitate of the metals in the soil which are precipitated by sodium hydroxide. We also decided that if the heavy metals in the soil were causing the trouble, to add more in the form of mercury and mercuric oxide would cause more trouble, so the Gunning method was tried and comparison made with the Kjeldahl method using mercury, the same dilutions being made in each method. It was found that where no mercury was used, there was no bumping.

<sup>2</sup> The Gunning method proved in every way satisfactory in respect to eliminating the bumping, but required considerable time for digestion, in some cases as much as 4 or 5 hours. As this length of time was objectionable, a catalyzer was thought necessary and copper wire was used in 0.08 to 0.1 g. amounts with excellent results. The time of digestion was reduced to an average of 2½ hrs. for each determination.

### METHOD USED AT THIS STATION

Place 10 g. of soil in an 800 cc.<sup>2</sup> Kjeldahl flask with 7 g. of powdered sodium sulfate, approximately 0.08 to 0.1 g. of copper wire and 35 cc. of pure concentrated sulfuric acid. Shake immediately to prevent the soil from adhering to the sides of the flask. Heat over a moderate flame, rotating or shaking occasionally so as to secure even and complete digestion. Continue the digestion one hour after the solution becomes colorless. Cool and dilute with 500 cc. or more of water. Add an excess of strong alkali and a small amount of

zinc dust or granulated zinc, preferably the latter. Connect the flask with the distilling apparatus, mix thoroughly and distil, etc.

In order to demonstrate more clearly the chemical efficiency of the method used at this Station, the results of some experimental work are given in comparison with the Official Method.<sup>1</sup> The results, given in Table I, show no marked differences in the two methods.

TABLE I—COMPARISON OF PERCENTAGES NITROGEN BY TWO METHODS

Sample	METHOD USED AT THIS STATION				OFFICIAL METHOD			
	No. of Det's	Max.	Min.	Av.	No. of Det's	Max.	Min.	Av.
1383	4	0.151	0.136	0.143	3	0.145	0.142	0.144
1384	2	0.147	0.144	0.146	3	0.147	0.145	0.146
1385	2	0.147	0.144	0.146	2	0.148	0.146	0.147
1386	2	0.153	0.154	0.153	2	0.160	0.158	0.159
1387	2	0.140	0.137	0.139	2	0.143	0.139	0.141
1388	3	0.146	0.137	0.141	2	0.143	0.140	0.142
1389	3	0.147	0.142	0.144	2	0.142	0.140	0.141
1390	3	0.151	0.145	0.148	2	0.146	0.143	0.145
1391	2	0.146	0.144	0.145	2	0.144	0.143	0.144
1392	2	0.156	0.154	0.155	2	0.153	0.153	0.153
1393	2	0.146	0.144	0.145	2	0.142	0.140	0.141
1394	2	0.147	0.146	0.147	2	0.146	0.145	0.146

As a means of showing the working efficiency of our method, some work may be described which was recently done with the aid of two student helpers, each working half time. We had 475 samples of soil to analyze for nitrogen which, including duplicates and the blanks on several lots of alkali and several repeats, made approximately 1000 determinations. We used one hundred and twenty 800 cc. Kjeldahl flasks and a 12-place block-tin condenser. Our average run was 100 determinations a day. Only two flasks broke, both of which fused dry in digestion. One of these broke after the distillation was completed. The other represents our sum total of losses in determinations due to breaking of flasks.

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## THE DETERMINATION OF PHOSPHORUS PENTOXIDE AFTER CITRATE DIGESTION

By O. C. SMITH

Received June 27, 1916

Considerable difficulty is experienced by most chemists in the digestion of the fertilizer and filter papers left after the removal of the reverted phosphate by the digestion with neutral ammonium citrate. The usual method consists in the digestion with differing proportions of hydrochloric and nitric acids, preferably 30 cc. concentrated nitric and 10 cc. concentrated hydrochloric. By this method a clear solution cannot be obtained with some fertilizers even after digestion for a whole day. By the use of the following method a clear solution can be obtained in less than an hour.

Two grams of the sample are weighed on a filter paper in a funnel and washed with about 250 cc. of water: the paper and sample are then transferred to a 200 cc. flask containing 100 cc. of neutral ammonium citrate, previously heated to 60° C. and heated at 60° with frequent shakings for ½ hr. The contents of the flask are then filtered immediately and washed with water at 60° until all of the citrate solution and soluble phosphorus are removed. The two filter

<sup>1</sup> The principle of diluting the digest has been in use in this laboratory for the last five or six years and the author claims no credit for this idea.

<sup>2</sup> Pyrex flasks were used exclusively in doing this work. We have found them superior to the well-known Jena flasks.



papers and remaining fertilizer are then ready to be dissolved.

The contents of the funnel, including both filter papers, are put back into the Erlenmeyer flask, 10 cc. concentrated sulfuric and 50 cc. of dilute nitric acid (1 : 1) are now added and the flask placed on the bare hot plate. The digestion is allowed to proceed undisturbed until all of the nitric acid has been boiled off which is shown by the appearance of the white sulfuric acid fumes. About 1 or 2 cc. of concentrated nitric acid is now added to the boiling sulfuric acid and the digestion continued until white fumes appear again. Concentrated nitric acid is then added again and the digestion continued. This is repeated till the solution is water-white, then it is allowed to cool, made up to volume and an aliquot taken. This is neutralized with ammonium hydroxide, ammonium nitrate added and the phosphorus precipitated in the usual way.

By using this method of digestion a clear solution is easily obtained in an hour or less. The second addition of the nitric acid will almost always clear it up. However, if the sample is heated after the sulfuric acid is added and then the dilute nitric acid added considerable difficulty with foaming will be experienced.

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## THE ANALYSIS, PURIFICATION AND SOME CHEMICAL PROPERTIES OF AGAR AGAR

By CARL R. FELLERS

Received May 8, 1916

### SOURCES OF AGAR

Agar is the commercial name applied to the dried and more or less purified stems of certain kinds of marine algae. Of these the group *Florideae* or red algae is by far the most common. They are char-

acterized by a leaf-like growth and upright thallus and grow almost exclusively in tropical waters. The most important of these are *Gelidium corneum*, *G. cartilagineum*, *Fucus amylaceus* (also called *Gracillaria confervoides*), and *Euchema spinosum* Ag., but agar may also be obtained from certain species of *Tenax* and *Gigartina*. In France as "gelose;" it is synonymous with Bengal or vegetable isinglass. The Ceylon and Chinese agars are derived mainly from *Gracillaria confervoides* and give with water a clear, transparent jelly. The product obtained from Java and Malaysia comes principally from *Euchema spinosum* and is of inferior quality. The Japanese agar, obtained from *Gelidium corneum*, is ordinarily accounted to be of superior quality to other agars. Mr. Y. S. Djang, of Tientsin, Southern China, has informed the author that the Japanese product is also considered best in China from a dietary standpoint. "Carragheen" or Irish moss should not be confused with agar. It is derived from *Chondrus crispus* mainly, an alga which is very abundant in the North Sea. It gives a gel resembling agar.

Agar is prepared for market in two ways: One method consists merely in drying and bleaching the thallus of the algae in the sun, previous to shipping. Such a product contains many impurities like diatomaceous refuse and other mineral or vegetable matter foreign to the plant. The other method consists in making a jelly of the seaweeds, allowing the water to freeze out, and finally cutting the residue into thin strips and drying thoroughly. The commercial product usually consists of a number of different species of algae and hence its composition is fairly constant.

### ANALYSIS OF AGAR COMPILED FROM VARIOUS SOURCES

The following analyses are thirty to forty years old except the one by Forbes, Beagle and Mensching<sup>1</sup> which is more recent and which gives a fairly complete analysis of a sample of dried agar.

These results show how widely the composition of agar varies from different sources or even from the same source. The high ash content shown by Analysis 2, points to gross mineral impurities, while the low

TABLE I—ANALYSES OF ALGAE PRODUCING AGAR  
Euchema &

SPECIES	<i>Gelidium</i> corneum	Unknown	<i>Euchema</i>	<i>Gelidium</i>	DRIED		<i>Fucus Amylaceus</i>
Analysis No.	1	2	3	4	5	6	7
Water	22.8%	18.5%	19.56	49.80	17.33	15.29	Water
Nitrogenous Matter	11.71	9.8	2.53	2.88	3.62	1.88	Albuminoids
Fat	.....	.....	0.24	0.20	0.37	0.37	Solution in Cold Water
Ash	3.44	12.02	3.15	18.96	2.89	4.23	Ash
Dried Plant	.....	.....	.....	.....	.....	.....	.....
Woody Fiber	.....	5.00	.....	3.20	0.47	0.89	Solution in Dilute NaOH
Carbohydrates	65.05	.....	.....	.....	S.	1.77	Gelose (Metarabin)
Fat + N-free Extract	.....	52.00	.....	.....	Ca,	0.66	.....
DRIED PLANT	.....	.....	.....	.....	Mg,	0.483	Solution in Alcohol
Nitrogenous Matter	14.06	12.02	3.15	.....	Na,	0.114	Wood gum
Nitrogen	2.35	1.92	0.50	.....	K,	0.112	Cellulose
N-free Extract + Crude Fiber	.....	.....	73.6	.....	Cl,	0.034	.....
Fat + Crude Fiber + N-free Extract	62.05	.....	.....	.....	P,	0.020	Matter removed by KNO <sub>3</sub> + Loss
N-free Extract	.....	.....	.....	19.16	45.00	77.34	.....
Date of Analysis	1884	1884	1883	About 1885	.....	1913	1882
ANALYST	Kellner(a)	Nagai & Murai(a)	Konig(a)	Sack and Van Eck and Greshoff	Forbes, Beagle & Mensching	Greenish	.....

(a) J. Konig, *Chemie der Menschlichen Nahrungs und Genussmittel*, Band I, S. 721.

acterized by a leaf-like growth and upright thallus and grow almost exclusively in tropical waters. The most important of these are *Gelidium corneum*, *G. cartilagineum*, *Fucus amylaceus* (also called *Gracillaria confervoides*), and *Euchema spinosum* Ag., but agar may also be obtained from certain species of *Tenax* and *Gigartina*.

Most of the agar of commerce comes from China, Japan, Malaysia, Ceylon and neighboring coasts. In China it goes by the name Hai-Thao or Ta-o,

ash and high carbohydrate percentages in Analysis 3 show careful purification. *Euchema* is seen to be inferior to *Gelidium* as a source of agar. Analysis 7 gives some interesting information as regards the organic composition of agar. Forbes' results show a very high percentage of sulfur. Frankland<sup>2</sup> reports that he found one liter of agar jelly to contain 0.3016 g. sulfur. Arsenic is reported to be present by Leroide

<sup>1</sup> Ohio Agr. Exp. Sta., Bull. 255.

<sup>2</sup> "Microorganisms in Water," p. 14.

and Tassidy.<sup>1</sup> They found 0.025 and 0.02 mg. As, respectively, in two samples which they tested. This arsenic may owe its presence to the fact that the agar may have been bleached by means of SO<sub>2</sub> gas, as this process is often used in Japan. Loewit and Bayer<sup>2</sup> show that no reaction for protein can be obtained with agar, unless the latter has been first hydrolyzed by means of H<sub>2</sub>SO<sub>4</sub> when the ninhydrin reaction is positive showing agar does contain protein. Czapek reports pentosans in agar to the extent of 1.66 per cent; Sebor<sup>3</sup> also attests to their presence, especially xylan. Bauer<sup>4</sup> states the carbohydrate principle of agar is galactin while Czapek<sup>5</sup> says there is enough iodine present to impart to CS<sub>2</sub> a red-violet color.

*d*-Galactan or gelose, the carbohydrate pectin-like basal principle of agar, gives the latter its characteristic swelling and jellyfying properties. It has been repeatedly investigated.

Payen<sup>6</sup> was the first to extract gelose from algae. He characterizes it by its ternary composition, absence of nitrogen, complete solubility in boiling water and its remarkable power of forming on cooling a colorless, transparent jelly, and coagulating in this form 500 times its weight of water. It is free from water and resembles closely the pectins. He called this interesting substance gelose, which recalls at the same time its origin, its applications and its most interesting property. He assigned to it the formula C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>.

Not until 1875 did Reichardt<sup>7</sup> again take up the subject of agar. He identified the carbohydrate principle as pararabin (C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>), a substance which he had previously prepared from carrots and beet roots. Morin<sup>8</sup> did much experimental work on gelose. He found it gave mucic and oxalic acids on hydrolysis with dilute HNO<sub>3</sub>. He determined the rotatory powers of solutions of gelose and concludes that its properties are very similar to those of the gums. Biot and Persoz<sup>9</sup> show it is not a true gum, while Poramuburn<sup>10</sup> assigns to it the formula C<sub>6</sub>H<sub>10</sub>O<sub>5</sub> and states it is analogous to lichenin and tunisin. The latter also determined the products of hydrolysis with various acids. In 1882, Greenish<sup>11</sup> repeated most of the work which had been done on agar previous to this time. To gelose he assigns the formula 4C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>H<sub>20</sub>. It does not reduce Fehling's solution and is not fermentable by yeasts even after hydrolysis with dilute H<sub>2</sub>SO<sub>4</sub>. He obtained seven carbohydrate-like compounds by various treatments of gelose. Among these were arabinose and glucose. A few years later Bauer<sup>4</sup> identified gelose with galactin, a product obtained by Muntz<sup>12</sup> from lucerne seeds and various non-starchy plants. It has the formula C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>. Pectins

have been mentioned as being very closely related to agar since the products of hydrolysis of both these substances are very similar. Seyfert<sup>1</sup> points out that 22 per cent mucic acid is obtained by hydrolysis of agar with dilute nitric acid. Tollens<sup>2</sup> states that lactose and a mixture of glucoses have been crystallized from agar treated with dilute acids. Rouvier<sup>3</sup> attests to the presence of small quantities of amidon in agar.

From these early investigations it may be concluded with a fair amount of certainty that the substance which is chemically the basal principle of agar and to which the latter owes its jellyfying properties is *d*-galactan.

Considerable work has been done on the jellyfying power of agar. It is an ideal substance for the study of reversible colloids. Hardy<sup>4</sup> used agar in his study on the theory of phases. He showed that the liquid phase of the system agar-water is a solution of agar in water while the solid phase is a solution of water in agar. Further work on the mechanism of gelatinization has been accomplished by Von Weimarn,<sup>5</sup> Voigtländer,<sup>6</sup> Wagner<sup>7</sup> and Levites.<sup>8</sup> Levites, for instance, found that chlorides, bromides, iodides, salts of di-, tri- and tetrabasic acids, polyhydric alcohols and carbohydrates to a lesser degree, all tend to accelerate the gelatinization of agar. The action depends mainly on the anion, the part played by the cation being less striking. Reidemeister<sup>9</sup> determined the influence of a large number of acids and salts on the solidity of agar gel. Cooper and Nutall<sup>10</sup> show the application of agar to photography. They show that an agar film need be but one-eighth as thick as a gelatin film. Of course this is a decided advantage. Other advantages which they state agar possesses over gelatin are cheapness and insolubility in water (except when the latter is very hot). Other investigators, however, do not advocate its use in photography.

The colloid chemistry of agar plays a very important rôle in the preparation of all agar media for bacteriological purposes. This is especially true as regards the concentrations of the agar and the other substances which make up the medium. Very little is known concerning the changes which take place when agar is sterilized at high temperatures. No systematic work has ever been done on the determination of the proper consistency or concentration of agar in the various media used so widely in bacteriological analysis. Antagonism between salts and the effect of salts upon the agar itself need further study. Possible reactions may occur during the process of making the media, especially when acids or alkalies are added to adjust the reaction (acidity). Agar which has been boiled a long time filters more readily than when boiled only

<sup>1</sup> Bull. soc. chim., **9**, 65.

<sup>2</sup> Centr. allgem. path., **24**, 745.

<sup>3</sup> Oesterr. Chem.-Ztg., **3** (1900), 441.

<sup>4</sup> J. prakt. Chem., **30**, 367.

<sup>5</sup> "Biochemie der Pflanzen," p. 520.

<sup>6</sup> Compt. rend., **49** (1859).

<sup>7</sup> Deut. chem. Ges. Berlin, **8** (1875), 807.

<sup>8</sup> Compt. rend., **90** (1880), 924.

<sup>9</sup> Ann. Chim. et Phys., **52**, 72.

<sup>10</sup> Compt. rend., **90** (1880), 1081.

<sup>11</sup> Arch. Pharm., **20**, [3] 241 and 321.

<sup>12</sup> Bull. soc. chim. de France, **37** [2], 709.

<sup>1</sup> Deut. chem. Ges., **21**, 298.

<sup>2</sup> Tollens et Bourgeois, "Hydrates de Carbone."

<sup>3</sup> Compt. rend., **104**, 128, 729 and 1366.

<sup>4</sup> Proc. Roy. Soc., **66**, 95.

<sup>5</sup> J. Russ. Phys. Chem., **43**, 653.

<sup>6</sup> J. Chem. Soc., Abs., **56** (1889), 817.

<sup>7</sup> Monatsh., **112**.

<sup>8</sup> J. Russ. Phys.-Chem., **34**, 110, and **35**, 283.

<sup>9</sup> Z. Wiss. Mikr., **25** (1908), 42.

<sup>10</sup> 7th Intern. Congr. of Applied Chem., London, p. 62.



a short time, hence it is probable that changes do occur when acid is used to neutralize the medium and the latter subsequently sterilized at high temperatures in an autoclave. The character of the precipitates formed during the sterilization, their effect on the nutritive value of the medium, and the changes which may take place when media are stored a long time are mentioned merely as suggestions for further work on agar media.

#### THE ANALYSIS OF AGAR

As a starting point for the study of agar media in more detail, it was decided that the composition of a product so widely used as agar, should be better understood. A large number of samples of commercial agar were collected. These were obtained from chemical and bacteriological supply houses in the United States. The foreign samples were procured for the author by Mr. Y. S. Djang, of Tientsin, China. They represent both crude and purified material. These results may also be of value from a dietary and nutrition point of view, to show the exact status of agar as a food for man.

#### DESCRIPTION OF SAMPLES OF AGAR

1—*Japanese Isinglass (Agar)*, Schieffelin and Co., New York. Guaranteed under Pure Foods and Drugs Act. This sample was finely ground, grayish white in color with a somewhat decided, aromatic odor. No dirt was visible to the naked eye but the microscope revealed a considerable amount of foreign matter.

2—*Shred Agar*, E. Leitz, New York. This sample consisted of long shreds of a dirty gray color, spotted here and there with a reddish stain. The microscope showed the presence of enormous numbers of diatom tests. The large amount of impurities was also noted on the filters through which media made from this sample were passed.

3—*Shred Agar*, Arthur H. Thomas & Co., Phila., Pa. The general appearance of this sample was good, no impurities being evident.

4—*Agar White*, E. Leitz, New York. A finely ground white, clean appearing sample.

5—An impure blackish colored sample obtained from China. This sample had not been purified in any way.

6—A reddish colored unpurified Chinese sample. This sample was derived from a different species of alga than was Sample V. 7, 8 and 9—Comparatively high-grade samples of white Chinese agar; this is the product used so widely in China as a food.

10, 11 and 12—Exceedingly pure white samples of Chinese agar. This is the best product obtainable on the markets of China, and so far as the author was able to determine was practically free from foreign matter.

13—*Shred Agar*, Eimer and Amend, New York. Guaranteed under Pure Foods and Drugs Law. The appearance of this sample was good.

14—Coarsely ground sample, Merck & Co., New York. Guaranteed under Pure Foods and Drugs Acts.

15—*Shred Agar*, Merck and Co., New York. This sample had a good outward appearance.

16—"Bacto," "Difco," Digestive Ferments Co., Detroit, Mich. An especially prepared purified agar for bacteriological purposes. The coarsely ground shreds or granules are of a grayish white color and are free from visible dirt. The product was packed in an air-tight container.

The methods used in the analysis are those of the A. O. A. C.<sup>1</sup> except in the determination of crude fiber, where the method given in *Ohio Bull.* 225 was followed.

In this method the use of fine sand on top of the asbestos film in a Gooch crucible greatly facilitates filtration. All determinations except those of crude fiber, ether extract and arsenic were run in duplicate, the figure recorded being the average. To determine the solubility in cold water, 5-g. portions of the air-dried substance were placed in a flask containing 200 cc. of water and allowed to stand 18 hours, with occasional shaking. Arsenic was tested for by a microchemical test,<sup>1</sup> and iodine by the carbon disulfide method. Sulfur was determined by the sodium peroxide fusion method and nitrogen by the Kjeldahl digestion method with  $K_2SO_4$ . To determine the acidity of agar, 5-g. portions were placed in 250 cc. of water (2.0 per cent solution) heated until the agar was dissolved and finally titrated while hot (100 cc. portions), using phenolphthalein as indicator.

TABLE II—PROXIMATE ANALYSES OF AGAR

No.	Moisture	Protein (N×6.25)	Nitrogen-free Extract	Ether Extract	Crude Fiber	Ash	SiO <sub>2</sub>
1.....	17.60	2.40	73.38	0.43	0.51	5.68	1.11
2.....	15.75	3.26	76.70	0.30	0.71	3.28	0.55
3.....	16.14	1.93	77.66	0.31	0.63	3.33	0.90
4.....	17.65	2.93	72.72	0.45	1.50	4.75	1.08
5.....	16.74	2.38	74.61	0.27	1.40	4.60	0.85
6.....	16.72	2.94	74.82	0.29	0.77	4.16	0.77
7.....	16.25	2.72	74.84	0.30	0.12	4.77	1.11
8.....	15.89	1.53	78.21	0.34	0.81	3.22	0.46
9.....	16.18	2.35	77.48	0.29	0.60	3.10	0.35
10.....	16.52	1.84	77.55	0.35	0.66	3.08	0.40
11.....	17.05	1.80	77.06	0.17	0.72	3.20	0.36
12.....	16.79	1.82	77.62	0.18	0.39	3.10	0.31
13.....	16.85	1.78	77.25	0.28	0.46	3.38	0.55
14.....	14.57	2.76	77.11	0.31	0.90	4.35	0.83
15.....	17.84	2.39	75.13	0.25	0.80	3.59	0.55
16(a).....	5.72	1.14	89.25	0.32	0.45	3.12	0.29
Av.....	16.57	2.34	76.15	0.30	0.80	3.85	0.68

(a) Sample 16 not included in the average.

The analyses in Table II show that a striking similarity exists among all of the samples. This is probably accounted for by the fact that the original sources of the samples do not differ greatly, all originating no doubt from the coastal waters of Japan, China and Malaysia. Another possible reason for this similarity is that the samples tested consist of several species of algae, which fact would tend to minimize any differences which may exist in single species. The percentage of moisture and fatty substance is very constant. Agar is hygroscopic and if left exposed to the air will absorb from 15 to 18 per cent moisture. The relative amounts of protein, ash and fiber, are, however, more variable. These constituents appear to have some relation to the purity of the sample, the more impure the sample, the greater the percentage of these constituents. On microscopic examination the impure samples showed much foreign material, including many species of diatoms, sand and foreign plant tissue. On the other hand, those samples which had been carefully purified were almost constant in composition, showing that impurities were not present. The siliceous diatom tests and sand in intimate contact with the agar shreds are the principal causes of the high percentage of ash in some of the samples. The very appreciable amount of protein present demands attention, as it is generally accepted by bacteriologists that agar adds no nitrogen to the cultural media. The fact is that there is present in agar an amount of nitrogenous matter equal in quantity

<sup>1</sup> U. S. Dept. Agr., Bur. of Chem., *Bull.* 107.

<sup>1</sup> Chamot, "Elem. Chem. Microscopy," p. 349.

to that present in our less rich foods. The high sulfur content of agar has already been shown by Forbes and by Frankland. The foregoing analyses check up these investigators. Since agar is sometimes bleached with  $\text{SO}_2$  gas, this may account for the high sulfur percentage in the samples. A point in favor of this view lies in the fact that less than one-half the amount of sulfur found in Samples 1 and 2 was obtained in the ash of Sample 16, a carefully purified product. Possibly the acidity of a water solution of agar may be ascribed to this water-soluble sulfur.

TABLE III—ANALYSIS OF AGAR (PERCENTAGES)

Sample No.	1	2	16(a)	AVERAGE
$\text{CaO}$ .....	1.02%	0.82	.....	0.92
$\text{MgO}$ .....	0.595	0.540	.....	0.568
$\text{Na}_2\text{O}$ .....	0.235	0.264	.....	0.25
$\text{K}_2\text{O}$ .....	0.062	0.072	.....	0.067
$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$ .....	0.57	0.052	.....	0.55
$\text{SiO}_2$ .....	1.11	0.55	0.29	0.83
$\text{SO}_2$ .....	2.65	0.264	1.11(b)	2.645
$\text{P}_2\text{O}_5$ .....	0.056	0.048	.....	0.052
$\text{As}_2\text{O}_3$ .....	—	—	—	—
$\text{Cl}$ .....	0.26	0.17	+	0.22
$\text{I}$ .....	+	+	.....	+
Pentosans.....	2.996	3.236	.....	3.12
Galactan.....	24.34	21.40	.....	22.87
Solution in $\text{H}_2\text{O}$ at $20^\circ\text{C}$ .....	19.1	18.9	3.08	19.00
Solution in $\text{H}_2\text{O}$ at $100^\circ\text{C}$ .....	96.5	95.9	98.77	96.20
Protein in alcohol precipitate.....	0.94	1.30	.....	1.12
Cc. excess $\text{N HCl}$ per gram agar	0.034	0.024	.....	0.029

(a) Not included in the average (—) Detected but not estimated.  
(b)  $\text{SO}_2$  in the ash. (—) Negative results in the tests.

No arsenic was detected by the microscopic methods used, hence the author was unable to check up Leroide and Tassidy's work already commented upon. A reddish violet color was imparted to the  $\text{CS}_2$  used in the test for iodine. It was very faint, however, showing that the amount of iodine in dried agar is very small. The inorganic elements Ca, Mg, Na, K, and P are present in varying amounts. These, together with the carbohydrate-like pentosans and galactan, form all the elements necessary for microbial development. It is possible that some of these substances may become available for bacterial food through the action of the acid present in the media or else by the high temperature used in media sterilization.

Agar is in itself acid to phenolphthalein as the data show. This also is contrary to the popular belief. A reaction of about 0.3 cc. of  $\text{N}/10$   $\text{HCl}$  per gram of agar is considerable and for this reason agar media should not be neutralized before the agar itself is added. Agar on being washed in water and precipitated by alcohol loses about 60 per cent of its original nitrogen content. This method of procedure may, therefore, be used to purify the crude agar, for use in refined bacteriological investigations.

#### PURIFICATION OF AGAR

The question of purification has received some attention in the literature of the subject. At least two patents have been taken out in Germany, one by Steinitzer<sup>1</sup> and another by Merck.<sup>2</sup> The former is of little value as the jellifying power of the agar is injured by treatment with acids. Merck's method consists essentially in dissolving low-grade agar in hot water, filtering and congealing by freezing. After it has become liquid again, it is separated from the aqueous solution and washed with cold water until the washings show little or no residue on evaporation

to dryness. This procedure removes the part soluble in cold water and which does not set. Among the investigators recommending the use of dilute acids to assist in the purification, are Mace,<sup>1</sup> Schottelius,<sup>2</sup> Marpmann<sup>3</sup> and Besson.<sup>4</sup> These methods appear to effect a sort of purification if the acid is not too concentrated, in which case the jellifying properties of the agar are injured. Dominikiewicz<sup>5</sup> published an article on the question of uniformity of composition and methods of preparation of agar. His method of purification is to precipitate a lukewarm solution by a large volume of alcohol which has been weakly acidified with acetic acid. This agar precipitate is then filtered, washed and dried.

A method used by the author in the preparation of "purified" agar has given uniformly good results. A brief account of the procedure follows.

Clean agar shreds are cut into pieces about  $\frac{1}{2}$  in. in length (a large paper cutter serves very well for this), transferred to a glass funnel containing a filter, and washed with ether. The ether is saved and may be used over and over. Then a little alcohol is poured over the shreds to dissolve out the ether. The agar is transferred to a beaker containing a sufficient quantity of a solution of 3 to 4 per cent acetic acid to cover the swelled shreds. In an hour or thereabouts the water is changed in the beaker, no more acid being added. In a few hours, during which period the water has been changed several times, the shreds are poured on a piece of cheese-cloth and as much liquid is squeezed out as possible. Washing a few times with water is sometimes advantageous at this stage, especially if the agar is still very acid. The swelled shreds are weighed and calculating back from the amount of original sample taken, enough distilled water is added to give approximately a 5 per cent solution of agar. This is flaked, melted in an autoclave and while still hot is poured through a cotton filter to remove foreign matter. The filtered solution is now poured very slowly into a large beaker containing 4 or 5 times its own volume of 95 per cent alcohol or acetone. The latter should be constantly agitated and the agar solution poured in a very thin stream for precipitation to take place properly. At first the alcohol becomes opalescent, but the snow-white precipitate soon appears. After standing for a short time, the alcohol is decanted from the precipitate which is thoroughly washed with water and dried at  $100^\circ\text{C}$ . This product, if kept in bottles with paraffined stoppers, will absorb a minimum amount of moisture and may be kept indefinitely. To test the efficiency of this method, the percentage reduction in nitrogen due to the purification process was determined in four samples, namely, 2, 4, 3 and 15. The reduction was 60, 82, 93 and 76 per cent, respectively, for these samples. These results show that a large part of the nitrogenous matter originally present in agar is eradicated by this method. Experiments were also made

<sup>1</sup> See Mace's "Traites de Bacteriologie."

<sup>2</sup> *Centr. Bakt.*, **2** (1887), 1042.

<sup>3</sup> *Ibid.*, **10**, 209.

<sup>4</sup> See Besson, "Bacteriologie," **42** (translation).

<sup>5</sup> *Centr. Bakt., Abl.* **1**, Bd. 47, S. 666.

<sup>1</sup> German Patent No. 269,088 (1912).

<sup>2</sup> German Patent No. 272,145.



to test out this purified product by comparison with ordinary agar, to see if bacterial development had been inhibited on plates where both kinds were used in media. These results are reported by the author in another place.<sup>1</sup> Here it is shown that as many bacterial colonies develop on "purified" agar media as on ordinary agar, made up in the same way and using a soil infusion as the inoculating material.

The "purified" agar gives a very clear medium, and since it contains a minimum amount of impurities and is constant in composition, its use is strongly to be recommended. The fact that it contains little or no moisture is an added point in its favor. The jellyfying power of the agar was not injured in any way as a result of the purification process. The question arises, can microorganisms make use of the protein compounds and other nutrients present in agar? From data presented elsewhere<sup>2</sup> it is shown that part of the nitrogen at least is available under certain conditions. This was determined by a series of ammonification experiments in which the agar itself was used as a basis of nitrogenous matter. However, in solid culture media, the amount used by microorganisms was shown to be very small, even though appreciable growths of a number of organisms including bacteria, yeasts and fungi, were obtained on plain agar. The failure of Warington,<sup>3</sup> the Franklands<sup>4</sup> and Winogradski<sup>5</sup> to isolate pure cultures of nitrifying bacteria on agar media, may probably be attributed to the food in the agar itself.

#### ACTION OF ACIDS ON AGAR

Three per cent HCl caused agar to lose its power of forming a gel with water. Alcohol or acetone cannot reprecipitate it from this acid solution. The agar on dissolving in the acid leaves a brown insoluble residue which on drying becomes a humus-like substance. The solution after neutralization with  $\text{Na}_2\text{CO}_3$  and evaporating to dryness, very slowly on a water-bath, gave a gray syrup, which tasted sweet and which on heating further gave the characteristic odor of caramel. All attempts to cause this sugar to crystallize failed. Solutions of this substance, with or without the nutrients, in concentrations of 0.5, 1 and 1.5 per cent gave no gas in fermentation tubes when inoculated with either Fleischmann's yeast or *B. coli*.

Three grains of each of Samples 1 and 2 gave on hydrolysis with  $\text{HNO}_3$  (sp. gr. 1.15) 0.6216 and 0.5358 g. of mucic acid, respectively. This is an average for the two samples of 28.93 per cent. Seyfert<sup>6</sup> obtained 22 per cent of mucic acid from *Fucus crispus*. Morin<sup>7</sup> states that oxalic acid is also formed but none was detected in this experiment.

Two per cent  $\text{H}_2\text{SO}_4$  solution, allowed to act on "purified" agar, dissolved it. The solution, after neutralization with  $\text{BaCO}_3$ , filtering and evaporating, yielded an amorphous grayish brown powder. Its

aqueous solution is precipitable by acetone or alcohol. One per cent solutions in fermentation tubes with or without added nutrients gave no evolution of gas in 5 days, on being inoculated with either Fleischmann's yeast or *B. coli*. No attempt was made to determine the identity of this substance. It had a slight sweetish taste and could not be made to crystallize. It probably is not a true sugar.

An experiment was performed for the purpose of determining the maximum concentration of KOH and HCl which will cause a 2 per cent solution of agar to lose its jellyfying properties. The effect of heat and the addition of peptone and KCl on these points was also determined. The sterilization of the agar was carried out in an autoclave at 1 atm. for 15 min.

TABLE IV EFFECT OF ACID AND ALKALI ON THE JELLYFYING POWER OF AGAR, BEFORE AND AFTER STERILIZATION

REACTION	PLAIN 2% AGAR		2% AGAR + 2% PEPTONE		+0.6% KCl (After Ster.)
	Not Ster.	After Ster.	Not Ster.	After Ster.	
5.0% HCl	Solid-Liquid	Liquid	Solid	Liquid	....
4.5% HCl	Solid	Liquid	Solid	Liquid	....
4.0% HCl	Solid	Liquid	Solid	Liquid	....
3.5% HCl	Solid	Liquid	Solid	Liquid	....
3.0% HCl	Solid	Liquid	Solid	Liquid	Liquid
2.5% HCl	Solid	Liquid	Solid	Liquid-Solid	Liquid
2.0% HCl	Solid	Solid-Liquid	Solid	Liquid	Solid-Liquid
1.5% HCl	Solid	Solid	Solid	Solid	Solid
1.0% HCl	Solid	Solid	Solid	Solid	....
Neutral	Solid	Solid	Solid	Solid	....
1.0% NaOH	Solid	Solid	Solid	Solid	....
2.0% NaOH	Solid	Solid	Solid	Solid	....
2.5% NaOH	Solid	Solid	Solid	Solid	....
3.0% NaOH	Solid	Solid	Solid	Solid	....
3.5% NaOH	Solid	Solid	Solid	Solid	....
4.0% NaOH	Solid	Solid	Solid	Solid	....
4.5% NaOH	Solid	Solid	Solid	Solid	....
5.0% NaOH	Solid	Solid-Liquid	Solid	Solid-Liquid	....

Table IV shows that practically all the concentrations of acid and alkali up to 5 per cent caused no delatinization of the agar; except when 5 per cent HCl was used, the gel was rather soft and crumbly. In these experiments the acid was added to the hot agar solution, thoroughly stirred and quickly cooled. Sterilization at 1 atm. in the autoclave for 15 min. caused all the agar containing more than 2 per cent HCl to become liquid. The 5 per cent alkali solution was also partly liquefied. Peptone seems to aid slightly in the gelatinization process, as 2 per cent agar with peptone was much firmer than the plain agar treated with a like amount of acid. A small amount of KCl may cause a slight decrease in jellyfying power, but the data are too scanty to draw conclusions. Where over 2 per cent NaOH was present the agar became brownish black in color. In connection with this experiment the least amount of clean pure agar which is able to form a firm gel with water was found to be 0.3-0.4 per cent. A 5 per cent agar gel is not harmed in any way by heating at a pressure of one atmosphere for 15 minutes.

#### ACTION OF OTHER CHEMICALS ON AGAR

Ether extracts an aromatic-scented, light, amber-colored, fatty substance of about the consistency of stearin. On account of the small quantity obtained no tests were made on the fat.

With hot aqueous solutions of agar ether gives a dirty, gray-brown colloidal gel. This is rather porous in character and on driving off the ether by gentle heat, ordinary agar is obtained.

Chloroform added to a boiling agar solution, and vigorously stirred, gives a two-liquid layer system

<sup>1</sup> See *Soil Science*, No. 3, 2 (1916), 260.

<sup>2</sup> *Ibid.*, p. 257.

<sup>3</sup> *J. Chem. Soc. London*, 59 (1891), 484.

<sup>4</sup> *Proc. Roy. Soc. London*, 47 (1890), 296.

<sup>5</sup> *Ann. inst. Pasteur*, 4 (1890), 213 and 257.

<sup>6</sup> *Ber.*, 21<sup>2</sup> (1888), 298.

<sup>7</sup> *Compt. rend.*, 90 (1880), 924.

with water-agar at the top and  $\text{CHCl}_3$ -agar beneath. The bottom layer consists of a snow-white porous, spongy mass, occluding large quantities of chloroform. On heating, the mass becomes less bulky, loses its chloroform, and apparently reverts to ordinary agar.

The precipitating action of alcohol and acetone has already been described.

#### SUMMARY

I—The sources, preparation and composition of agar have been discussed.

II—The analysis of sixteen samples of agar, obtained from widely different sources, show a remarkable uniformity in composition. High ash or silica content is indicative of an inferior product. Considerable amounts of nitrogenous substances were found in all of the samples. Part of this nitrogen, and possibly some of the other nutrients may serve as a food for microorganisms, if grown on a medium containing agar. Some aqueous solutions of agar are acid to phenolphthalein.

III—A method of preparing a "purified" agar is described. It consists essentially in washing the agar shreds in a solution of dilute acetic acid, washing out the acid and precipitating, while hot, a 5 per cent

solution of the agar, by means of a large volume of alcohol or acetone. It is shown that much of the nitrogenous matter of the agar is removed by this method of purification. The method is recommended to be followed for the preparation of agar substrata to be used in refined bacteriological work, especially where a jellifying medium containing a minimum of nutrients is desired.

IV—Solutions of agar will solidify at all concentrations of HCl and NaOH between 4.5 per cent HCl and 5 per cent NaOH. Heating at one atmosphere pressure for 15 minutes in an autoclave narrows the range of solidification to from 2 per cent acid to 4.5 per cent alkali. Peptone increases the jellifying power of agar. KCl appears to decrease it slightly.

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## LABORATORY AND PLANT

### FORMULAS FOR THE FLOW OF GASES

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In the formulas ordinarily employed for the flow of gases through orifices, pipes, and conduits, use is seldom made of the simplifications which the gas laws make possible, with the result that in our engineering handbooks and textbooks we find formulas for the flow of steam, other formulas for the flow of air, and occasionally formulas for use with illuminating gas. On the other hand, all these formulas can be expressed in terms of fixed constants (the same for all gases) and the molecular weight of the particular gas with which the engineer is dealing. While such modification of the formulas involves nothing new in the dynamics of gases, none the less such simplification is of great value, most especially to the chemical engineer, who frequently deals with gases other than those familiar to mechanical engineering practice. This is true to such a degree that it seems worth while to develop and present such formulas in general form so as to make them available to the profession.

The mechanical engineer always uses the gas law in the form  $pV = RT$ , applying this formula to one pound of the gas in question. On the other hand, the chemist has learned to use the gas law in the form  $pV = nRT$ , where  $n$  is the number of mols of gas in question and  $R$  is the gas constant, the same for all gases. The chemist, it is true, has hitherto used this formula exclusively in the metric system, but its advantages over the older form are no less real in the English system than in the metric, and throughout the following we shall therefore express the gas law

in this way,  $pV = nRT$ , using throughout English engineering units, so that  $p$  = the pressure on the gas in lbs./sq. ft.,  $V$  = the volume of gas in question expressed in cu. ft.,  $n$  = the amount of gas in pound mols, one pound mol being a weight of the gas in question in pounds equal to its molecular weight,  $R$  = the gas constant in English units, 1545, and  $T$  the temperature in ° F. absolute. By the use of this formula and this nomenclature all the ordinary formulas for the flow of gases may be written in a common form applicable to all gases, merely inserting into the formula the molecular weight or average molecular weight of the gas or mixture of gases in question. The molecular weight of a gas may be defined as the weight in pounds of 359 cu. ft. of the gas reduced to or measured under standard conditions, this definition being identical with the ordinarily accepted definition familiar to the chemist.

The measurement of gas by volume when this is not absolutely necessary is intolerably bad practice, especially on the part of a chemical engineer. To state the volume of gas tells nothing of its amount unless its temperature and pressure also be given. It is true that gas quantities may be expressed as weight, but weight relationships in gases are always complicated in comparison with molal relationships, and the rational way to express gas quantities is in mols. Inasmuch as most engineering work has to be done in the English system, the most satisfactory unit is the lb. mol, *i. e.*, a number of pounds of the gas equal to its molecular weight. The formulas for the number of pound mols of gas are therefore given below, and in general it will be found that these are the easiest and best to use.



## DERIVATION OF FORMULAS

Bernoulli's theorem in hydro-mechanics is merely the statement of the equality of input or output of energy into any section of a system through which a fluid is flowing. As applied in hydraulics and in the hydro-mechanics of liquids in general, it is usual to equate the mechanical energy at inlet and outlet, inasmuch as there is no transformation of heat energy into mechanical energy or *vice versa*, except that due to friction; where friction loss occurs this is subtracted from the energy input before equating to the energy output. On the other hand, whenever a compressible fluid, *e. g.*, a gas, enters and leaves a section under differing pressures, the gas must have expanded within the section itself from the higher to the lower pressure or *vice versa*. In such an expansion, a gas will do work upon itself, thereby increasing its mechanical energy at the expense of the heat content of the gas itself or of its surroundings, and its expansion work must be added to the input of mechanical energy in the gas in order to get the output. This expansion work is evidently the integral of  $p dv$ , and Bernoulli's therefore becomes

$$z_1 + \frac{p_1}{\rho_1} + \frac{u_1^2}{2g} + \int_{v_1}^{v_2} p dv = z_2 + \frac{p_2}{\rho_2} + \frac{u_2^2}{2g}$$

The integral may have all possible values from zero up to the value of an isothermal expansion at the highest temperature in the apparatus in question and the actual value will frequently be difficult, if not impossible, to ascertain. On the other hand, this term can rarely be neglected and Bernoulli's theorem for the flow of all compressible fluids must be corrected by the introduction of this integral.

In the flow of gases it is usually allowable to neglect the variations in  $z$ , because gases are so light that the differences in level above data encountered are usually negligible compared with the other terms in Bernoulli's equation. On the other hand, if the pressure differences encountered are small, the vertical distances may no longer be negligible. We shall, however, neglect these terms consistently in the following discussion.

I—FRICTIONLESS ISOTHERMAL FLOW OF A GAS  
(LOW PRESSURE ORIFICES)

Let it be assumed that a gas flows isothermally through a given part of an apparatus with a drop in pressure. The gas entering the section at the higher pressure will in its expansion do work upon the gas ahead of it, and this work being done isothermally, the increase in mechanical energy in the gas will be equal to  $\int p dv = p_1 v_1 \ln p_1/p_2$ .

$$\frac{u_2^2 - u_1^2}{2g} = \int_{v_1}^{v_2} p dv = bT \ln \frac{v_2}{v_1} = bT \ln \frac{p_1}{p_2}$$

This condition of isothermal flow is practically quantitatively realized for the passage of air through an orifice through which the drop in pressure is small

compared with the total pressure of the gas, *i. e.*, not exceeding 10 per cent of that total pressure.<sup>1</sup>

The best results are obtained in manipulating such an orifice when the orifice chamber is very large compared with the orifice itself. This makes  $u_1$  negligible compared with  $u_2$ . To secure this condition it has been found experimentally that the cross section of the orifice chamber should be not less than twenty times the area of the orifice itself. Under this condition our equation becomes  $u_2^2 = 2g bT \ln p_1/p_2$ .

If  $\ln(1 + h)$  be expanded by Maclaurin's theorem it gives  $h - \frac{h^2}{2} + \frac{h^3}{3} - \frac{h^4}{4}$ , etc.; if  $h$  be small this series is sensibly equal to  $h$  itself. Since  $p_1$  is very nearly equal to  $p_2$ , the logarithm of  $p_1/p_2$  may be written

$$\ln\left(1 + \frac{p_1}{p_2} - 1\right) = \frac{p_1}{p_2} - 1$$

The error involved in this simplification is only 1 per cent when  $p_1$  is 2 per cent greater than  $p_2$ . Therefore,

$$u_2^2 = 2g bT (p_1 - p_2)/p_2 = 2g v_2 (p_1 - p_2) = 2g h_2$$

where  $h_2$  is the height of a column of liquid of the density of the gas at the point in question which would exactly support the impact or dynamic pressure which the gas possesses in consequence of its velocity. The volume of gas,  $V_2$ , passing the orifice should therefore be the area of the cross section of the orifice times the velocity  $u$ . Inasmuch, however, as there is a frictional loss in the orifice so that the velocity is slightly less than calculated, and a contraction of the stream flowing from the orifice so that the effective area of the orifice is decidedly lower than the actual area, this volume of discharge must be corrected by the use of a coefficient of discharge, namely,

$$V_2 = cA u_2 = cA \sqrt{2g v_2 (p_1 - p_2)} = \frac{2g c^2 A^2}{W} (p_1 - p_2) = cA \sqrt{2g h_2}$$

$$\text{and, } W = \frac{cA u_2}{v_2} = cA \sqrt{\frac{2g(p_1 - p_2)}{v_2}} = cA \sqrt{\frac{2g}{b} \frac{p_2}{T} (p_1 - p_2)}$$

$$\text{which may be written } n = cA \sqrt{\frac{2g p (p_1 - p_2)}{\text{BMT}}}$$

$$\begin{aligned} & \text{Writing Bernoulli's theorem, } z_1 + p_1 v_1 + \frac{u_1^2}{2g} + \int p dv = z_2 + p_2 v_2 + \frac{u_2^2}{2g} \\ & \text{and neglecting } z, \quad \frac{u_2^2 - u_1^2}{2g} = p_1 v_1 - p_2 v_2 + \int p dv \end{aligned}$$

The velocity changes are therefore determined by the expression on the right-hand side of this equation. For isothermal expansion this function is

$$p_1 v_1 \ln \frac{p_1}{p_2} \text{ and for adiabatic } p_1 v_1 \left( \frac{k}{k-1} \right) \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right]$$

$$\text{The ratio of these two expressions, } \ln \frac{p_1}{p_2} \bigg/ \frac{1}{k-1} \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right],$$

is unity if  $p_2 = p_1$ , as is shown by the calculus; *i. e.*, for small pressure changes the velocity changes are the same whether the process be isothermal or adiabatic. So nearly coincident are these curves that even though the pressure change be 10 per cent of the initial pressure, the difference in the velocity changes for the two curves is only 1/2 per cent, *i. e.*, isothermal expansion represents the result within the usual experimental error. Wherever the pressure change is less than 10 per cent, or frequently even 20 per cent, the assumption of isothermal expansion is entirely justified. This statement applies to calculating the power output of fans and the performance of all apparatus handling gases under low pressure drops.

The value of the coefficient  $c$  for circular orifices in thin plates (0.057 in. thick), varies between 0.59 and 0.62; an average value of 0.605 will give results very near the truth. *This formula applied to the use of orifices of this type offers one of the most satisfactory methods for measuring the flow of gases under reasonably steady conditions at low pressure drops.*

## II—FRICTIONLESS ADIABATIC FLOW OF A GAS (HIGH PRESSURE ORIFICES)

For adiabatic flow,  $\int p dv = \frac{p_1 v_1}{k-1} \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right]$ .

Bernoulli's theorem therefore becomes,

$$p_1 v_1 + \frac{u_1^2}{2g} + \frac{p_1 v_1}{k-1} \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right] = p_2 v_2 + \frac{u_2^2}{2g};$$

or,

$$p_1 v_1 \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right] + \frac{p_1 v_1}{k-1} \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right] = \frac{u_2^2 - u_1^2}{2g};$$

or, neglecting  $u_1$ , as before,  $\frac{k p_1 v_1}{k-1} \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right] = \frac{u_2^2}{2g}$ .

This gives<sup>1</sup>  $V_2 = c A u_2 = c A \sqrt{\frac{2gk}{k-1} p_1 v_1 \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right]}$ .

$$\begin{aligned} W = \frac{V_2}{v_2} &= c A \sqrt{\frac{2gk}{k-1} \frac{p_1 v_1}{v_2^2} \left[ 1 - \left( \frac{p_2}{p_1} \right)^{\frac{k-1}{k}} \right]} \\ &= c A \sqrt{\frac{2gk}{k-1} \left( \frac{p_1}{v_1} \right) \left[ \left( \frac{p_2}{p_1} \right)^{\frac{2}{k}} - \left( \frac{p_2}{p_1} \right)^{\frac{1+k}{k}} \right]}. \end{aligned}$$

This equation applies to the flow of gases through orifices under a drop in pressure large compared to the total pressure. In this case the velocity of the gas is so great that the possibility of inflow of heat from the surroundings while the gas is passing through the orifice itself is negligible. It is self-evident that the transition from isothermal to adiabatic flow, produced as it is by increase in the pressure drop through the orifice, cannot be a sharp one, and it is therefore highly probable that intermediate values of the pressure drop will not satisfactorily follow either equation. It has been proposed to take care of such intermediate states by the utilization of an experimentally determined constant,  $n$ , instead of the ratio of the specific heats of the gas  $k$  in the equation for adiabatic flow, as is done in the calculation of the work consumption of air compressors, but on the other hand, the complications involved in such a correction are so great that engineers have never adopted the suggestion.

The expression for adiabatic flow contains the

function,  $\left[ \left( \frac{p_2}{p_1} \right)^{\frac{2}{k}} - \left( \frac{p_2}{p_1} \right)^{\frac{1+k}{k}} \right]$ .

This expression is one which increases from zero with decrease in  $p_2/p_1$  from unity, but on the other hand, as  $p_2/p_1$  is further decreased a maximum value of this expression is reached below which the expression decreases. This maximum is obtained at the point

$$\frac{p_2}{p_1} = \left( \frac{1+k}{2} \right)^{\frac{k}{1-k}}.$$

According to the equation, therefore, for pressure ratios less than this, the flow through the orifice should actually decrease. This, of course, is highly improbable. As a matter of fact experiment has shown that at approximately this value of the pressure ratio, the discharge through the orifice reaches a maximum value which is maintained constant however much the pressure ratio may be further decreased. The opinion of engineers is that when the pressure  $p_2$  has decreased to this extent, the velocity of the gas in the orifice has reached a value so great that further decrease in pressure in the receiving chamber on the down-stream side of the orifice cannot reduce the pressure in the throat of the orifice itself, and hence cannot increase the velocity. The gas leaving the orifice cannot get out of the way of the gas following it; in consequence the pressure at the outlet of the orifice itself cannot fall beyond this limiting value, and remains constant however much the pressure in the low pressure chamber may be decreased. This argument assumes constancy of the initial high pressure. In other words, the ratio of the pressure in the orifice to the initial pressure cannot fall below this limiting value. The bracketed expression,

$$\left[ \left( \frac{p_2}{p_1} \right)^{\frac{2}{k}} - \left( \frac{p_2}{p_1} \right)^{\frac{1+k}{k}} \right] = \left[ \left( \frac{1+k}{2} \right)^{\frac{2}{1-k}} - \left( \frac{1+k}{2} \right)^{\frac{1+k}{1-k}} \right],$$

therefore has a limiting and constant value for all pressure ratios below the critical ratio given above. This constant value may be grouped with the other constants of the equation, giving an expression,

$$\begin{aligned} W &= \frac{c A p_1}{\sqrt{T b}} \sqrt{\frac{2gk}{k-1} \left( \frac{1+k}{2} \right)^{\frac{1+k}{1-k}}} \\ &= c A p_1 \sqrt{\frac{M}{B T}} \sqrt{g k \left( \frac{1+k}{2} \right)^{\frac{1+k}{1-k}}}, \end{aligned}$$

which for the case of air, where  $k = 1.404$ , becomes

$$W = \frac{A p_1 c}{\sqrt{T_1}} \sqrt{\frac{2gk}{(k-1)b}} (0.0675) = (0.533) \frac{A p_1}{\sqrt{T_1}},$$

which may be written in the form  $W = (a \text{ constant}) \frac{A p_1}{\sqrt{T_1}}$ .

This last expression is ordinarily known as Fliegner's formula, and is merely the simplification of the general formula for adiabatic flow for the special case that the ratio of the pressures on the two sides of the orifice is less than the critical value given above. Inasmuch as this simpler formula holds whenever the pressure ratio is sufficiently low, it is highly desirable whenever possible to arrange conditions so that the pressure ratio is well below the critical value. For air this

<sup>1</sup> It must be kept in mind in deriving these formulas that  $\frac{v_1}{v_2} = \left( \frac{p_2}{p_1} \right)^{\frac{1}{k}}$ .



pressure ratio should be below 0.50 and for steam below 0.55. For the flow of air the coefficient (0.53) varies slightly with the area of the orifice, which must be standardized for the most accurate work. The area,  $A$ , in this particular formula may be taken in sq. in. if the pressure  $p_1$  is in lbs. per sq. in., and the coefficients quoted apply only to an orifice in a hardened steel plate between  $\frac{3}{8}$  and  $\frac{1}{2}$  in. thick with the inside edge rounded to a circular section, the radius of which is  $\frac{1}{16}$  in. less than the thickness of the plate itself.

It is to be noted that the orifice coefficient  $c$  is occasionally *greater than unity*. This is due to the fact that the flow is not adiabatic, but some heat comes in from the surroundings. *This formula is the one to use for the measurement of gases flowing under large pressure drops.*

For this purpose the pressure on the down stream side of the orifice should be adjusted to a value sufficiently low so that the formula unquestionably applies. This value can be calculated from the formula

$$\frac{p_2}{p_1} = \left( \frac{1+k}{2} \right)^{\frac{k}{1-k}}.$$

### III—VENTURI METER

The principle of the Venturi meter, *i. e.*, the measurement of the decrease in static pressure consequent upon the increased velocity of a fluid stream caused by reduction in cross section of path, is used for the measurement of gas flow. A great advantage lies in the fact that the permanent reduction in pressure is very small, as the velocity head is reconverted to pressure head by again enlarging the section to the original value. The pressure drops can be made very large by large changes in section, thereby producing large changes in velocity, and these pressure drops can be recorded by suitable instruments. This makes possible a continuous record of the gas flow, and the method is used in the illuminating gas industry and elsewhere with great success. Since the flow through such a meter will be practically isothermal, the isothermal expression for Bernoulli's theorem given above may be employed to determine the increase in static pressure between any two sections, but the readings of such an instrument must be experimentally corrected by careful standardization for friction losses in the throat of the instrument. On account of the simplicity of the instrument and the continuous nature of the record obtained, it is very satisfactory for use where continuous streams of gas are flowing.

$$\text{Assuming isothermal flow,} \quad \frac{u_1^2}{2g} + bT \ln \frac{p_1}{p_2} = \frac{u_2^2}{2g}.$$

For pressure drops small compared with the total,

$$u_2^2 - u_1^2 = 2g bT \frac{p_1 - p_2}{p_2}.$$

This gives

$$\begin{aligned} W &= c p_1 A_1 \sqrt{2g(p_1 - p_2) \cdot p_2 bT \left[ \left( \frac{p_1 A_1}{p_2 A_2} \right)^2 - 1 \right]} \\ &= c A_1 p_1 \sqrt{2g bT \left( \frac{p_1}{p_2} - 1 \right) \left[ \left( \frac{p_1 A_1}{p_2 A_2} \right)^2 - 1 \right]} \end{aligned}$$

$$\begin{aligned} \text{or } n &= c p_1 A_1 \sqrt{\frac{2g}{BMT} \left[ \frac{\frac{p_1}{p_2} - 1}{\left( \frac{p_1 A_1}{p_2 A_2} \right)^2 - 1} \right]} \\ &= c p_1 A_1 \sqrt{\frac{2g(p_1 - p_2)}{BMT p_2 \left[ \left( \frac{A_1}{A_2} \right)^2 - 1 \right]}} \\ u_1 &= c \sqrt{\frac{2g bT \left( \frac{p_1}{p_2} - 1 \right)}{\left( \frac{p_1 A_1}{p_2 A_2} \right)^2 - 1}} = c \sqrt{\frac{2g bT (p_1 - p_2)}{M p_2 \left[ \left( \frac{A_1}{A_2} \right)^2 - 1 \right]}} \end{aligned}$$

\* For small pressure drops only.

### IV—PITOT TUBE

If an orifice be inserted into a gas stream at right angles to the direction of flow, there is developed a pressure in this orifice greater than the static pressure under which the gas exists by an amount corresponding to the kinetic energy possessed by the gas in consequence of its velocity. This dynamic pressure is given by the formula  $h = u^2/2g$ , where  $h$  is the height of a column of fluid of the same density as the gas corresponding to the dynamic impact pressure.

$$\begin{aligned} \text{Whence, } u &= \sqrt{\frac{2gHsBT}{M\rho}}; \quad V = A \sqrt{\frac{2gHsBT}{M\rho}}; \\ W &= A \sqrt{\frac{2gHsM\rho}{BT}}; \text{ and } n = A \sqrt{\frac{2gHs\rho}{BMP}}. \end{aligned}$$

It has been experimentally demonstrated that if the static pressure be accurately obtained, the difference between the impact pressure upon a small orifice in the gas stream and the static pressure exactly correspond within the experimental error, which can frequently be reduced to 1 per cent, in the formula given above. On the other hand, the determination of the static pressure requires care. It has been experimentally proven that the safest way to determine this static pressure is by means of a piezometer ring, *i. e.*, into the sides of the conduit pipe a series of small holes, not less than four in number at approximately equal spaces around the pipe, should be drilled. These holes should all be connected, and from this connection the static pressure obtained. The difference between static and total pressure, *i. e.*, the dynamic impact pressure, is measured by means of an ordinary U-tube, best inclined at an angle of 1-10 to increase the readings, and usually using gasoline or a mixture of gasoline and chloroform to eliminate errors due to adhesion of the liquid in the U-tube to the sides.

This gives the exact velocity at the point where the orifice is inserted. On the other hand, the velocity of a gas flowing in any conduit varies at different points in the conduit. This variation is extremely erratic at points near the entrance or exit to any straight section of pipe. While theoretically it is possible to explore the pipe thoroughly by moving the impact orifice, practically this is unsatisfactory on account of the wide variations in velocity unless the orifice be inserted in the pipe at not less than 20—and indeed better 40 diameters from the point where the gas enters the straight section in question and not less than 20 diameters from the point where it leaves. Even

these lengths should be increased if possible. To get accurate results it will even now be necessary to explore the pipe, but on the other hand, experiment has demonstrated that if the above conditions be met in pipes up to about 12 in. in diameter and probably higher, the average velocity in the pipe is about 0.8 of that at the center of the pipe. It is therefore allowable to measure the velocity at the center of the pipe using the above formula and multiply this velocity by the factor 0.8 in order to get the average velocity in the pipe. For high precision, however, exploration of the pipe is essential.

There are certain cases where the velocity of flow of a gas is extremely erratic, but where the determination of the velocity at practically every point in the section through which the gas is flowing is the only available means of measuring the current. This, for example, applies in determining the air supplied by a fan operating in the middle of a short tube drawing from and delivering into open spaces. In this case the pitot tube is of great value because, while exploration of the cross section of flow is essential, the pitot tube enables us to measure with precision the exact velocity at every point, and almost no other means would give us the possibility of determining the flow. The one grave disadvantage with the pitot tube is the fact that owing to the low density of gases, the readings at low velocities are very small and their measurement, therefore, liable to error.

Having developed the formulas applying to the measurement of the gas flowing past any point by the determination of a pressure drop or difference, it may be well to mention the other methods available for the measurement of gases.

(1) The gas may be collected in a gasometer or a storage tank and the amount flowing may be measured by measuring the decrease of gas in this storage reservoir. The decrease in amount of gas in the reservoir may be determined by measuring the decrease in volume of gas in a gasometer, the decrease in pressure in a storage tank of constant volume, or the decrease in weight of such a storage tank. The first two of these methods are very satisfactory where applicable, because they give a direct measure of the gas, but on the other hand, their applicability is extremely limited because the storage capacity of such reservoirs is relatively small. Measuring gases by weight is very unsatisfactory because the differences are so small that large errors are likely to be encountered.

(2) The amount of gas flowing past a given section may be determined by injecting a measured amount of something into the gas, securing perfect distribution of it throughout the gas, and measuring the proportion of the admixed substance in the final product. Knowing the amount admixed makes possible the calculation of the amount of gas to which it is added. Theoretically any gas which is not present in the gas to be measured, or which is present in known amount, may be utilized for this purpose, but actually it is far better to add energy in the form of heat and to measure the increased energy content of the gas by measuring the rise in temperature. This energy can best be added

in the form of electrical energy. On this principle is based the *Thomas Gas Flow Meter*. This consists in an enlargement of the pipe carrying the gas, in which is inserted first a thermometer of the electrical resistance type, then an electrical resistance wire uniformly distributed across the whole section of the pipe in which a known amount of electrical energy is transformed into heat, this energy being measured by a wattmeter, and finally, another thermometer similar to the first which records the rise in temperature. The Thomas meter automatically controls the electrical input so as to maintain a constant temperature rise between the thermometers, and measures the electrical input necessary to maintain this rise. This electrical input is, of course, proportional to the amount of gas passing the section. Knowing the specific heat of the gas at constant pressure the weight of gas is immediately obtainable. This apparatus is of wide applicability and worthy of wide-spread adoption because it is the only really satisfactory method of measuring absolutely the amount of gas flowing when the quantities are large. On the other hand, the construction must be automatic in type in order to get satisfactory results, because under ordinary conditions the temperature fluctuations of the entering gas are very large compared with the rise in temperature of the gas in the meter, so that an attempt to measure the quantity of gas by admitting a constant amount of energy and determining the temperature rise is highly unsatisfactory. This and the previous method are the only absolute ones for determining gas quantities. All others must be standardized against one of these.

(3) The amount of gas flowing past a section may be measured by the insertion of a mechanical gas meter of which various types are obtainable. These meters must be carefully standardized, generally by method (1) above. They are mechanical devices which are clumsy, expensive, sensitive to corrosion, and liable to get out of order. Where large quantities of gas are constantly to be measured they are employed (illuminating gas industry); but for special work they are practically out of the question.

(4) *The Anemometer* is a small windmill, the friction of which is reduced to a minimum, and the velocity of which should therefore be proportional to the velocity of the gas current in which it is placed. The instrument must, however, be standardized with the greatest care at velocities as nearly as possible equal to those to be measured, and even when so tested is liable to wide variations in behavior. While very convenient, the instrument is unsatisfactory on this account.

#### V FLOW OF GASES WITH FRICTION; FLOW THROUGH PIPES AND CONDUITS UNDER SMALL PRESSURE DROP

It is important to be able to estimate the carrying capacity of pipes and other conduits for gases under definite pressure drops. It is experimentally determined that the flow of gases even under high pressure drops through pipes which are not short enough to be considered orifices, is practically isothermal, and the formulas are therefore developed upon this as-



sumption. It has also been experimentally confirmed that, as in the case of flow of liquids, there is a drop in head due to friction loss which is proportional to the square of the velocity of the gas, to the length of the pipe traversed, and inversely proportional to the mean hydraulic radius, *i. e.*, the area of the cross section of the conduit divided by its perimeter. Bernoulli's theorem therefore becomes

$$v_1 + p_1 v_1 + \frac{u_1^2}{2g} + bT \ln \frac{p_1}{p_2} - f \frac{u^2}{2g} \frac{l}{m} = v_2 + p_2 v_2 + \frac{u_2^2}{2g}$$

Assuming that the pipe is sufficiently nearly horizontal so that the differences in level may be neglected, and remembering that for isothermal flow the  $p v$  product

$$\text{is constant, we obtain } \frac{u_2^2 - u_1^2}{2g} = bT \ln \frac{p_1}{p_2} - f \frac{u^2}{2g} \frac{l}{m}.$$

On the other hand, this expression cannot be applied directly except for very slight changes in velocity and correspondingly slight changes in pressure because the friction loss varies with the velocity. In case the pressure drop is slight and the difference in the squares of the velocity therefore negligible, remembering as above that the logarithm of  $p_1/p_2$  for this case equals  $(p_1 - p_2)/p_2$ , we obtain

$$f u^2 / 2 g m = bT (p_1 - p_2) / p_2 = v_2 (p_1 - p_2) = h, \text{ or}$$

for circular pipes,

$$u = \sqrt{\frac{ghd}{2fl}} = \sqrt{\frac{v(p_1 - p_2)gd}{2fl}} = \sqrt{\frac{gBTd}{2flM_p}(p_1 - p_2)};$$

$$n = \sqrt{\frac{\pi^2 d^5 g p (p_1 - p_2)}{32 fl MBT}};$$

where  $h$  is the drop in static head caused by the friction loss in the pipe. *This formula applies only for flow of gas with small drop in pressure, but this is by far the most important case.*

#### VI—FLOW THROUGH PIPES AND CONDUITS UNDER LARGE PRESSURE DROP

If the drop in pressure be large, we must consider a differential length of pipe and write

$$\frac{u^2}{2g} + p dv = \frac{(u + du)^2}{2g} + \frac{f u^2 dl}{2gm}, \text{ or } \frac{f u^2 dl}{2gm} = -\frac{u du}{g} + p dv.$$

$$\frac{f W^2 v^2 dl}{2gm A^2} = -\frac{W^2 v dv}{g A^2} + \frac{b T dv}{v}.$$

$$\frac{f W^2}{2gm A^2} dl = -\frac{W^2}{g A^2} \frac{dv}{v} + \frac{b T dv}{v^3}.$$

$$f W^2 l / 2gm A^2 = -\frac{W^2}{g A^2} \ln v - \frac{b T}{2v^2} + \text{const.}$$

$$= \frac{W^2}{g A^2} \ln \frac{v_1}{v_2} + \frac{b T}{2} \left( \frac{1}{v_2^2} - \frac{1}{v_1^2} \right) = \frac{W^2}{g A^2} \ln \frac{p_2}{p_1} + \frac{1}{2bT} (p_1^2 - p_2^2).$$

$$b T \frac{(p_1^2 - p_2^2)}{p_1^2} - \left( \frac{W b T}{p_1} \right)^2 \frac{1}{g A^2} \ln \frac{p_1}{p_2} = \frac{f l}{2gm A^2} \left( \frac{W b T}{p_1} \right)^2.$$

$$\frac{W b T}{p_1} = W v_1 = A u_1 = \sqrt{b T \frac{(p_1^2 - p_2^2)}{2 p_1^2}} / \frac{1}{g A^2} \left( \frac{f l}{2m} + \ln \frac{p_1}{p_2} \right).$$

For reasonably long pipes the  $\ln p_1/p_2$  is negligible, and we write,

$$u_1 = \sqrt{\frac{b T g d}{4 f l} \frac{(p_1^2 - p_2^2)}{p_1^2}}; \quad n = \pi \sqrt{\frac{g d^5 (p_1^2 - p_2^2)}{64 f l B M T}}.$$

This formula becomes identical with the one previously derived for conditions of low pressure drop.

The simpler formula (Case V) for low pressure drop may be employed with safety provided the pressure drop be not greater than 10 per cent of the total pressure, but above this condition the more complicated formula for the general case must be employed. The more complicated formula, while theoretically applicable to all cases of isothermal pressure drop, certainly fails to apply for very short pipes and very high velocity (probably due to disturbances at entrance and exit), *i. e.*, whenever the conditions become comparable to those in orifices, and it must not be applied to such cases. It is designed to give the flow of gases through pipe lines with reasonable drops in pressure although these drops in pressure may in some cases, as for example in the transportation of natural gas or similar products for long distances, be several fold the final pressure. The coefficient,  $f$ , in these equations has been found experimentally by Unwin to be of the form

$$f = f_0 \left( 1 + \frac{3}{40d} \right),$$

where  $f_0 = 0.005$  for rough pipes and 0.0028 for smooth ones. These coefficients are practically the same for both steam and air, and indeed are practically identical with the coefficients for the flow of water, a fluid 1000 times as dense. If the coefficient changes so slightly for a change in density of a 1000-fold, we shall be introducing very little error in assuming that this same coefficient applies for the flow of all gases.

#### VII—WORK OF COMPRESSION OF GASES

It will not be out of place to give also simpler formulas than those usually found for the work of compression of gases. For isothermal compression, the expression

$$U = p_1 v_1 \ln \frac{p_2}{p_1}, \text{ becomes } U = n B T \ln \frac{p_2}{p_1} = n B T \ln \frac{v_1}{v_2};$$

$$\text{which simplifies to } U = \frac{n B T}{p_1} (p_2 - p_1) = \frac{n B T H_s}{p_1},$$

for small pressure changes (*e. g.*, low pressure fans). These expressions being in work per second, division by 550 gives horse power.

$$\text{For adiabatic compression, } U = \frac{n B T k}{k-1} \left[ 1 - \left( \frac{p_1}{p_2} \right)^{\frac{k-1}{k}} \right],$$

which includes the necessary corrections for expulsion of the compressed gas, and for the intake of the incoming gas.

#### NOMENCLATURE

- A = area in sq. ft.
- B = gas const. = 1545.
- b = gas const. for 1 lb. of gas = B/M.
- c = experimentally determined coefficient, expressing divergence of practice from theory.
- d = diameter in feet.
- g = 32.2, acceleration of gravity.
- H = "head" = a pressure or pressure drop, expressed in ft. of liquid, *i. e.*, the observed vertical height of the column of the liquid used to measure it. N. B.,  $H_s = p_1 - p_2$ .
- h = "head" = a pressure or pressure drop expressed in ft. of gas column of the given density.
- HP = horse power =  $U/550$ .
- k = ratio of specific heats of gas in question.
- l = length of pipe in feet.
- M = average molecular weight of the gas or gas mixture.
- m = mean hydraulic radius in feet =  $\frac{\text{area of cross section}}{\text{perimeter}}$ .
- n = number of lb. mols/sec.
- p = absolute pressure in lb./sq. ft.
- s = density of liquid used to measure H, in lbs./cu. ft.
- T = ° F. abs.
- U = work per sec., in ft. lbs./sec.
- u = velocity in ft./sec.
- v = specific volume of 1 lb. of gas in cu. ft.
- V = total volume of whole quantity of gas under conditions in question, in cu. ft./sec.
- W = weight of gas, in lbs./sec.

## SUMMARY OF FORMULAS

In the following formulas the Subscripts 1 and 2 frequently used indicate that the quantity in question is to be measured at the corresponding section. In all cases Section 1 is at the entrance of the gas to the device under consideration, and Section 2 is the point at which the second pressure measurement is taken. For example, in the formulas for flow through orifices,  $p_1$  is the pressure on the upstream side of the orifice and  $p_2$  the lower pressure on the downstream side.

In all these formulas the expression  $p_1 - p_2$  may be replaced by  $H_s$ .

## I—FLOW OF THE GAS THROUGH ORIFICE UNDER SMALL PRESSURE DROP

$$u_2 = c \sqrt{\frac{2gBT(p_1 - p_2)}{M p_2}} = c \sqrt{\frac{2g v_2(p_1 - p_2)}{p_2}} = c \sqrt{\frac{2gh_2}{p_2}}$$

$$V_2 = A u_2 = c A \sqrt{\frac{2gBT(p_1 - p_2)}{M p_2}} = c A \sqrt{\frac{2gh_2}{p_2}}$$

$$W = c A \sqrt{\frac{2gM p_2(p_1 - p_2)}{BT}}; \quad n = c A \sqrt{\frac{2g p_2(p_1 - p_2)}{BMT}}$$

**Limitations:** The pressure drop through the orifice must not exceed 2 per cent of the total pressure.

For flow through sharp-mouthed, circular orifices in thin steel plates, the coefficient  $c$  equals approximately 0.605.

The orifice chamber must be not less than 20 times the area of the cross section of the orifice itself.

## II—FLOW OF GAS THROUGH ORIFICE UNDER LARGE PRESSURE DROP

$$W = c A_1 p_1 \sqrt{\frac{M g k}{BT} \left( \frac{1+k}{2} \right)^{\frac{1}{k-1}}}; \quad n = c A_1 p_1 \sqrt{\frac{g k}{BMT} \left( \frac{1+k}{2} \right)^{\frac{1}{k-1}}}$$

**Limitations:** The downstream pressure,  $p_2$ , must be less than

$$p_1 \left( \frac{2}{1+k} \right)^{\frac{k}{k-1}}$$

For circular orifices in steel plates, rounded to a circular section on the upstream side, with straight section  $1/16''$  long on the downstream side,  $c$  is approximately unity, but standardization is necessary for precision.

The orifice chamber on the upstream side must exceed in area of section, 20 times the orifice.

## III—VENTURI METER

$$u_1 = c \sqrt{\frac{2gBT \left( \frac{p_1}{p_2} - 1 \right)}{M \left[ \left( \frac{p_1 A_1}{p_2 A_2} \right)^2 - 1 \right]}} = c \sqrt{\frac{2gBT(p_1 - p_2)}{M p_2 \left[ \left( \frac{A_1}{A_2} \right)^2 - 1 \right]}}$$

$$W = c A_1 p_1 \sqrt{\frac{2gBT \left( \frac{p_1}{p_2} - 1 \right)}{M \left[ \left( \frac{p_1 A_1}{p_2 A_2} \right)^2 - 1 \right]}} = c A_1 p_1 \sqrt{\frac{2gBT(p_1 - p_2)}{p_2 M \left[ \left( \frac{A_1}{A_2} \right)^2 - 1 \right]}}$$

$$n = c A_1 p_1 \sqrt{\frac{2g}{BMT} \left[ \left( \frac{p_1 A_1}{p_2 A_2} \right)^2 - 1 \right]} = c A_1 p_1 \sqrt{\frac{2g(p_1 - p_2)}{BMT p_2 \left[ \left( \frac{A_1}{A_2} \right)^2 - 1 \right]}}$$

\* This second expression in each case can be used only when the pressure drop is small compared with the total pressure.

**Limitations:** The pressure drop must be measured between two sections of widely different area, the pressure at the first and larger section  $A_1$ , being  $p_1$ , at the second and smaller section  $A_2$ , being  $p_2$ .

The sections must be connected by a smooth tapering tube, the angle of divergence of which should not exceed  $10^\circ$ .

The coefficient  $c$  must for accurate work be determined by calibration of the specific instrument, but is usually in the neighborhood of 0.97.

## IV—PITOT TUBE

$$u = \sqrt{\frac{2gH_s BT}{M p}}; \quad V = A \sqrt{\frac{2gH_s BT}{M p}}; \quad W = A \sqrt{\frac{2gH_s M p}{BT}}; \quad n = A \sqrt{\frac{2gH_s p}{BMT}}$$

**Limitations:** The head  $H_s$  is the pressure difference between the impact and static orifices. The area of these orifices must

be small (not exceeding  $1/8$  in. diameter and preferably smaller). The plane of the impact orifice must lie perpendicular to the direction of flow, and the static pressure in pipes should be taken from a Piezometer ring, i. e., from small orifices uniformly placed around the pipe, but not projecting into it, and connected for obtaining the average pressure.

In pipes the pitot orifices should be in a straight length of pipe not less than 40 diameters from the point of entrance of the gas nor less than 20 diameters from its exit.

If possible the pipe should be very completely explored by means of the impact orifice, and the results averaged. For precision this is necessary.

The average velocity in the pipe is approximately 0.8 times the velocity at the center.

## V—FLOW OF GASES THROUGH PIPES AND CONDUITS UNDER SMALL PRESSURE DROP

$$u = \sqrt{\frac{2gBTm(p_1 - p_2)}{M f l p_2}} = \sqrt{\frac{gBTd(p_1 - p_2)}{2 f l M p_2}}$$

$$V = A \sqrt{\frac{2gBTm(p_1 - p_2)}{M f l p_2}} = \pi \sqrt{\frac{gBTd^3(p_1 - p_2)}{32 f l M p_2}}$$

$$W = A \sqrt{\frac{2gM p_2 m(p_1 - p_2)}{B T f l}} = \pi \sqrt{\frac{gM p_2 d^3(p_1 - p_2)}{32 f l B T}}$$

$$n = A \sqrt{\frac{2g p_2 m(p_1 - p_2)}{B M T f l}} = \pi \sqrt{\frac{g p_2 d^3(p_1 - p_2)}{32 f l B M T}}$$

For rough pipes

$$f = 0.005 \left( 1 + \frac{3}{40d} \right)$$

For smooth pipes

$$f = 0.0028 \left( 1 + \frac{3}{40d} \right)$$

\* For any cross section whatever.

† For circular section only.

**Limitations:** Apply theoretically to straight pipes only. In any case curvature must be small.

Pressure drop must not exceed 2 per cent of the total pressure if a precision of 5 per cent is required. Since frictional coefficients are not accurate unless determined on the specific pipe involved, pressure drops of 10 per cent may be estimated by these formula.

## VI—FLOW THROUGH PIPES AND CONDUITS UNDER LARGE PRESSURE DROP

$$u_1 = \sqrt{\frac{gBT \left( \frac{p_1^2}{p_2^2} - 1 \right)}{2M p_1^2 \left[ \frac{f l}{2m} + \ln \frac{p_1}{p_2} \right]}} = \sqrt{\frac{BTgd \left( \frac{p_1^2}{p_2^2} - 1 \right)}{4M f l p_1^2}}$$

$$V_1 = \sqrt{\frac{BTGA^2 \left( \frac{p_1^2}{p_2^2} - 1 \right)}{2M p_1^2 \left[ \frac{f l}{2m} + \ln \frac{p_1}{p_2} \right]}} = \sqrt{\frac{\pi^2 BTgd^3 \left( \frac{p_1^2}{p_2^2} - 1 \right)}{64M f l p_1^2}}$$

$$W = \sqrt{\frac{MGA^2 \left( \frac{p_1^2}{p_2^2} - 1 \right)}{2BT \left[ \frac{f l}{2m} + \ln \frac{p_1}{p_2} \right]}} = \sqrt{\frac{\pi^2 gMd^3 \left( \frac{p_1^2}{p_2^2} - 1 \right)}{64BT f l}}$$

$$n = \sqrt{\frac{GA^2 \left( \frac{p_1^2}{p_2^2} - 1 \right)}{2BMT \left[ \frac{f l}{2m} + \ln \frac{p_1}{p_2} \right]}} = \sqrt{\frac{\pi^2 gd^3 \left( \frac{p_1^2}{p_2^2} - 1 \right)}{64BMT f l}}$$

\* For any cross section

† For circular section and long pipes only.

For values of  $f$ , see under Section V.

**Limitations:** Apply theoretically to straight pipes only; curvature if present must be small.

Do not apply to extremely short tubes or orifices, as these formulas ignore losses at entrance and exit, i. e., at points of change in section

## VII—WORK OF COMPRESSION OF GASES

For isothermal compression,

$$HP = \frac{nBT}{550} \ln \frac{p_2}{p_1} = \frac{nBT}{550} \ln \frac{v_1}{v_2} = \frac{nBT(p_2 - p_1)}{550 p_1} = \frac{nBTH_s}{550 p_1}$$

\* For pressure change less than 2 per cent of the total pressure, error being less than 1 per cent.

For adiabatic compression,  $HP = \frac{nBTK}{550(k-1)} \left[ 1 - \left( \frac{p_1}{p_2} \right)^{\frac{k-1}{k}} \right]$ , this being the total work.



*Limitations:* Apply to theoretically perfect compression under the conditions indicated.

The starred formulas are for low pressure fans, and such apparatus.

The approximate values of  $k$  for ordinary temperatures may be found from the following table:

Monatomic Gases, Argon, Helium, etc.	$k = 1.66$
Permanent Diatomic Gases, Air, $O_2$ , $N_2$ , $H_2$ , HCl, HBr, CO, etc.	$k = 1.41$
Triatomic Gases, $CO_2$ , $H_2O$ , $SO_2$ , etc.	$k = 1.28$

RESEARCH LABORATORY OF APPLIED CHEMISTRY  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
BOSTON, MASSACHUSETTS

## A GRAPHIC CHART FOR THE EVALUATION OF COAL

By A. F. BLAKE

Received August 9, 1916

In any heating or power plant it is of primary importance to determine which coal of all those which may be available is actually the cheapest to use; *i. e.*, from which can the most heat be obtained for the least cost, the cost including both the purchase price of the coal and the labor involved in handling and burning it. The relative costs of different coals depend upon the price per ton and upon the quality of the coals. The quality is determined either by boiler tests or by a chemical analysis. The latter is by far the simplest and in the majority of cases the only applicable method. To correctly estimate, however, the comparative cost of the heat obtained from different coals, given the cost per ton and the analysis, when all factors of importance, including labor, are to be considered, involves calculations, the performance of which, arithmetically, is tedious. To facilitate these calculations a general equation may be developed and to solve this equation a special graphic chart may be constructed.

It is believed that the accompanying chart (9/40 actual size) is more comprehensive in its scope, more generally useful, and easier in its application than any which has yet been described in the literature. By means of a T-square applied to the chart, properly framed, the calculation of the actual cost of the heat obtained from any coal may be accurately performed in a few seconds. Longhand, this would require several minutes and necessitate in addition a consideration, each time, of all the principles involved. This chart has been used continually and with entire satisfaction in this laboratory for more than a year. The soundness of the theoretical principles involved has been shown by the close agreement of these results with those obtained from boiler tests run under actual operating conditions.

The comparative costs of the heat obtained from different coals depend principally upon the following four factors:

- (1) Cost per ton of the coal;
- (2) Water contained in the coal as received;
- (3) Ash content;
- (4) Heating power.

Other factors, such as the tendency of the coal to clinker, and to incomplete combustion, and other individual peculiarities, have some bearing on the cost of the heat but are not of such fundamental importance and in any case do not admit of mathematical expression. As a means of expressing on a strictly

comparable basis the cost of the heat obtainable from different coals it is convenient to calculate the cost in cents per million B. t. u. We have given, then, the cost per ton, the per cent of water, the per cent of ash, and the B. t. u., to find the cost per million B. t. u.

Water in coal increases the cost of the heat inasmuch as it is weighed and paid for as coal but does not produce any heat. On the other hand, it absorbs heat by its vaporization. This latter effect, however, is very small proportionately, and is not here considered. In the development of our general equation allowance is made for water by correcting the price per ton as received to the price per dry ton.

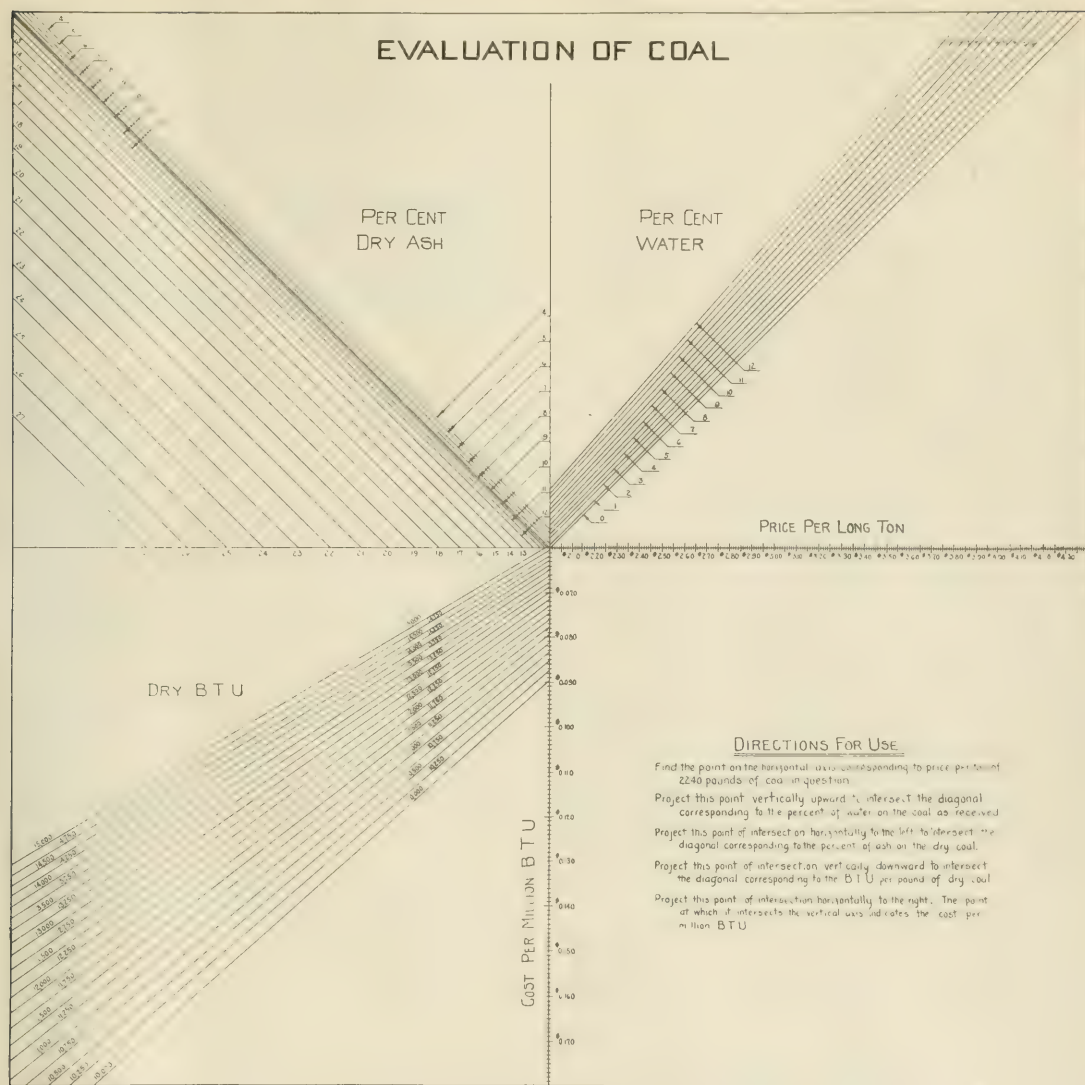
Let  $a$  = Price per long ton (in dollars) of the coal as received  
 $b$  = Per cent water in coal as received.  
 $c$  = Cost per long ton (in dollars) of the dry coal

$$\text{Then } c = \frac{100a}{100 - b} \quad (1)$$

In the commercial evaluation of coal the ash content is of great importance. First, by its presence, it dilutes the combustible, heat-producing matter of the coal and thereby reduces the heating power. This effect, however, need not be considered under this head inasmuch as it is fully taken care of below when allowance is made for the calorific value as determined by the calorimeter. But aside from this the cost of the heat increases largely with the ash content for a number of reasons. The efficiency of combustion decreases, the air supply is restricted and unevenly distributed and labor charges are increased due to the greater quantity of coal handled, the increased quantity of refuse to be disposed of and the greater attention to the fire which is required. It is now necessary to reduce these effects to a mathematical basis and incorporate them in our general equation. To do this we can hardly do better than to use the figures published by the United States Bureau of Mines. In the purchase of coal for the government under specifications it is provided that the contract price per ton after having been corrected for variations in the heating power from that specified shall be further corrected for any variation of ash content from that established in the proposal in the following manner:

For all coal that by analysis contains less ash on a "dry coal" basis than the percentage specified, a premium of 2 cents per ton for each whole per cent less is paid. For all coal containing an excess of ash over that specified, deductions are made from the price to be paid according to a table given in the Bureau of Mines Bulletins. An inspection of the table shows that the deductions depend only upon the difference between the actual ash per cent and the standard ash. Further examination shows that the cents per ton to be deducted are in all cases almost exactly equal to one-half the square of the difference between the ash content and the standard ash. This is shown by the following table:

Ash minus Standard Ash	Cents per Ton Deducted (Taken from Table)	One-half Square of Ash minus Standard Ash
2.....	2	2
3.....	4	4.5
4.....	7	8
5.....	12	12.5
6.....	18	18
7.....	25	24.5
8.....	35	32



This, then, gives us a mathematical expression for the influence of ash on the cost of the heat. The values which the government deducts from the price per ton to be paid we add to the cost per ton of the coal.

Let  $c$  = Cost per long ton (in dollars) of the dry coal;  
 $d$  = Per cent of ash on the dry basis;  
 $e$  = Per cent ash selected as the standard;  
 $f$  = Cost per long ton (in dollars) of the dry coal, corrected for ash.

$$\text{Then for ash above standard, } f = c + \frac{(d - e)^2}{200} \quad (2)$$

or, for ash below standard  $f = c - 0.02(e - d)^2$  (3)

The standard per cent of ash is usually taken as the lowest found in the series of coals under consideration, in which case only Equation 2 is used, or one standard may be selected for any one laboratory and all determinations referred to it as a common basis. The former is the better.

From this corrected cost per ton we now calculate the cost per million B. t. u.

Let  $f$  = Cost per long ton (in dollars) of the dry coal, corrected for ash;  
 $g$  = B. t. u. per pound dry coal;  
 $x$  = Cost per million B. t. u. (in dollars).

$$\text{Then } x = \frac{1,000,000f}{2,240g} \quad (4)$$

Combining Equations 1, 2 (or 3) and 4 we obtain the general equation sought:

For ash above standard,

$$x = \left[ \frac{100a}{100 - b} + \frac{(d - e)^2}{200} \right] \left[ \frac{1,000,000}{2,240g} \right] \quad (5)$$

For ash below standard,

$$x = \left[ \frac{100a}{100 - b} - 0.02(c - d)^2 \right] \left[ \frac{1,000,000}{2,240g} \right] \quad (6)$$



As an example of the use of the equation suppose it is desired to know which of two coals, A or B, is the more economical, the prices and analyses being as follows:

	A	B
Cost per long ton.....	\$ 3.00	\$ 3.50
Per cent water.....	4.25	3.50
Per cent dry ash.....	10.25	8.00
B. t. u. per pound dry coal.....	13,500	13,900

Taking 8 as the standard ash we obtain by substitution in (5) \$0.1044 for A and \$0.1167 for B as the relative costs per 1,000,000 B. t. u. A is therefore the cheaper coal and the extra price of B is greater than is justified by its better quality.

The chart for the solution of these equations is 30 inches square. It is divided by a horizontal and a vertical line into four quadrants. On the horizontal axis to the right of the vertical axis is indicated the price per long ton,  $a$ , from \$2.00 to \$4.40 by \$0.01 (scale,  $1/16$  in. = \$0.01). The vertical line above the horizontal represents the cost per long ton dry coal,  $c$  (same scale), but the values are not indicated. In the first quadrant are diagonal lines representing percentages of water from 0 to 12 and are plotted according to Equation 1. Any two points are plotted for each line. Zero per cent water is of course the diagonal of the square, and the others are above it.

Distances along the horizontal axis to the left of the vertical axis represent the cost per long ton of dry coal corrected for ash,  $f$  (same scale as before), but the values are not indicated. In the second quadrant are diagonal lines representing the difference between the percentage of dry ash and the standard ash. In the cut the standard ash is taken as 8 per cent and is so marked, the others being the actual percentages of dry ash. These lines are plotted according to Equation 2 for positive values of  $(d - e)$  and by Equation 3 for negative values of  $(d - e)$ . The standard ash, 8 per cent dry ash in the chart, is, of course, the diagonal of the square. The others are parallel and range from  $e - d = 4$  (in the chart 4 per cent ash) to  $d - e = 19$  (in the chart 27 per cent ash).

On the vertical line below the horizontal are indicated the cost per million B. t. u. from \$0.060 to \$0.180 (scale  $1/8$  in. = \$0.001). In the third quadrant are diagonal lines representing the dry B. t. u. from 10,000 to 15,000. They are plotted according to Equation 4.

This chart is framed with a thick glass plate with bevelled edges such that the wooden frame comes just level with the face of the glass. It is then fastened to the wall and used in the following manner: A T-square with the head against the left side of the frame is laid along the horizontal axis and the point corresponding to the price per ton of the coal in question is marked upon it or indicated by holding the thumb nail at the point. This point is then projected vertically upward by raising the square until the point intersects the line corresponding to the per cent of water. Without moving the square the point in the third quadrant where it intersects the line representing the difference between the ash and the standard ash

(or in the chart the per cent ash) is marked. This point is projected vertically downward by lowering the square until it intersects the line representing the B. t. u. The point where the edge of the square intersects the vertical axis indicates the cost per million B. t. u. Fractions of per cents, etc., are easily estimated and even when this is done the result obtained can always be checked by \$0.0004 or less.

ATLANTIC SUGAR REFINERIES, LTD.  
ST. JOHN, NEW BRUNSWICK, CANADA

## A THERMOSTAT OR CONSTANT-TEMPERATURE CABINET FOR THE FLOUR-TESTING LABORATORY

By C. H. BAILEY

Received October 11, 1915

The making of yeast-leavened bread is a biochemical process, involving the use of living cells in the production of the gases of fermentation. The  $\text{CO}_2$  which expands the dough is derived from certain sugars by the action of the yeast enzyme, zymase. The activity of this enzyme, or group of enzymes, is influenced by several factors, one of the most important of which is temperature. Aberson<sup>1</sup> found that 2.7 times as much sugar was fermented by yeast at 28° as at 18°. The other ferments in the dough, including the natural enzymes of the flour, and those due to the presence of bacteria and fungi, are similarly affected by temperature variations.

It is evident therefore that in making comparative tests involving the use of living yeast cells, the control of the temperature is an important item. This may be eliminated as a variable by the use of suitable thermostats or constant temperature chambers. Many laboratories are making flour tests, which embody yeast-fermentation, without adequate means for the production of maintenance of the proper temperature. Chambers or cabinets are in use which are not uniformly heated. Electric lamps are frequently used as the heating element in a manner which precludes uniform heating unless fans are employed for the circulation of the air. Usually no provision is made for the automatic control of temperature, which may fluctuate within rather wide limits, depending upon the vigilance of the operator, and the facilities which are afforded for varying the heat supplied.

Since this laboratory has had occasion to conduct a number of investigations requiring the use of a thermostat for dough fermentation, our attention was turned to the construction of an adequate device for this purpose. It was desired to make this of a type which would not only be capable of the proper control, but which could be duplicated at a reasonable cost, and operated by a person without much knowledge of physics. The thermostat when completed proved so satisfactory for this purpose that it is believed a description of it, and a statement of the reasons governing the style of construction adopted, might be of interest to others engaged in a similar line of work.

The electrical heating element offers marked ad-

<sup>1</sup> Aberson, *Rec. trav. chim. Pays-Bas*, **22** (1903), 100. Cited by Euler, "General Chemistry of the Enzymes," translated by Pope, p. 241, New York, 1912.

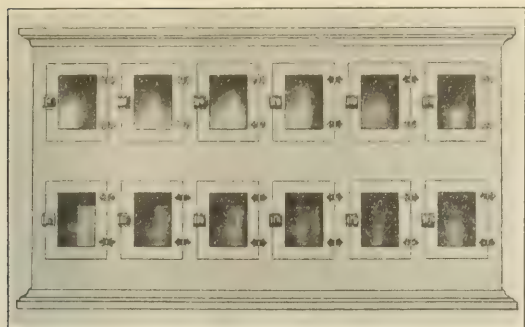
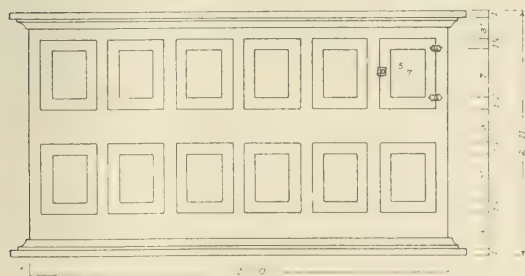


FIG. I—CABINET IN USE

vantages over other possible sources of heat. It is clean, dependable, easy of operation and control, and involves no serious risks of shock or fire if properly constructed and installed. This method of heating was accordingly adopted. Neither this nor any other heating system, where an accurate control is necessary, can be made entirely fool-proof. Some knowledge of the properties of electricity is desirable to secure the best results. This is especially true if the specifications and details of construction given in this paper are to be departed from. While all the work of making and installing the heating elements in the cabinet in this laboratory was done by the writer, the services of an electrician may be necessary when one is not familiar with such work, or where certain shop facilities are not available.

The cabinet was made with sufficient space for conducting 24 baking tests simultaneously if used from

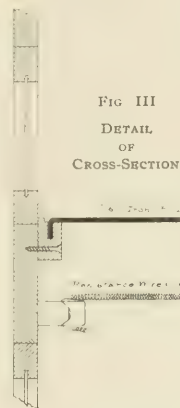
FIG. II—FACE OF CABINET



both sides. One face is provided with twelve doors, and the other has a "piano-box back" which can be removed in one piece and a face having twelve doors substituted. If the work of the laboratory is voluminous enough to justify it, doors may be provided on both faces at the outset. Where the cabinet can be used only from one side, the back may be glued on. A depth of 18 inches permits of setting two ordinary fermentation vessels or baking-pans one behind the other. This depth can be reduced if the cabinet is used only from one face. Any reduction in the cubical contents of the cabinet must necessarily be accompanied by an increase in the length of wire used in the heating element.

The doors were made 8 in. wide  $\times$  10 in. high, with panes of glass 5  $\times$  7 in. Where the space is limited, the width of the doors may possibly be reduced 1 in. each, thus shortening a cabinet of this capacity 6 in. The 8-in. door is more desirable, as it reduces the liability of striking dishes and pans when introducing or removing them. Small doors are preferable to fewer large doors because of the reduced exposure when the doors are opened to introduce or remove the vessels. A space of 5 in. between the upper and lower rows of doors was provided so that the heating coils between shelves would not be too close to the doughs on either side of them.

The inside of the box is virtually an undivided space. The two shelves were made by bending the ends of  $\frac{3}{16}$ -in. iron rods at right angles and inserting the bent ends into holes provided in cleats screwed to the inside of the box. These rods were placed at distances of  $1\frac{1}{2}$  in. from center to center. The cleats were located so that they serve as stops for the doors, as shown in Fig. III.

FIG III  
DETAIL  
OF  
CROSS-SECTION

The electrical heating elements were made by winding No. 20 Advance resistance wire around a  $\frac{1}{4}$ -in. iron rod. Coils wound in this manner possess sufficient resiliency to eliminate any considerable sagging and to take up the expansion on heating. The wire was manufactured by the Driver-Harris Wire Co., of Harrison, N. J., and has a rated resistance of 287 ohms per 1000 ft. For use on a 220-volt current, 20 coils, each 15 ft. long, were suspended beneath the lower shelf, and 10 coils, each 10 ft. long, beneath the upper shelf. The coils were supported by porcelain knobs at

a distance of  $3\frac{1}{2}$  in. below the shelves in each instance. The end coils under the lower shelf parallel the end of the box at a distance of 2 in., while the other coils of this set zigzag back and forth across the box, the knobs to which they are attached being 6 in. apart. The end coils of the upper set parallel the end of the box at a distance of 3 in., and the porcelain knobs are 13 in. apart. These knobs should be attached by the cabinet maker while the cabinet is in course of construction. The scheme of attachment is shown in Fig. IV.

This method of distributing the heating elements has been found to give reasonably uniform temperatures in all parts of the box. Uniform heating cannot be effected when the coils (or lamps if used) are all beneath the lower shelf of a two- or three-shelf cabinet, and there is no provision for air circulation by fans. The 400 ft. of wire has a resistance of 115 ohms, and since the 30 coils are in series, a current of 1.9 amperes is drawn on 220 volts. This furnishes more heat than is necessary to maintain the air in the cabinet at from 28 to 32° C. when the air of the room is 22° C. The



current is accordingly flowing only part of the time when the thermostat is used under these conditions. The cabinet may be employed for other lines of investigation at higher temperatures, which would be

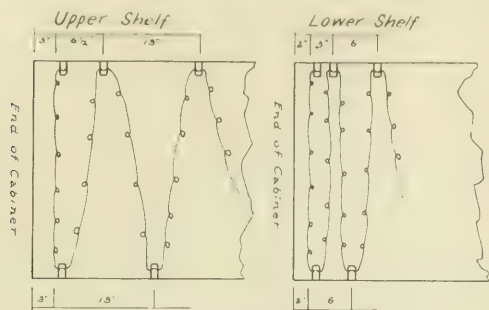


FIG. IV—METHOD OF ATTACHING HEATING COILS

impossible were it wired for use at only one temperature. If desired for dough fermentation exclusively, at the temperatures mentioned above (28 to 32° C. or 82.4 to 89.6° F.) from 600 to 700 feet of wire should be used instead of 400 feet. This should be distributed between the upper and lower sets in the same proportions as given for the 400-foot coil, *viz.*, 25 per cent above and 75 per cent below.

The temperature of the air in the box is controlled by a thermoregulator. For this purpose the device manufactured by the Apparatus and Specialty Company of Lansing, Michigan, has been found quite satisfactory.<sup>1</sup> If the heating elements were in series with the thermoregulator the contact points of the latter would be rapidly destroyed. A circuit-breaking device or relay switch was accordingly devised, the magnets of which are in series with the thermoregulator. Two 16-candle-power carbon lamps in series are used as resistance to reduce the current which flows through the thermoregulator and relay magnet series. The current which passes to the heating elements is broken

thus arranged does not vary more than 0.5° C. if properly adjusted.

The heat-regulating system may be rendered more efficient by having a variable external resistance or rheostat in series with the heating elements. While not essential, this can be employed to reduce the number of makes and breaks occurring in the thermostat. A little experience with a thermostat enables one to judge of the proper additional resistance to insert by means of the rheostat when the surrounding air temperature is known. A rheostat of this kind can be purchased for about \$8.00, while a satisfactory one may be constructed by anyone with mechanical ingenuity for \$4.00 or even less.

The cost of the completed thermostat is shown below. The cabinet in this laboratory was built of clear cypress, although white pine could possibly be used at a slightly reduced price. It was finished inside and outside with white enamel paint. The figures represent only the price of the materials. A rheostat is not included, as this is a non-essential though desirable accessory. The cost of winding and installing the heating elements is omitted as this would vary with the efficiency of the person employed. About 4 hours were required to wind and install the coils and make the electrical connections described in this paper.

#### COST OF COMPLETED THERMOSTAT

Cabinet.....	\$40.00
1.25 lbs. No. 20 advance resistance wire.....	1.88
Thermoregulator.....	7.00
Circuit breaker or relay.....	8.30
2 16-c. p. carbon lamps.....	0.30
1 15-ampere knife switch with fuses.....	0.75
25 feet No. 14 insulated copper wire.....	0.25
3 doz. split porcelain knobs.....	0.75
<b>TOTAL.....</b>	<b>\$59.43</b>

The writer does not claim that the features of this cabinet possess any marked originality. The ideas expressed in its construction were gained from several sources. The device as finally assembled possesses a serviceability that is outstanding, however. It gives added value to tests conducted by empirical methods, as any fermentation or baking test must be. No laboratory concerned with such work can long afford to be without a uniformly heated, automatically controlled device of this character which can be obtained at such a reasonable cost.

CEREAL AND FLOUR LABORATORY  
DIVISION OF AGRICULTURAL CHEMISTRY  
MINNESOTA AGRICULTURAL EXPERIMENT STATION

#### NOTE ON THE RESULTS OF ANALYSES ON FERTILIZER SAMPLES TAKEN WITH DIFFERENT STYLES OF SAMPLERS<sup>1</sup>

By F. B. CARPENTER

Received October 20, 1916

Having noticed the low results in ammonia on samples of fertilizer taken with the ordinary half round sampling tube, on goods which we had every reason to believe contained the guaranteed percentage of ammonia, an experiment was made to determine the

<sup>1</sup> Presented at the 53rd Meeting of the American Chemical Society, New York City, September 25 to 30, 1916.

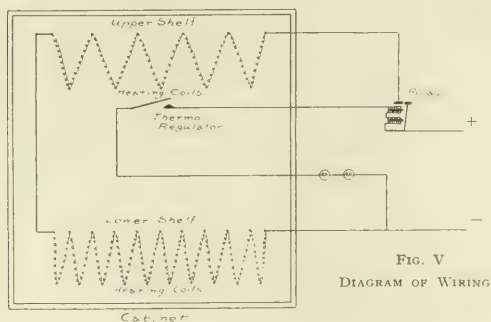


FIG. V  
DIAGRAM OF WIRING

through carbon contacts in the relay. These contacts are moved in one direction by a spring, and in the other by the electromagnets. The general scheme of the wiring system is shown in Fig. V. The thermostat

<sup>1</sup> Since writing this paper the No. 5 thermoregulator with condenser manufactured by the Chicago Surgical and Electrical Company has been tested and found satisfactory for use in this thermostat. It costs \$10.00, and since no relay and carbon lamps are required when it is employed, the cost of the complete thermostat is reduced by \$5.80. The wiring system is also simplified.

relative efficiency of different types of samplers. For this purpose two bags of fertilizer were carefully made at one of our factories containing 7.20 per cent ammonia or a guaranteed percentage of 7 per cent. Part of the nitrogen was derived from nitrate of soda and the remainder from organic ammoniates. This fertilizer was sampled by three different persons at different times with three different types of samplers and the samples analyzed. The results of the analyses were as follows:

SAMPLED BY	Per cent Ammonia		
	No. 1	No. 2	No. 3
Assistant Manager.....	6.48	6.90	.....
Chemist.....	6.90	7.21	.....
Superintendent.....	6.43	7.17	6.27
Average.....	6.67	7.09	6.27

The results under No. 1 are from samples taken with old style half round tube; No. 2 new style round sampler, which opens and closes; No. 3 what is known as a rice sampler. The first result under No. 2 is lower than the others for reason that the sample was not properly manipulated; the tube was inserted into the fertilizer without being closed. The proper way to handle the sampler is to push the closed tube into the fertilizer the full length of the bag, open, turn until filled, close and withdraw.

The results of these different analyses show that the sampler which closes gives results on ammonia nearest to theory, while with the other types the results are very much too low.

As many of the agricultural departments still use the old style sampler, it is more than probable that many of the deficient analyses on samples taken by official inspectors are a result of using improper sampling devices. This is a very important matter from the manufacturers' standpoint and, while there has been no intentional neglect on the part of the fertilizer controls, it is to be hoped that they will make a thorough investigation of the whole system of sampling and make such changes in existing methods as may be found necessary.

VIRGINIA-CAROLINA CHEMICAL COMPANY  
RICHMOND, VIRGINIA

#### BETTER SAMPLES FROM THE FERTILIZER FACTORY<sup>1</sup>

By A. J. LAWRENCE

Received October 20, 1916

A great many useless analyses are made through lack of cooperation between the laboratory and the factory and even where there is a strong desire on the part of the superintendent to have representative samples sent to the chemist, trouble often arises through incorrect methods of sampling.

In the fertilizer industry the methods of collecting samples vary to some extent in nearly every plant and we believe that by standardizing these methods, much trouble could be eliminated and more accurate and reliable information would result.

In receiving raw materials, some contracts specify as to the number of bags to be sampled. The large majority of sellers, however, leave the actual method

of sampling to the sworn weigher. We have found considerable variance in the methods used by different weighers, many of whom do not realize the importance of their work and the trouble that may arise between buyer and seller owing to disagreement in analysis. An example of this is shown in a case in which there was considerable difference between the buyer's and the seller's chemists on a cargo of garbage tankage. The source of trouble lay in the fact that the sworn weigher, without consulting the chemist or sample-boy, had quartered the fluffy, dusty material during a very high wind, in which a large amount of the fine particles were blown away, and in leaving, told the sample-boy that he had gotten his sample and the remainder was in the barrel. The boy got his sample, not mentioning the incident, the results of which he did not realize.

Also, at times, where the samples are carefully mixed and quartered and the duplicates and triplicates agree excellently, still, lack of judgment in quartering on moist or dirty floors, or using brooms or shovels which are contaminated with foreign materials, will result in the analysis of the goods differing to some extent from that actually received.

A considerable loss of money can very easily result through using the "bought" analysis on a lot of goods, which analysis may be slightly different from that in the pile. In one instance, a low-grade tankage was sampled, the sworn weigher requiring the unloaders to take a handful from each cart and drop same into a burlap bag tacked to the side of the scales. A large tin bucket was put on the other side of the scale house, and the men were required carefully to take a cupful of sample from each cart and place same in the bucket. This experiment was tried because it was believed that in dropping the tankage into the bag, some of the fine ammoniated particles were lost by being blown away from the mouth of the same; also it was noticed that a considerable portion sifted through as each handful was thrown in. On several occasions the sample in the tin bucket showed a higher analysis, running from 25 to 90 cents per ton in valuation above that obtained on the sworn weigher's sample. The observance of these points would save considerable trouble later on should analysis be made in the piles and found to disagree with the "bought" test.

In batching stock brands which are to be shipped after being cured, we do not believe that enough stress is laid on the method of sampling. In the majority of plants, the usual plan is for the superintendent to run up several tons of a brand and either have a sample drawn from the mill or the carts as they dump into the pile, or have the sample-boy dig down a few inches into the pile at several places. In most instances, with careful sampling, fairly reliable results can be obtained in this way. However, from several experiments we find that quite often very bad analyses result from this method of sampling and cause numerous retests in the laboratory as well as new samples from the pile.

We believe that this trouble can be eliminated to a large extent by using a large prospecting auger

<sup>1</sup> Presented at 53rd Meeting of the American Chemical Society, New York City, September 25-30, 1916.



such as is used in sampling soils and clays. This consists mainly of two blades arranged to cut a 6 in. hole and so bent as to pick up the material each time. Sufficient amount of handle can be attached to enable a pile of nearly any depth to be thoroughly sampled. In this way uniform sections can be bored into a pile in several places and duplicate samples invariably check, showing that if the materials are put into the mixture, a correct sample of same can be obtained.

The following tests were made on four brands of about 1000 tons each. Four samples were bored from each bin with the sampler as well as a sample being drawn from the mill during the run of the entire lot. The brands being figured to the exact analysis, the slight overrun is evidently due to shrinkage.

	"12 1/2-5" BRAND P <sub>2</sub> O <sub>5</sub> K <sub>2</sub> O	"10-8" BRAND P <sub>2</sub> O <sub>5</sub> K <sub>2</sub> O	"1-8-4" BRAND NH <sub>3</sub> P <sub>2</sub> O <sub>5</sub> K <sub>2</sub> O	"2-8-10" BRAND NH <sub>3</sub> P <sub>2</sub> O <sub>5</sub> K <sub>2</sub> O
12.55 4.96	10.05 7.91	1.15 8.05 4.00	2.18 8.15 10.20	
12.42 5.10	9.92 8.08	0.99 8.18 4.16	2.01 8.10 10.20	
12.48 5.12	9.96 8.10	1.03 8.15 4.06	2.11 8.17 10.01	
12.63 5.00	9.93 8.04	1.13 8.02 4.06	1.96 8.18 10.14	
Av. (Bored)	12.52 5.04	9.97 8.03	1.07 8.09 4.07	2.06 8.15 10.13
Mill sample (Not Bored)	11.96 4.66	10.67 7.83	1.10 8.50 3.60	2.16 7.80 10.30

On these "mill" samples it would be necessary to change the formula which would result in incorrect analyses, whereas the bored samples show that the piles actually run about as figured. Bad analyses on bored samples can invariably be traced to faulty mixing in which either wrong amounts were weighed in or the actual materials fail to analyze as figured.

In sampling bagged shipments, we believe that much more reliable information can be obtained as to their analyses by the use of the double tube sampling trier which is inserted into a bag, closed, and withdrawn, giving an exact section of the material therein.

If methods of sampling could be as rigidly enforced in the factory as in the laboratory, we believe that more dependable information would result.

The average factory chemist does not bestir himself sufficiently to see when samples are being drawn correctly and the average superintendent does not realize the importance of the small details in sampling, which have a vital bearing on the plant and its reputation for uniform analyses.

CHEMICAL LABORATORY, F. S. ROYSTER GUANO COMPANY  
NORFOLK, VIRGINIA

## A NEW SPECTRUM MAP PAPER

By R. P. ANDERSON

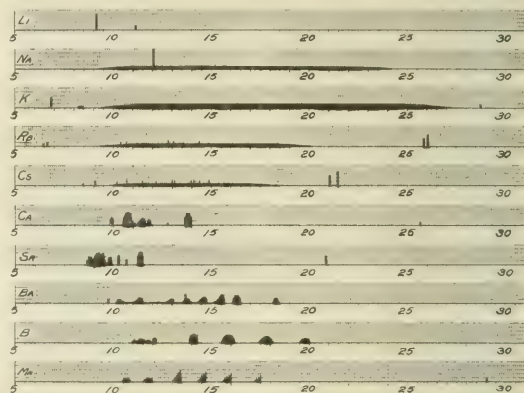
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The method of mapping emission spectra which was suggested by Bunsen<sup>1</sup> has proven of value in the course in Opticochemical Methods at Cornell University as an aid in familiarizing the student with comparatively simple emission spectra. Bunsen's method consists in plotting the lines and bands of a spectrum on a millimeter scale, numbered to correspond to the arbitrary scale of the spectroscope. Each line or band is placed at the position on the scale that corresponds to its

position on the scale of the instrument, representing its width and intensity by the width and height, respectively, of the drawing.

The spectrum map paper here described differs from that ordinarily employed in that there is provided above each scale a cross-sectioned area one centimeter in height on which the maps are made, using the heavy line as the base line. The vertical lines of the cross-sectioned area are useful as guides in mapping spectrum lines, while the horizontal lines simplify the comparison of the intensity of lines and bands in different parts of the spectrum.

The spectra that are shown were mapped as an illustration of Bunsen's method as applied to this new map paper. The compounds employed were respectively: lithium carbonate, sodium carbonate, potassium carbonate, rubidium carbonate, caesium alum, calcium chloride, strontium chloride, barium chloride, boric acid, and manganese chloride. The spectra were produced in the usual fashion by introducing the sub-



stances into a Bunsen flame on a platinum wire. In the case of the chlorides of the alkaline earths, where rapidly shifting spectra are first obtained, the maps represent the fairly stable spectra that are produced after a preliminary heating of the chlorides on the wire.

This map paper can also be conveniently employed for the mapping of absorption spectra at different concentrations for the determination of the point of "minimum brightness" of the substance in solution.

The illustration shows a sheet of the spectrum map paper about one-third natural size. This paper is furnished by the Cornell Coöperative Store, Morrill Hall, Ithaca, N. Y., in packages of fifteen sheets, together with three sheets of millimeter cross section paper, at a cost dependent upon the price of paper. Until recently a package was sold for fifteen cents, postage prepaid, with lower prices on ten or more packages.

CORNELL UNIVERSITY, ITHACA, NEW YORK

<sup>1</sup> *Ann. der Phys. und Chem.*, 195 (1863), 10.

## ADDRESSES

### THE NEW ASPECTS OF CHEMICAL SCIENCE<sup>1</sup>

By J. MERRITT MATTHEWS

The past two years have offered great inspiration both in thought and accomplishment to the American chemist. The past recent meeting of the chemical societies in this city, together with the elaborate Exposition of the Chemical Industries, has formed what might be termed the apotheosis of Technical Chemistry.

The American Chemical Society has heretofore confined its attention probably more to the consideration of pure chemistry of an academic character rather than to the industrial aspects of the science. This latter point of view has been left more to the technical societies. There has, however, been a more or less growing demand for an added emphasis to the features of applied chemistry. This demand has found its expression in the remarkable development of THIS JOURNAL so ably and successfully edited by Professor Whitaker. The general trend of our meetings has also shown the influence of this same leading force; the American chemist is evidently becoming vitally interested in the application of his science; it might almost be said that he is seeking to bring it up from the state of an art to the true dignity of a science.

This growing tendency in our Society naturally leads to some philosophical reflections on the relations of technical chemistry and pure chemistry—the human relations of chemistry as distinguished from its purely academic features.

Technical chemistry must, of course, be considered as a branch of applied science, and as such more or less in opposition to "pure science." In using the term "pure science" it is my purpose to convey the meaning of science studied as an end and an ideal in itself: science that seeks for nothing beyond its own development, and having no ulterior motive than that of its own aggrandizement. Like virtue, it is its own reward; and like virtue, it also demands many sacrifices from its devotees. Its domains are vast; its treasures are countless; its followers are those to whom the lust of knowledge is the ambition of life. It is the science of the schools and the scholars, of the life-long student and the philosopher. Its wealth is not measured in money, but in the understanding of the phenomena of Nature. It seeks after a knowledge of the laws of the world, and probes deeply into the mysteries of the universe; no fact is too humble for its recognition, nor too vast for its comprehension; no problem is too trifling for its attention, nor too sanctified for its solution. Its object is truth for the sake of truth alone; knowledge for the mere sake of gratifying the desire of knowing. The astronomer seeks for the cause of a star's variation in color, the biologist studies the life-history of a jelly-fish, the chemist prepares a thimbleful of some newly discovered compound, the mathematician speculates on the laws of a fourth dimension to space, while the mineralogist measures the angles of a microscopic crystal. These are the offerings on the altar of pure science; these are the theses of philosophers, and the life-works of scientists.

To the layman, the matter-of-fact man of the world, the study of pure science is a useless bit of mental recreation; an exercise in intellectual gymnastics which may strengthen and develop the mind, but which serves no other purpose. "*Cui bono?*" he asks, with a shrug of the shoulders. What good is it all? For as humanity is more apt to reckon its honesty in terms of policy, so will it judge of knowledge by its usefulness. We have reached a period where utility is more and more in demand; a utility, moreover, which is reckoned in dollars and cents rather than in the more esthetic currency of beauty and

truth. Things either have a money value or no value at all; ideas which cannot be patented are scarce worth the brain tissue used up in thinking them out. In an age when even the emotions are definitely assessed at certain money valuations, we should not be surprised to find that culture is rated below utility, and that the genius of the intellect is a servant in waiting to the God of Mammon. We do not rub the Lamp of Knowledge just to polish it up and keep it clean, but to summon the Slaves of Science that they may transmute for us the wealth of intellect into the wealth of the world.

The study of pure Science is essentially a study for culture. Leaving aside the consideration of any application of its results, it makes for increased intellectual powers by extending the intellectual vision; it elevates the type of knowledge and broadens the character of the individual. It differentiates from the universal "thought-stuff" another form of truth—a form, perhaps, which may exist as a piece of statuary which appeals to the artistic contemplation of the scientist, but which will never be animated with the energies of life. The question is narrowed down to one of appreciation and taste, and we must put to ourselves the query: Is the cultivation of pure science the essential element in the advancement of knowledge; or is it but a plaything and a hobby for the enthusiast, and does applied science become the absorbing purpose of knowledge and the ultimate foundation of truth? On the very threshold of this discussion we are struck with the disparity and wide separation of these two sides of scientific thought. On the one hand we see pure science being carried out in the laboratories of universities and colleges, taking little or no thought of anything but itself. It labors faithfully and diligently onward to the working out of some engrossing idea—perhaps its end is the preparation of a hexachloride of molybdenum, or a determination of a velocity of a star through the shifting of lines in its spectrum; or possibly its goal is the tracing back of some English word to its derivation amidst its Aryan ancestors. But whatever the subject may be, the student of pure science will almost invariably lose sight of everything outside of that focus towards which all his lines of thought converge. He never stops to think for a moment what practical advantage to the world in general it will be whether Capella is moving away from the earth with a velocity of seventeen miles a second and not thirty-two, as some previous observer may have erroneously computed. He may spend five years in preparing a single gram of the hexachloride of molybdenum, and after having established its composition and formula, and having used up all his product in so doing, he will experience a feeling of satisfaction at having so successfully completed a difficult problem in scientific research. After all, do not such things appear somewhat outside of the world's interests; are they really as much in touch with humanity as they should be? Can we altogether blame Swift for his little sarcasm about extracting sunbeams from cucumbers? It brings us around to the opinion that all science should be animated with a human motive; it should appeal to a wider interest than that of the mere student; it should be a living and organic force active within the life-history of thought itself. The truths of astronomy should appeal to more than a mere personal gratification of the star-gazer himself; every discovery of science should possess a universal significance before it becomes embodied in the general form of knowledge.

But on the other hand pure science, or science *par excellence*, is essentially a mode of intellectual culture, and as such cannot be regarded too highly as an end in itself. Whatever makes for the further development of the mind is more truly a factor in human progress than that which merely serves a utility in supplying the momentary demands of sense. The money value

<sup>1</sup> Chairman's address, New York Section American Chemical Society, Chemists' Club, October 13, 1916.



of a thing does not in any manner represent its final utility, but merely serves to measure the present ratio between its demand and supply. Calvin spent years in patient study and research in observing the twitchings of the hind legs of a frog, he did it purely for the interests of the science to which he had devoted his life, and no one paid him a cent for his trouble. But his seemingly trivial and ridiculous studies into the causes of the twitchings of the frog's legs proved to be the fount of inspiration from which flowed in a direct stream the discovery and knowledge of the electric current, and all the possibilities to which modern ingenuity has applied it. There is not a fact, however humble, but which by its understanding adds a dignity to human knowledge; there is not a theory, however abstruse, but which by its confirmation and comprehension adds a new purpose to and widens the possibilities of human life. Our lives, in reality, are not made up so much of "things" as of "thoughts," and whenever science broadens the field of thought, she not only enlarges, but elevates the sphere of life. In estimating the utility of things we are inclined more to regard their individual practicability than their universal significance; a specific invention which earns its originator a material fortune is considered of more value in the opinion of most people than the broad law of nature to which that very invention owes its possibility and its conception. Men of science seldom patent the result of their research; they bend their energies towards the general expression of the truth of which they are in search; they care little, and in fact, know little, of the practical applications of that truth to the various needs of life. They find their greatest satisfaction and recompense in the consciousness of having advanced the general type of knowledge.

Perhaps we of the present time are inclined to depreciate the value of pure culture below that of mercantile utility, and give more attention to the transactions of commerce than to the speculations of science, literature, and art. The cry is often heard that we are rapidly going away from a civilization of pure culture to one of specialized utility; nor is this movement one peculiar to science alone, for we find it as an active factor in the fields of literature and art. Even the most conservative mind must admit the apparent fact that there is a strong force continually active in the direction of specialization, with the ultimate object in view of practical utility. The cause of its existence is found in the fact that human life is no longer commensurate with the infinite possibilities afforded for its activity; the ramifications of science have become so extended and numerous that should the individual desire to develop further, he must take up the burden of some specialized line and carry it forward in the rapid march of progress.

This is a period in which we are becoming steeped in education, flooded with knowledge. Our motto is becoming "It pays to know," and the particular knowledge which most pays to know appears to be of the scientific type. This is no doubt necessitated by the predominating influence science is exerting upon the numerous branches of industry and commerce. And our scientific education must be of a technical character in order to fulfil the exactions placed upon it. The development of technical sciences so closely allied to the arts is the direct result of the specializing of higher education so needful in the forming of acutely and minutely trained minds. This influence is becoming a potent factor in the educational problem of the times, giving knowledge a practical tendency and a body more in keeping with the flesh and blood of human needs. In making science assume a technical character there is an attempt to infuse the facts and energies of living industries into the rather inert and spiritual mass of general principles and theorems. What we know of as "pure science" has little to do with the real problems of human life; these must be met and answered by the technical sciences, dealing as they do with practical applications of human knowledge.

You will pardon, I trust, these rather generalized reflections on the two aspects of chemical science, but I cannot help but feel that we are realizing a higher dignity for our science as a *profession* in contrast with its dignity as a purely academic form of scholarship and culture. Perhaps it was not so long ago that the Chemical Engineer was regarded somewhat as a pipe fitter and plumber, rather than as a real scientist. The chemist in England is still a drug clerk, and even to the layman in this country the chemist has been considered as a compounder of pills and hair tonics. The past two years I think, however, has seen a better appreciation by the layman and the press as to just what the chemist is and what his profession consists of and can accomplish. There is still that idea, however, prevailing that chemistry is a hodge-podge of mysterious secrets, the discovery of which is made by accidental and haphazard methods. The popular mind has evidently not yet progressed beyond the age of the alchemist. In things chemical the public has still the innocently receptive mind of a child; it will accept as gospel truth the most absurd and illogical statements of supposed discoveries. Some so-called chemist announces the remarkable discovery that by the addition of a few drops of a mysterious green liquid to water he creates a perfect substitute for gasoline for use in automobiles. The daily press devotes column after column to this truly remarkable process, and the public evidences the keenest and most serious interest. The thing could not be more absurd than if a physician announced that he had discovered that he could make new legs grow where those members had been amputated, by rubbing a decoction of hen's teeth on the parts affected. I hardly believe either the press or the public would take this latter announcement seriously and any editor would consider it too foolish to be printed. And yet how often have we been regaled at breakfast table with glaring head-lines announcing with all seriousness that Dr. So-and-So, a celebrated chemist (whom none of us had ever heard of before), has just discovered the *secret* of the German dyes.

Fortunately, however, I think the public and the press are becoming perceptibly educated to a saner idea of chemistry. We have all appreciated more or less the wide publicity given by the press to the recent meeting of our Society and we surely have not failed to notice the remarkably sensible and rational reports that were printed in our daily papers. We also could not but be impressed with the fact that the great throng of visitors to the Chemical Exposition was made up quite largely of laymen and the unscientific public, and they seemed interested and appreciative.

It is apparent, therefore, that chemistry is coming into closer contact with human life; it is becoming more and more a part of the every-day life of the world, and as such is acquiring a breadth and a dignity which only a wide understanding can give it. And not only is the world at large being benefited by this wider understanding, but chemistry itself, as a profession, is acquiring new forces and inspiration from this wider contact with human life.

50 EAST 41ST STREET  
NEW YORK CITY

## THE DAY OF THE CHEMIST<sup>1</sup>

By FRANK S. WASHBURN  
President American Cyanamid Company

"Si monumentum quaeris, circumspice!" (If you seek his monument look around you.) As we look around us, we see hardly a single object that has not required in its preparation the service of a chemist. The tungsten lights illuminating this room are the product of many years of patient toil. The glassware on the table and the eye-glasses that many of you are wearing are representative of two thousand different grades of glass

<sup>1</sup> Address delivered at the banquet of the American Chemical Society, Waldorf-Astoria Hotel, September 29, 1916.

that can be produced by the skilled glass maker who works under chemical control.

The cutlery on the table represents several immense branches of chemical industry—the iron and the steel industry and the mining industries. The making of iron and steel is in its every step controlled by chemical analyses, and recently many forms of steel have been produced as a result of systematic chemical experimentation. The extraction of silver and gold from their ores by means of cyanide solutions, and their purification, are chemical operations of great importance.

The clothing we wear would be a far different commodity if it were not for the chemist. The dye industry is attracting a great deal of attention since the war cut us off from German sources of supply. The American chemist and American capital are making good headway in their efforts to place this country on a basis, which if it is not independent, will at least not be entirely at the mercy of foreign sources of supply.

Cotton, which supplies such a large portion of the clothing of mankind, has a host of other uses. Fabrikoid, an artificial leather, is produced by nitrating cotton in a particular way and applying it to cotton cloth. For many purposes it is superior to ordinary grades of leather, and is much cheaper. Celluloid and similar compounds are made from cotton and have the widest variety of applications. Photographic films familiar to all of us are also made from nitrated cotton.

Perhaps the largest use of nitrated cotton to-day is in explosives, and this product of the chemist's art is playing a considerable part in determining the future of Europe.

Then, coming to the food, even the butter may not be above suspicion of having been tampered with by the chemist, and it is not unlikely that a great part of what we have partaken to-night was grown with the aid of chemical plant foods. Nitrogen drawn from the air, from coal, from distant Chile, and from various seeds, phosphorus from phosphate rock and potash separated by careful crystallization from the mother ores in Germany, have all helped to sustain the life of the plant and made it grow abundantly and well. Over \$100,000,000 are invested in fertilizer manufacturing plants in this industry, and for its products the farmers of this country pay \$175,000,000 per annum.

The scientific preparation of new food products, the principles underlying the canning of fruits, all require the chemist. The preservation of foods by artificial refrigeration is made possible with ammonia produced from the air or in the coke ovens.

Cottonseed oil, in its raw state unfit for human consumption, is purified by chemical means and becomes a substitute for olive oil, or it is treated with hydrogen in the presence of a nickel catalyzer and becomes a semi-solid.

Fruit oils, flavoring extracts, perfumes are made to-day synthetically, in a great variety and of high purity—some of these products surpassing the natural substances.

And when you ride home in your automobile to-night, the motive force in the engine will be gasoline, which with some two hundred other products, represents the petroleum chemists' contribution to mankind.

The present is to be valued as a day of opportunity for the chemist rather than the high noon of accomplishment. Agriculture requires the help of the chemist more than any other human activity, but the benefit of his work has been tremendously handicapped by the ignorance, isolation and restricted horizon of the farmer which makes extremely slow the adoption of new methods and materials, and right here we see wherein the thing called government fails us, for it is hopeless to rely on the individual initiative of the farmer to seek out improvements. Society must place them in his hands for its own benefit, and where government is so ordered that it neither uses to a legislative appreciation of this fact nor could efficiently

perform even if it had the appreciation, then it may be justly called an ineffective form of government.

There is an almost untouched field in new agricultural products, the commercialization of weeds, if you please, such as the sunflower. There is only partial utilization of potatoes, of cotton and of wood fiber. We are at the very threshold of the possibilities in the development of new fibers and fabrics. Synthetic rubber still challenges the chemical world. The secret of electrical conductivity is still hidden from man although some progress is reported in the treatment of steel conductors which make them slightly, if at all, inferior to copper. The economic conversion of natural insoluble potash-bearing rocks into soluble potash salts is not yet demonstrated. There is a world of undiscovered country in the conversion of the initial products of the fixation of atmospheric nitrogen, to the myriad nitrogenous substances. Photo-chemistry as yet counts comparatively little in the way of practical accomplishment. And so far in the distance does the production of synthetic foods from inorganic substances appear to be that one does not mention it seriously for fear of being counted irredeemably impractical.

Chemistry will have admirable running-mates along the course stretching on into the future. Even the purely mechanical discoveries and developments do not all belong to the past. There is still place in this field, which ordinarily does not challenge the highest scientific attainments, for marvelous performances based on a profound knowledge of physical laws and mathematics. The evidence of this we see, for example, in the Sperry gyroscope; originally an interesting mysterious toy which with twelve years of devoted study and experimentation displaces in a night the magnetic compass, stabilizes the ponderous battleship and the feathery aeroplane, and promises to be the agency by which ice-bound ports may be unlocked and kept open to commerce the year round. And far removed from mechanics in the long list of subjects of human interest is the psychopathic laboratory and the Binet-Simon system of analyzing—not a physical substance, but the mind of the defective human being, determining the degree of his responsibility to society, and constituting what has been designated as a mental finger-print method of identification of the specific type of mental trouble. The defective and feeble-minded are not only detected at an early age but by prescribing thyroid or other treatment, carefully and persistently given, these cretin children may be grown to normal stature, mentally and physically.

That the genius, devotion and labors of the chemist may be expressed in valuable accomplishment demands the existence of certain favorable conditions which do not exist at present in this country, and therefore must be brought about. The laborer is worthy of his hire and, furthermore, unless he receives it, he cannot, even if he would, give his labor. One of the greatest discouragements to chemical research work is the absence of any adequate provisions under American law for safeguarding the individual's title to the product of his brain and energy. The patent laws are inadequate to this end. Their first requisite is publicity and such protection as they do afford is seriously threatened with dissolution by each succeeding session of the National Congress. The average constituent does not distinguish between an odious monopoly which takes from society a right and bestows it upon an individual without recompense to society, and the recognition of a property right in the product of one's brain to be guaranteed for a limited period in return for its assignment to mankind thereafter. The average legislator cannot hold to views nor act upon them beyond the prejudice or insistence of his constituents or he would cease to be a legislator, average or otherwise.

Let us not fail to give adequate consideration to the personal factor. The carrying out of involved chemical processes demands a "feeling," on the part of the workmen, that, while it



falls short of the fine sentiment of the artist, lifts artisanship almost to the level of art itself. After all, the chemical plant is only a chemical laboratory on a large scale and we all appreciate, in the laboratory at least, the technique and touch, in other words, a feeling for the work is a necessary characteristic of the operator who expects to gain accurate and successful results.

In countries of modern income a life-long pride and satisfaction on the part of the highly trained chemist in a simple subordinate calling is universal. The mono-technic schools of Germany are in the belief of many, the chief factor in that nation's unexampled advance in the arts, particularly in the chemical industries. One cannot travel far in chemistry without coming to Germany. Few branches of the subject can be properly dealt with except we draw examples from Germany. I trust no one here will read into my references to Germany any expression of opinion as to Germany's place in this horrible world tragedy being enacted abroad. We can all meet on the common ground of mourner over the sufferings of the admirable individuals who compose the greater part of every nation. To return to the mono-technic school: it is more than a great economic factor; it represents and examples that unique social principle that sets the German people politically apart from every other nation of the world, the placing of the Fatherland above the individual, the sacrifice of individual opportunity to the principle of the greatest good to the greatest number. There are, as I recall it, over 400 mono-technic schools, and taking the dye schools as an example, the curriculum is of a higher standard than in any save one or two universities in the United States—four years of laboratory practice in neighboring dye establishments and specialization in the most involved chemical theory, on the intricate differentiations of the myriad color compounds and by-products, and on the psychology of color. What American parent would be satisfied to have his son give four years of high-class intellectual effort as a college student and have nothing ahead of him in a long life beyond a foremanship in a dye establishment? And yet this subjugation of the individual has made Germany, in a broad sense, the only producers of dyes in the world and the greatest of dyers.

So we say the Day of the Chemist is not to be measured by the personal gain of the chemist so much as by the opportunity for service, and applying to the modest thing the trained analytical mind. So we come back to our original statement that without devoted personal service many scientific undertakings otherwise possible will prove failures with us. The German estimate of our limitations in this regard is well expressed by the dry comment on the merits of the Diesel Engine—"It works well—except where English is spoken."

There is little appreciation among American financiers, bankers, or the investing public of the value of an idea, and therefore we are without a recognized basis for seeking capital with which to exploit the result of research work, either in the initial stages of the development or for later expansions. The average banker is more impressed with an asset item of buildings, plant and equipment even without knowledge as to whether they can be converted to any practical use, than he is with an idea the potential value of which may be substantially unlimited. He will not give value to an idea. There is another obstacle to establishing the value of chemical developments, namely, the absence of any body of recognized consultants whose reports are universally accepted as reliable. The failure to use such men as there are of this type is a handicap to the good project and an imposition always upon the persons whose assistance, financial or otherwise, is sought in the development of a project. No enterprise, regardless of the ability and standing of its sponsors, should be presented in an effort to secure financial coöperation, without being accompanied by a report on the project with conclusions as to its technical and commercial merits from some highly regarded man of scientific attainments.

I would point in passing to another difficulty for which I think the chemist himself is chiefly responsible, and that is that no distinction as to commercial value is made between the bare thought or invention and the developed process or material. Too many chemists view as synonymous the theory which applies to an idea and the processing by which the theory may be converted to practical accomplishment. Chemical theories are innumerable and of those who present them in the aspect of practical accomplishments there are a vast multitude. I was interested in looking over the report of one of our great mining companies, which maintains a department for the investigation of projects presented for investment. Last year out of 780 projects so presented only 13 were worthy of extended investigation: substantially 2 per cent. I am quite positive that the experience of those engaged in the chemical industries as to new projects which are brought to them by chemists, will confirm in this branch of human endeavor as low a percentage of worthy projects as in metal mining.

American problems have been primarily the problems of a pioneer community in a sparsely settled country, where virgin national wealth is to be had by stretching out the hand, where simple direct means backed by energy, daring and courage accomplish results by main strength and awkwardness. We are going out of that phase of existence into a period where to compete in accomplishment with other nations scientific methods must be employed. The day of the typical "practical man" is passing and there is dawning the day of the efficient scientific man. The latter is not yet appreciated, he is not generally understood nor honored. As he grows in public esteem and receives social recognition there will be attached to his ranks more of ability, ambition and the stronger personalities by whom honor and the consciousness of serving society is more prized than the money wage.

This nation's greatest asset is its thinking men. Our country faces its greatest peril as well as its greatest opportunity. The Day of the Chemist is a day of opportunity for service. It is the blessed privilege of the man of science that his value is measured in proportion to the service he renders society. It lifts him to a plane of nobility unattainable by those who amass even the greatest fortunes without contributing to mankind a comparable return.

But the chemist's most valuable contribution to the world will not lie in the economic value of his process or product. It will come from his moral example and influence. We of this country are not yet awake to the value of truth. I mean the truth that is fact. So little of our national life is ordered on a basis of fact. Contemplate our National legislators, in whose hands are the destinies of this great nation and the waste or the useful fulfillment of our individual lives. One of the most depressing experiences in the life of any observing, thinking American must be the contemplation of the most important and complicated of human activities, government, conducted in an age of scientific approach to every other subject and striving for efficiency in every other activity, without any realization that such a basis might exist for it. Government with us, like the study of contemporaneous European geography, is largely a matter of personal opinion.

Were some fearful scourge running an unchecked course through the greater part of the civilized world, killing, crippling and blinding the vigorous youth and middle aged of sixteen nations of Europe would not the mind and soul of every lover of mankind be enlisted in the service of stamping out the scourge and establishing a quarantine thereafter that would for all time prevent its recurrence? This horrible, unexampled war has been called the Chemist's war—and it is to the honor of any man that he shall do great service for his nation at war, and yet how immeasurably greater would be the accomplishment of any class of men who had contributed something effective to

the prevention of war. What will the Day of the Chemist bring forward as his contribution to war's prevention? And yet despite the possession by the German nation of a highly honored body of the world's greatest scientists the scourge came and none could stay it. Something more than is required than simple devotion to scientific truth. Is it "reasonableness?" In other words, that spirit of mind which is not allied to partisanship—the balanced, considerate and open mind. When that shall be the recognized mental equipment of every scientific man, then shall dawn the True Day of the Chemist.

200 FIFTH AVENUE, NEW YORK CITY

## NITROGEN AND NITRATES FROM BITUMINOUS COAL<sup>1</sup>

By C. G. ATWATER

Received September 23, 1916

Every few years a wave of nitrogenous famine seems to sweep over the daily press, arousing more or less interest and apprehension on the part of the public. Coincident with these waves, discoveries which remove the danger of famine and therefore deliver posterity from the prospect of perishing of starvation, are brought to public view.

Some eight or nine years ago Sir William Crookes sounded a "note of alarm" and our deliverance by the recovery of atmospheric nitrogen through the electric arc was predicted. A few years later commercial cultures of nitrogen-fixing bacteria were discovered and their beneficial activities were greeted with more or less journalistic and public enthusiasm. The *New York Tribune*, commenting editorially on the appearance of electrolytic fixation and of the nitrogen-fixing bacteria at that time, proclaimed its entire willingness to credit the inventors of either process with the preservation of our descendants from death by hunger, but admitted its inability to give both credit for the same beneficent work.

I have not seen in the public prints any wide-spread announcement of the fact that the recovery of nitrogen from bituminous coal is destined to save future generations from starvation, but in view of the fact that this process has always had and still has as great a promise as either of the others and is much closer to our ordinary manufacturing operations and industrial organization, I feel that such a proclamation may be expected at any moment. While there is an attractive touch of romance in the idea of converting the atmosphere into food, even though somewhat overworked of late, it must be remembered that even in the legend, the rainbow was in the air, while the pot of gold had to be dug out of the ground at its foot.

These circumstances furnish me with some shadow of excuse, at least, for this paper. Additional color is given to this excuse by the fact that the immediate demand of nitrogen for producing food for the preservation of life is supplemented by a dire need for it in the production of explosives to be used in quite the opposite direction. It might be interesting, but would probably be quite useless, to speculate as to whether these two needs could not be so manipulated as ultimately to neutralize each other in the outcome.

### AMMONIA FROM BITUMINOUS COAL

In speaking of the potential amounts of ammonia recoverable from bituminous coal, as has been done for years past in the public prints, it has been the habit to limit such speculation to the amount of coal actually made into coke. There were at least two good reasons for this, one being that this coal was already being subjected to the process of destructive distillation and hence was commercially eligible for treatment by the by-product recovery process. A second was that the amount of ammonia recoverable from the coking operation was until recently so far in advance of the amount actually being recovered, the ratio being about 4 to 1, that any argument for

conservation or contrast with European practice could be sufficiently enforced with this simple illustration without going further afield. Such statements, so far as I have been guilty of them, erred only on the conservative side. They limited themselves to the replacement of beehive coke, used almost exclusively in iron smelting, with by-product coke. They took no account of the extremely probable increase in the iron industry and they passed by, in rather a cursory fashion, the immense production that would ensue if even a moiety of our ordinary fuel consumption were conducted with by-product recovery. A little closer examination of the actual conditions will show how important these omissions were.

In order to get the data in proper sequence, I will first state the present figures. The ammonium sulfate production in the United States for the year 1915 is estimated at 220,000 net tons, figuring all forms of ammonia as sulfate. The largest amount of coal made into coke in any one year, as reported to date, including beehive, by-product and gas-house coke, was in 1913, and amounted to over 73 million tons. This should have yielded over 700,000 tons of ammonium sulfate. In other words, the maximum recovery is a little less than one-third of the maximum amount possible. It is highly probable, however, that the year 1916 will increase the total figures, though it may not change their ratio. The beehive coke production for the past half year, if maintained, will give the largest year on record, and the same is true of the by-product coke output. An increase of 25,000 to 50,000 tons of ammonium sulfate for the year is considered probable. There are estimated to be 2,600 new by-product coke-ovens actually under construction, and 1,100 more that have been definitely decided upon. These will add about 15,000,000 tons of by-product coke to the annual capacity when completed, so that within two years an output of 375,000 to 400,000 tons of ammonium sulfate per year is quite possible if business conditions favor complete operations.

The output of bituminous coal for the year 1915 was 438,550,000 tons and the Geological Survey's estimate for 1916 is 500 million tons. If we figure a recovery of 1 per cent in ammonium sulfate this would amount to 5 million tons per annum. All of this ammonia is recoverable, and all but the modicum recovered is now wasted. The first objection to this statement that will occur is, of course, the difficulty of recovering by-products from the simple furnaces in which most of this coal is consumed. These difficulties are by no means so great as has been popularly accepted and a notable amount of progress has recently been made along the line of substituting methods of fuel treatment that permit of ammonia recovery.

In the first place a great deal of coke is now being used in place of anthracite coal. The latter has constantly risen in price and its production is decreasing. In many districts of the Middle West, coke has taken its place as a smokeless fuel. There are a number of coke-oven plants which regularly turn a respectable portion of their output into domestic coke and this business is steadily increasing. Domestic coke is regularly distributed from the coke plants at Chicago, Ill., Milwaukee, Wis., Duluth, Minn., St. Louis, Mo., Muncie and Indianapolis, Ind., Hamilton, Ohio, Detroit, Mich., Glassport, Pa., Geneva, N. Y., Everett, Mass., Camden, N. J., and is obtainable in many other cities. Some domestic coke will also be supplied to the local market from the new plant now building near Newark, N. J. These conditions are emphasized by the fact that there is no prospect of any diminution in the price of anthracite, nor is it to be expected that the present burners of smokeless fuel will ever return to the former smoky and undesirable conditions.

An additional impulse in this direction is the increasing domestic and industrial consumption of gas. Large areas of the Middle West have been accustomed to natural gas at a low price. The supply seems to be finally on the wane and it is only

<sup>1</sup> Paper read before the American Chemical Society, New York City, September 25-30, 1916



a question of time when this territory will have to be supplied with artificial coal-gas, which will necessarily be made with the recovery of by-products, including ammonia, or for industrial uses, with producer gas, which may well be made with by-product recovery. Some years ago much was expected in the way of ammonia recovery from bituminous coal by the agency of the Mond gas producer. The expected development in this direction did not take place. Certain drawbacks stood in the way of its wider introduction and its coadjutor in power development, the large gas engine, found difficulty in competing in cost of installation and operation with the steam turbine. Later developments in modified forms of the Mond producer, as in the Lynn type of apparatus, have brought about the introduction and successful commercial operation of a number of such ammonia- and power-producing plants in Great Britain and in Germany, Italy, Spain, China, and Japan as well. There is good reason to believe that progress in this country in this direction will not be much longer delayed. It must be noted in this connection that the ammonia recovery from coal treated in these producers is approximately *four times* as great as in the by-product coke-oven. With our accepted practice of concentrating power generation in large central stations, there is good reason for considering this development as an immediate commercial possibility.

Another reason for an increased use of ammonia from bituminous coal is the low cost of production, compared with the electrolytic or synthetic processes, when necessary transportation costs are included. The advantage that coke-oven ammonia has in this respect been stated frequently, and by various acceptable authorities, and so far as I know this has never been contradicted by anyone even approximately without bias. It therefore seems of little use to set up a man of straw in order to overturn him. Coke-oven ammonia, being recovered as a by-product of the main product, coke or gas, is produced with but minor regard as to the demand for it, hence must be sold for the best price obtainable. Therefore, in any event, the argument for it, in view of the existing coke industry and undertakings, would probably partake of the nature of a request to "Come on in, the water's fine!" Certainly a statement that ammonia could be made more cheaply on a commercial basis by resort to water-power development would hardly seem to be an adequate reason for asking the Government to lend financial aid to such an enterprise, more particularly when such a project includes the making of fertilizers in times of peace, as well as explosives in war. There are a half-dozen other good reasons why coke-ovens are our best source of ammonia, in peace or war—geographical distribution, immunity from enemy attack, speed with which new units can be erected, production of other essential materials, conservation of natural resources, I cannot stop to go into them all, more especially as they have been adequately covered elsewhere.<sup>1</sup>

#### TRANSFORMATION OF AMMONIA TO NITRIC ACID

The oxidation of ammonia to nitric acid is practically a new process in this country. Commercially, its prospects seem to offer little attraction, as the ordinary method of producing nitric acid by treating sodium nitrate with sulfuric acid is a less expensive one. Its principal function would be in time of war when sodium nitrate would possibly not be obtainable.

As the great resource of this country for combined nitrogen lies in the recovery of ammonia from bituminous coal, the adaptability of this form of ammonia to oxidation by the Ostwald or some other process is most important. The Ostwald process, as is well known, depends upon the action of a catalyst

on a mixture of ammonia and air, or air and oxygen, such catalytic action being more or less subject to derangement or poisoning by certain impurities. Granted that the Ostwald process is capable of producing nitric acid from ammonia in large quantities, which in view of the present European experience we may safely assume, the question resolves itself into an investigation of the effect of the impurities and the process of their removal if necessary.

That the impurities in coke-oven ammonia can be successfully removed so as to deliver a gas that is to all intents and purposes pure, has been amply demonstrated. This is regularly done in the manufacture of anhydrous ammonia, aqua ammonia, and ammonia for the production of pure ammonium salts. The methods employed, it is not necessary here to describe. It is probably possible to modify these methods for the purification of ammonia for oxidation on a scale of, say, one hundred tons per day, at a reasonable cost, and what modifications, if any, are permissible in order to lessen this cost without interfering with the practical operation of the catalyst, are problems that can be solved only by diligent experimentation on a laboratory and on a factory scale. In addition to the successful work which has unquestionably been done abroad, such investigations have been recently undertaken by several different agencies in this country and considerable progress has been made. From one source of unquestioned authority, I am authorized to make the following statement:

"Independent laboratory investigations have definitely shown that we can purify coke-oven ammonia on a commercial scale quite well enough to permit satisfactory oxidation to nitric acid. The expense of purification is well within reasonable limits, and the experiments indicate that there is no practical obstacle to the use of coke-oven ammonia for nitric acid manufacture. Definite statements on this point are withheld until an actual commercial demonstration can be made."

As further evidence of the practicability of the oxidation process, I am indebted to Mr. Lewis A. Riley, of New York City, for the following brief statement of the Ostwald process for the oxidation of coal ammonia to nitric acid:

"In the year 1900 Professor Ostwald made arrangements to carry on his experiments with the Central Station for Scientific Technical Investigations in Neubabelsberg, near Berlin, which was an Institution supported by a number of explosive works in Germany to undertake industrial investigations and work out technical processes. These experiments were under the general direction of Herr Geheimrath von Duttenhofer of the Rottweiler Explosive Works. Before the conclusion of this experimental work in the year 1903 Herr von Duttenhofer died and his successor abandoned the work in an unfinished condition."

"The Chemical Works Griesheim-Elektron next interested themselves in the matter and carried on some experimental work in which the previous apparatus from Berlin was used."

"In the summer of 1904 official tests gave only 70 per cent conversion efficiency which appeared insufficient for commercial success. This led the Griesheim Works to abandon the experiments, although immediately subsequent to these tests the cause of the low yield was discovered and remedied, it being found that the platinum contacts required more frequent changing."

"The process was then taken up by the Gewerkschaft des Steinkohlenbergwerks Lothringen at Gerthe, near Bochum, and in 1906 a small plant was put down and operated there, which gave a conversion of 85 per cent on which results the Lothringen Company decided to proceed with the building of a large plant."

"The construction of this large plant was badly handled and resulted in some unfortunate litigation, owing to the constructing engineers and manufacturers having departed from the designs and specifications in certain parts and some of the auxiliary apparatus gave considerable trouble."

"The plant was in certain respects rebuilt and although the first cost of the plant was on this account considerably higher than should have been the case, it was, nevertheless, satisfactorily completed in 1908 and since December of that year it has operated continuously."

"Sometime during the year 1910 the operation of this plant was carefully investigated and tested by the Nitrate Products Company, Ltd., of London, and was purchased by this com-

<sup>1</sup> See paper "Ammonium Sulfate as a Source of Combined Nitrogen," by J. W. Turrentine, *This Journal*, 8 (1916), 584; H. Koppers Company, Pittsburgh, Pa., Pamphlet, May, 1916; "Position of Gas Industry in the Nation's Scheme for Preparedness," by W. H. Gantley, *Gas Institute News*, 5 (1916), 302; paper "Sources of Nitrogen Compounds in the United States," by Chester G. Gilbert, Smithsonian Institution, June, 1916.

pany which is understood to be closely affiliated with the cyanamide interests. The purchase was made based on this investigation and tests which were stated to show a conversion efficiency of 85 per cent on the basis of ammonia to nitric acid, corresponding to the tests of the experimental plant of the Lothringen Company and on which the latter company originally accepted the process.

"The plant since beginning operations in 1908 down to a period just preceding the present war had operated practically continuously, using coal-ammonia from the Bochum coke-ovens for the production of nitric acid.\* The nitric acid produced was then used for the further absorption of additional ammonia in the production of commercial ammonium nitrate which has been disposed of on the market as such. This plant and process was, therefore, developed and perfected in the use of coal-ammonia as the nitric acid raw material and its success on this material was thoroughly demonstrated both by the operations conducted by the original owners, the Lothringen Company, and subsequently by the Nitrate Products Company.

"A further development of this plant and process has been its application to the oxidation of cyanamide ammonia and it is understood that the second plant built for the commercial oxidation of ammonia which was located in Belgium was designed for the utilization of cyanamide-ammonia.

"Test figures on the operation of this plant for a 20-month period show 83 per cent nitric acid conversion with 97 per cent ammonia absorption.

"The ammonia oxidation process has, since 1910, been controlled by the Nitrate Products Company. It is understood that its application by this company has been restricted to the oxidation of cyanamide-ammonia although the Gerthe plant was being successfully operated on coal-ammonia up to the start of the present war."

To this statement I may add that, according to Lunge<sup>1</sup> on the authority of the Deutsche Ammoniak-Verkaufs-Vereinigung, the sales of ammonium nitrate produced by the Ostwald process at the Lothringen plant, were as follows: 651 tons in 1908; 1,096 tons in 1909; 1,237 tons in 1910; about the same in 1911. All these amounts and the subsequent production to the opening of the war are to be credited to coal-ammonia.

In conclusion I may cite the following summary, from the last edition of Lunge, which carries additional weight, coming as it does from Central Europe, where they have produced more ammonia from coal, and more from the atmosphere, and have transformed more of it into nitric acid, than in any other country:

"The synthetical production of ammonia from atmospheric nitrogen must find its limits in the impossibility of producing the requisite enormous amount of electrical energy *in infinitum*, whether by water-power or otherwise. As far as we can look forward, the principal source of ammonia will be always the nitrogen of coal, just as this has been the case for a long time past in the case of the comparatively small fraction of coal consumed for the manufacture of illuminating-gas, and more recently by carrying out the coking of the coal in such a way that the formerly lost by-products, ammonia and tar, are recovered. This last proceeding is sure to be more and more extended. Even the general conversion of the coal to be used for heating, into gaseous fuel, with recovery of its nitrogen in the shape of ammonia, is within visible distance."

THE BARRETT COMPANY

17 BATTERY PLACE, NEW YORK CITY

## EARLY CHEMICAL MANUFACTURING IN PHILADELPHIA<sup>2</sup>

By SAMUEL P. SADLER

Received October 24, 1916

The earliest efforts at chemical manufacturing in Philadelphia, as in other parts of the American Colonies, were undoubtedly due to the feeling of the colonists that they must free themselves from the oppressive trade regulations of the mother country. We read in the sketch of the career of one of the pioneers of Philadelphia chemical industry, the following:

"The earliest efforts of the colonists—the manufacture of coarse, woolen fabrics in 1719—so excited the jealousy of Great Britain that the English Parliament declared 'that the erecting of factories in the colonies must be discouraged at all cost,' so

every enterprise met with great opposition. It was not, however, until 1774 that Pennsylvania became so aroused by English oppression of her industries that a convention of delegates from all the counties was held in Philadelphia. Joseph Reed was president, Jonathan B. Smith, John Benezet and Francis Johnston were secretaries. The convention earnestly enforced the strict observance of non-importation agreements and to provide against the inconvenience which might result, recommended the preservation of sheep until they were four years old, and the immediate establishment of the manufacture of woollens, salt, saltpetre, iron, nails, copper in sheets and kettles, malt liquors and gunpowder especially, 'as there existed a great necessity for the latter, particularly in the Indian trade.' The convention advised the exclusive use of home manufactured articles and urged that associations be immediately formed for the encouragement of all domestic productions."

This feeling only came to a head about the time of the beginning of the Revolutionary War. Prior to that, in the Colonial period, the production of potashes and lime, some attempts at the extraction of salt from brines, tentative efforts at the making of gunpowder, and domestic utilization of the potashes in soap-boiling about comprised the chemical manufacturing industry. Of these the most important was the manufacture of potash from wood-ashes. Scharf and Westcott's "History of Philadelphia" states that in 1772 the value of the potashes manufactured in America was £50,000.

As before stated, the oppressive trade regulations of England acted as an impelling force in the establishment of chemical industries. Thus the exportation of powder and its materials from England was prohibited by an order of Council of October 19, 1774, so that the American Colonies were made dependent on other sources for their supply.

"The Continental Congress in various ways encouraged the erection of powder mills and also the production of nitrate of potash. Congress in 1775 published a manual giving directions for making saltpetre, and about the same time the 'Committee of the City and Liberties' erected a large saltpetre works on Market Street for the double purpose of making saltpetre and also to instruct such as were willing to engage in the making of this very necessary article for the powder mills.

"The manufacture of gunpowder was very extensively carried on during the Revolution in nearly all of the American Colonies. A very large proportion of this powder, however, was made in Pennsylvania. Philadelphia was among the first places in which powder mills were successfully operated.

"Early in the Revolution a public powder mill was established in or near Philadelphia by the Assembly, while Congress opened, and for some time operated, what was known as 'The Continental Powder Mill.' Congress also offered advances to such persons as would be willing to establish powder mills within 50 miles of the city of Philadelphia, and this offer was taken advantage of by many who subsequently supplied a liberal proportion of the powder used in the Continental Army."

But to come back to the efforts of the Colonists to free themselves in other lines from dependence on the mother country, we read in the sketch of the career of Samuel Wetherill, from which we previously quoted:

"Samuel Wetherill was one of the promoters and managers of the 'United Company of Pennsylvania for the establishment of American Manufactures.' He embarked his whole soul in the business, and in 1775 set up at his own dwelling house in South Alley, then called Hudson Square, now Commerce Street, a factory for jeans, fustians, everlastings and coatings (Fustian is a cloth, the warp of which is linen and the woof thick cotton; it derived its name from Fusht, a town on the Nile where it was first made). This business was just for spinning and carding and did not necessitate any heavy machinery, but in order to prepare these goods properly it was necessary to have them dyed. There being no dyers in Philadelphia equal to the task, Samuel Wetherill was obliged to undertake this branch of the business also. His house on South Alley is described as being of two frames, which I suppose means what we would call a double house, and he was probably able to turn one frame into a factory and let his family live in the other. However that may be, a little inconvenience more or less in those days did not matter, where all were working together for the common good and for the highest principles. \* \* \* So it was that Samuel Wetherill, who started as a carpenter, became a weaver, then chemist, etc., and when the war broke out he did

<sup>1</sup> "Coal-Tar and Ammonia," 5th ed., 1916, p. 1572.

<sup>2</sup> Address before the Philadelphia Section of the American Chemical Society, October 19, 1916.



not scruple about entering into a contract with Congress to furnish clothes for the patriot troops, being a patriot himself; and it is said that his timely shipment of supplies to Washington's little army at Valley Forge saved it from disbanding. This, his allegiance to his country, and his expressed approval of bearing arms for its defense, were the cause of his being 'dealt with' by the Society of Friends and cut off from religious communication and fellowship with them. Thereupon he and a few others who had publicly taken the oath of allegiance to the American cause started the Society called the 'Free or Fighting Quakers.' "

"Probably the first to inaugurate the manufacture of chemicals, as such, in this country, was the firm of Christopher, Jr., and Charles Marshall, sons and successors of Christopher Marshall, an early druggist and one of the original 'fighting Quakers' of Philadelphia. This firm had, as early as 1786, entered quite extensively into the business of making muriate of ammonia and Glauber's salt. The factory is described by Watson, in his 'Annals of Philadelphia,' as being a grim and forbidding-looking building on Third Street near the stone bridge over the Cohocksink Creek. This firm is said to have developed an annual output of upwards of 6,000 lbs. of muriate of ammonia: quite an achievement for that time."

#### MANUFACTURE OF SULFURIC AND OTHER ACIDS

Let us now take up the beginnings of the manufacture in Philadelphia of one of the fundamentally important chemicals, *vis.*, sulfuric acid. This substance is recognized as the basis of all chemical industries and its manufacture must precede that of most other chemicals. The theory of the lead-chamber process was already understood by chemists, by the middle of the eighteenth century. Ward had made it in England in 1740 on a large scale in glass vessels, and Dr. Roebuck first used leaden chambers instead of glass in Birmingham in 1746. The first lead chamber was erected in France at Rouen in 1766.

Mr. John Harrison, the son of Thomas Harrison, a member of the Society of Friends, was an early Philadelphia druggist who had completed his education by spending two years in Europe, in part under the instruction of Dr. Joseph Priestley, the famous English chemist. Upon his return he began, in 1793, the manufacture in Philadelphia of various chemicals, and notably of sulfuric acid. He had at first a lead chamber capable of producing 300 carboys of acid per annum, and his laboratory at this time was on the north side of Green Street, west of Third. In 1804, he established a new factory at Second and Huntingdon Streets, near Frankford Road, Kensington, but continued for a time the work on Green Street. In 1807 he built what was for that time quite a large lead chamber; it was 50 ft. long, 18 ft. wide, and 18 ft. high, and capable of making nearly 500,000 lbs. of sulfuric acid annually, the price of which was then as high as 15 c. per lb.

"As is well known, acid produced in lead chambers is not the Oil of Vitriol of commerce, and the only method known at that time to concentrate it to the required strength was by boiling it in glass retorts—a very precarious and dangerous process. The constant breakage of the glass largely increased the cost of the concentrated acid and the dangers of the work. To obviate this great trouble Mr. Harrison, in 1814, introduced the use of platinum for the manufacture of sulfuric acid, for the first time, at least in this country. In the previous year, 1813, Dr. Eric Bollman, a Dane, had come to Philadelphia. Dr. Bollman was familiar with the metallurgy of platinum, and a highly scientific man. He brought with him from France Dr. Wollaston's method for converting the crude grains of platinum into bars and sheets. About the first use that Dr. Bollman made of these platinum sheets was the construction, early in 1814, of a still for the concentration of sulfuric acid for the Harrison works. It weighed 700 oz., had a capacity of 25 gal. and was in continuous use for 15 years. This early application of platinum for such purposes was highly characteristic of the sagacity and ingenuity of the American manufacturer. At the time the use of this rare metal was a novelty in Europe and known only to a few persons and certainly entirely unknown in this country. It follows, therefore, that Mr. John Harrison was not only the earliest successful manufacturer of sulfuric acid in America, but the first in this country to concentrate it in platinum."

Farr and Kunzi were next in Philadelphia to follow the lead

of Harrison in making sulfuric acid which it is stated they did in 1812, and shortly thereafter Wetherill & Bros. also began the manufacture of sulfuric acid on the east bank of the Schuylkill River. Chas. Lennig, the founder of the present firm of Chas. Lennig & Co., Inc., also began the manufacture of sulfuric acid in 1829, Rosengarten & Sons shortly thereafter, and Carter & Scattergood in 1834 also were early manufacturers of sulfuric acid.

Nitric acid, under the name of *aqua fortis*, is mentioned in Scharf & Wescott's "History of Philadelphia" as made by Christopher Marshall, Jr., a Philadelphia druggist, at the close of the last century. A communication from Mr. Thos. Skelton Harrison says his grandfather, John Harrison, began to make both nitric and muriatic acids in 1804. Carter & Scattergood had it on their list of manufactures in 1834. Muriatic acid is also mentioned as made by this latter firm in the year 1834, as were tartaric acid and citric acid.

#### MANUFACTURE OF PAINT COLORS

We have here another record of which Philadelphia may be proud. We have already referred to the energetic work of Samuel Wetherill in starting American lines of manufacture just prior to the opening of the Revolutionary War. About 1789 he began the manufacture of white lead in Philadelphia and persisted in it, despite great efforts made on the part of the importers to hinder him by underselling and misrepresenting him. The first white lead factory of Samuel Wetherill & Sons was built in 1804 at the corner of Broad & Chestnut Streets, but it was burned down a few years later, and in 1808 they erected a new factory at 12th & Cherry Streets.

"His son, Samuel Wetherill, Jr., was the active man of the concern, and assisted his father in all business matters. The enforced experience which was pressed upon them during the revolution, concentrated their attention upon the manufacture and sale of chemicals, and they went into the drug business. In 1785 Samuel Wetherill & Son were located in Front Street above Arch. Here, for many years, 'Wetherill's drug store' was an old landmark, and the place at which sons and grandsons were brought up to the business. The Wetherills were the pioneers in the manufacture of white lead. They established it before the year 1790. They erected extensive white lead works near Twelfth and Cherry Streets, which were burnt down in 1813, but afterwards rebuilt.

"The fire which destroyed the white lead works proved to be incendiary and started by a young English officer the day before he sailed for England.

"In October, 1811, Samuel Wetherill, Jr., obtained patents for a new mode of washing white lead and for screening and separating metallic from corroded lead in the process of making red lead, and using the first machine ever used for manufacturing purposes in the United States. This method has been generally adopted and used by all makers of lead.

"The name of the first white lead firm was Samuel Wetherill & Son, Samuel Wetherill, Jr., evidently being the active member. After his father's death in 1816, Samuel Wetherill, Jr.'s, sons joined in the business and the firm became Samuel Wetherill & Sons. After the death of Samuel Wetherill, Jr., in 1829 it became Wetherill Brothers. The store of the firm was at 65 N. Front Street; the warehouse and mill of the old establishment were on Coomb's Alley, back of Second Street.

"When the residence part of the city spread to Twelfth & Cherry Streets, Samuel Wetherill, having bought ten acres of land on the bank of the Schuylkill River below Chestnut Street, moved there in 1847; his sons (Wetherill and Brother) built the white lead and chemical works and continue to this day."

John Harrison also began the manufacture of white lead in 1806. The firm of Mordecai & Samuel N. Lewis, which afterwards became John T. Lewis & Brothers, also began the manufacture of white lead in 1812, making three Philadelphia firms manufacturing paint colors at that time. These three earliest manufacturers of white lead and paint colors or their lineal successors have continued in business to the present time, for considerably over a century, and have done much to give Philadelphia its long-continued prominence as a chemical manufacturing center.

"Chromates were probably first made in Baltimore, though as early as 1816 a Mr. Wesener, a German chemist, had established himself in Philadelphia, in the neighborhood of Broad & Cherry Streets, where he made chrome salts and chrome pigments in considerable quantities. Being nearer the source of supply of the raw material, the Baltimore manufacturers had a decided advantage, so much so that before the middle of the last century the business had drifted back to that city."

The manufacture of varnishes followed that of paint colors. Christian Schrack, who was a manufacturer of paints in Philadelphia in 1816, later established the varnish manufacture, and already in 1836 an export trade in American-made varnishes had begun.

The manufacture of shot by the granulation of lead, while not properly called a chemical industry, is closely related to the lead pigment manufacture. This manufacture of lead shot was one of Philadelphia's earliest industries. From Winslow's "Biographies of Successful Philadelphia Merchants," page 142, we quote:

"On the fourth of July, 1808, the corner-stone of the South-wark shot tower, in John Street, between Front and Second, was laid by the firm of Cousland, Bishop and Sparks, and the building was pressed forward rapidly to completion. Thomas Sparks paid particular attention to this branch of the business, and in a short time the patent shot of the firm became celebrated throughout the country. So long as this article was used by sportsmen and hunters, there seemed to be no difficulty about the property of the manufacture in the firm. But when the war of 1812 broke out, the firm then being Bishop and Sparks, the senior partner, who was a consistent member of the Society of Friends, felt conscientious scruples as to the rightfulness of continuing a manufacture which the United States now demanded should be turned to the production of munitions of war. John Bishop, therefore, withdrew from the firm, and retired from business.

"Thomas Sparks, therefore, continued the business for several years alone. In 1818 he took into partnership his brother, Richard Sparks, and the firm continued at No. 49 South Wharves, as Thomas and Richard Sparks, the shot tower operations being in full play. It was necessary that they should reside near the tower, and accordingly Thomas had his house at No. 476 South Front Street and Richard at No. 478. This partnership did not last very long. Richard Sparks fell a victim to the yellow fever in the year 1821, and for many years Thomas Sparks continued at No. 49 South Wharves, and at the shot tower, without a partner. In the year 1838 he took in with him his nephew, Thomas Sparks, Jr., a son of Richard. The business was then conducted under the firm name of Thomas & Thomas Sparks, Jr., at the old stand, which from No. 49 South Wharves had become No. 49 South Delaware Avenue."

One of the lines of manufacture that contributed to make Philadelphia a great chemical center early in the last century was that of the yellow and red prussiates of potash. I have been furnished a private memorandum concerning the activities of the firm who began this industry and were active in it for many years.

"Under the firm name of Carter & Scattergood a profitable chemical manufacturing business was conducted from 1834 to 1911; and was absorbed in the latter year by The Henry Bower Chemical Mfg. Co.

"John Carter and Joseph Scattergood bought out the old established business of 'John & Daniel Elliott' founded in 1754 by their grandfather, John Elliott.

"The Elliotts' place of business and factory was originally on Front St. between Chestnut & Walnut Streets, but in 1812 the manufacturing work was transferred to a new factory which they erected at 19th & Pine Streets, John Carter becoming their apprentice January 1, 1816.

"The list of chemicals produced by Carter & Scattergood was an extensive one, John Carter being the manufacturer and Joseph Scattergood the business man of the concern. It included citric, tartaric, oxalic, nitric and sulfuric acids, bichromate and prussiates of potash and many other articles, but their operations during the first 10 years of their business were on a scale which in this day would be considered quite small.

"Yellow prussiate of potash was first made by them in 1834 (that being so far as known the first production of the article in America), but the demand was very small, only 472 lbs. being absorbed by the market in that year. In 1835 the sales in-

creased to 6443 lbs. but it was not until 1843 that the demand became large, the sales amounting in that year to 69,470 lbs. and rapidly increasing in the next two years, the sales in 1845 being 207,522 lbs.

"The high price, over 50 c. per lb., and the keen demand, of course resulted in active competition, and the market for many years was oversupplied.

"In the year 1846 Carter and Scattergood began to produce red prussiate of potash, being the first in America. This was a highly profitable branch of the business until the introduction of coal-tar dyes, as substitutes for prussiate colors on woolen goods, gradually displaced it in the most important field of consumption. Except for the manufacture of *Blue-Print Paper*, there is now very little demand for it."

Potash and ammonia alums were first made in Philadelphia by Chas. Lennig in 1837 and by Harrison Bros. in 1840.

Coming now to the early manufacture of medicinal or pharmaceutical chemicals which has long made Philadelphia famous, we find that George D. Rosengarten and Charles Zeitler as Rosengarten & Zeitler began the manufacture of chemicals in St. John Street, Philadelphia, about 1822. They were the first to manufacture the alkaloids of cinchona and opium in this country, having begun the manufacture of sulfate of quinine in 1823, of sulfate of morphia in 1832, and strychnine in 1834. The salts of quinine were also manufactured by John Farr in 1825.

These two firms and their successors have had much to do with the establishment of Philadelphia as a chemical manufacturing center. After the withdrawal of Mr. Zeitler which took place within a year, Mr. Rosengarten continued alone, later taking in a Mr. Dennis. When this partner withdrew some 20 years later, the firm became Rosengarten & Sons, which business continued until the formation of the present combination with the other large Philadelphia manufacturer of medicinal chemicals, Powers & Weightman.

"Farr & Kunzi began the manufacture of chemicals about 1818. Abraham Kunzi, a Swiss by birth, retired in 1838, and the senior partner, John Farr, who had been born and brought up in England, associated with himself Thomas H. Powers and William Weightman, two young Philadelphians, who had been in the employ of the firm for some time. The new firm name was John Farr & Co. This was later changed to Farr, Powers & Weightman, and, on the death of the senior partner in 1841, the firm name was again changed; this time to the title—Powers & Weightman, by which it was so long known throughout the entire country."

These two firms in 1905 united under the name of the Powers-Weightman-Rosengarten Co. and continued as probably the best-known manufacturers of general and medicinal chemicals in the United States.

The history of the commercial production of pure glycerine is also of interest in this account of Philadelphia's chemical achievements.

The late Robert Shoemaker while making medicinal plasters had his attention directed by Prof. Wm. Procter to the residuum liquid which was obtained. From this he prepared the first glycerine made in this city, if not in America, in 1846, and this was exhibited by Prof. Procter to his class at the Philadelphia College of Pharmacy at the time. Mr. Shoemaker manufactured it for sale according to his statement for some years in connection with the manufacture of lead plaster.

The later development of the refining of waste lyes containing glycerine was also a Philadelphia achievement and was worked out by the late Henry Bower. By the courtesy of his son, Mr. W. H. Bower, I am allowed to quote from a private letter which gives the account of his work, in his own words:

"Quite early in life, say in 1857, my attention was keenly directed to some mode of purifying these waste liquors of the stearine candle factories, and in that year I could have purchased the entire product of crude glycerine of the United States for a sum not exceeding \$5000, although the manufacture of it was nearly if not quite as large then, as now.

"I commenced work in earnest to experiment in purifying glycerine in 1858—and expended long and weary efforts, all my



earnings, as well as some borrowed money. I at first succeeded in producing an article sufficiently pure for use in gas meters (a place of alcohol) to prevent freezing and stoppage of the instrument. It was not however until about the middle of 1860 that I succeeded in making and placing in the market a "pure inodorous glycerine," even then the amount sold was quite insignificant. Inferior grades made their appearance about the same time in the West. The bland and neutral nature of the article, and the discovery of various uses for it, soon increased the demand to a marked extent; I was enabled from time to time to increase my works, and in increasing them was making steady inroad into the supply of the crude article. At this period, say in 1863, the business of refining glycerine was scarcely known on the continent of Europe, and I exported small quantities to Hamburg paying a profit; Belgium, France, Germany and Austria were immense producers of crude glycerine, but like its sister product here in previous years, it only found its way to the sea. As before stated, the use and sale of the refined continued to improve, the crude growing more scarce each season, until a point has been reached when every available pound is worked into a valuable product. It would not be out of the way to place the total value of all the glycerine sold in the United States at this time at \$500,000. This sum could never have been reached had it not been for the discovery of a mode for refining, to which, so far as this country is concerned, I lay claim; by a careful management of my business for some years I kept the process a secret; but in time some portions of it came to the knowledge of other persons, who have been enabled to produce very fair articles. There are besides myself, here, two refiners in Cincinnati, one in Chicago, and one in New York."

There were of course other drug and chemical firms who were well and favorably known in the early half as well as the later half of the nineteenth century.

We have already mentioned the name of Christopher Marshall, Jr., who was active in Revolutionary days. Himself the son of a druggist, he was succeeded by his son, Charles Marshall, and his grandson, Charles Marshall, Jr., who in 1814 established himself in the wholesale business at 310 Market Street.

With this Charles Marshall, Jr., entered as an apprentice Geo. W. Carpenter, who later became one of the most prominent as well as successful of wholesale druggists in Philadelphia. The old store of Carpenter & Henszey at Eighth and Market Streets I remember quite well as it stood about 40 years ago.

A very well-known drug firm of the latter half of the nineteenth century was that of Bullock & Crenshaw. They were the successors to Smith & Hodgson who established themselves as druggists at the corner of 6th and Arch Streets in 1819 where they continued until 1849 when they disposed of their drug business to two of their employees who then formed the firm of Bullock & Crenshaw. This firm carried on not only a wholesale drug business but handled fine chemicals and chemical apparatus, supplying many colleges and schools throughout the country. In September, 1868, they moved to 528 Arch Street where in larger quarters they carried on a flourishing business until the death of Mr. Chas. Bullock, the surviving partner.

The firm French, Richards & Co. was for many years one of the best known of Philadelphia drug firms at its centrally located store, Tenth and Market Streets. The founder of this firm was Clayton French who in 1840 entered the drug business as an apprentice with a Dr. Edward S. Wilcox. This firm was disbanded in 1890 on the death of its founder, but in the meantime its extensive cement and plaster department which was started in 1852 at Callowhill Street and York Ave., had been erected in 1883 into a separate business of Samuel H. French & Co. This has since developed into a very extensive cement, plaster and dry color firm, now under the leadership of Howard B. French, a son of Samuel H. French of the original French, Richards & Co. firm.

In conclusion I wish to acknowledge my indebtedness to various friends for furnishing special information and the loan of papers, books and pictures of early chemical establishments. I would specially mention Mr. Wm. H. Bower, Mr. W. C. Carnell, Mr. Thos. S. Harrison, Dr. Ewing Jordan, Librarian of the Uni-

versity Club, and Mr. Spofford, the Assistant Librarian of the Historical Society, Mr. Howard B. French, Prof. Henry Kraemer of the Philadelphia College of Pharmacy, and Mr. Martin I. Wilbert, formerly in this city but now in Washington, D. C. The last named published a valuable paper in the *Franklin Institute Journal* for May, 1904, on "Early Chemical Manufactures," from which I have quoted in the preparation of this paper.

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## NECESSITY OF PROPER TARIFF LEGISLATION TO INFLUENCE THE DEVELOPMENT OF THE MANUFACTURE OF MEDICINAL CHEMICALS IN THE UNITED STATES<sup>1</sup>

By GASTON DUBOIS

The Tariff Act of Oct. 3, 1913, can best be defined as a jungle through which no human being could find his way, but which to some extent has been remedied by the Revenue Bill recently enacted into law. We can find in the 1913 Tariff Act such anomalies as benzol, naphthol, resorcin, jammed together in one paragraph at 5 per cent *ad valorem*, followed by chloroform and carbon tetrachloride 1 c. per lb., and then after the coal-tar intermediates at 10 per cent *ad valorem* comes cobalt oxide 10 c. per lb. Surely Mark Twain himself could not have written a better tariff.

We all know and appreciate, however, the enormous amount of work entailed by a tariff revision, and although it is often difficult for our legislators to understand the relation existing between the several products found in any one paragraph of the tariff, we may safely trust them, knowing that every item was thoroughly considered. Even though political opinions may often have thrown the balance to one side or the other, we must admit that every tariff, even though far from perfect, was the result of an honest intention to give the country the best that could be had.

A few months ago, when the Revenue bill was being discussed in Washington, the purpose of which was also to encourage the production of dyes in this country, some Congressman suggested a very brilliant division of the Coal-Tar Products, this division to form the basis of a tariff revision which had become imperative. You are probably familiar with this new revision now in force since Sept. 8, 1916.

Group 1, *Free list*, contains products of coal-tar distillation.

Group 2, with a duty of 15 per cent *ad valorem*, contains all the intermediates, and also some refined products of coal-tar distillation, obtained in whole or in part from products of Group 1.

Group 3, with a duty of 30 per cent *ad valorem*, contains all colors, dyes, photographic chemicals, medicinals and flavors, phenolic resin and explosives, obtained in part or in whole from products of Group 2.

Following this division is a paragraph providing for a 2½ c. per lb. additional duty upon all articles contained in Group 2, and a duty of 5 c. per lb. upon all articles contained in Group 3, excepting, however, alizarin, indigo, medicinals and flavors.

Unquestionably, the above division appears perfectly logical to chemists as it has the great advantage of being based on a scientifically logical foundation. One point, however, is most striking, and that is the exemption of medicinals and flavors, made from products contained in Group 2, from the additional duty of 5 c. per lb.

We are confronted here with a puzzle in an otherwise most harmonious composition. It should be noted that only the medicinal products produced from coal-tar intermediates are exempt of the 5 c. per lb. duty, while other medicinal products not derived from coal tar are not here considered and retain the duty (provided for in the Tariff Act of 1913) of 15 per cent.

<sup>1</sup> Written for the Industrial Conference on Manufacture of Medicinal and Pharmaceutical Products, 53rd Meeting of American Chemical Society, New York, September 25 to 30, 1916.

The manufacture of dyestuffs and that of coal-tar medicinals are so closely interwoven that the interests of both are identical and practically inseparable.

Both the manufacturers of dyes and those of medicinal products have heretofore imported their raw materials or intermediates from Germany, and to a small extent from England. This, to a certain extent, demonstrates the similarity of the position of the above mentioned manufacturers, for to both industries, conditions in this country previous to the war were not such as to encourage an attempt to manufacture these materials.

Another striking illustration of the close relation of the two named industries is the fact that in Germany there is not a single large dye manufacturer, who does not also manufacture medicinals. This is not an accident but the result of a logical development of two industries working hand in hand and depending one upon the other.

Speaking to chemists, it is unnecessary to further elaborate, as I am convinced that no well informed chemist would contradict the above statements.

Why is it, then, that our legislators apparently fail to fully grasp this situation? And why is it that those interested in a proper rate of duty for dyestuffs omit in all their arguments and all their discussions any reference whatever to medicinals produced from coal tar, and why is it also that even photographic chemicals from coal tar are favored as against medicinals? Why are we confronted by this apparent discrimination in favor of dyes, photographic chemicals and explosives and against medicinals and flavors, when all belong to the same class of chemicals?

Of the many explanations which might be brought forward to explain this anomaly, let us believe that the desire for cheap medicines for the people brought about the above mentioned discrimination. The question now to determine is whether this particular action on the part of Congress is justifiable or not.

Let us answer this question by a second question.

Why was the duty on dyes, explosives, and photographic chemicals raised?

It unquestionably was in order to aid in developing those industries in this country.

The logical conclusion would be, that in view of the discrimination against medicinals and flavors, it was not the intention of Congress to aid in developing the manufacture of these valuable coal-tar products in this country.

Will this situation tend to cheapen these medicinals in this country?

The National Association of Manufacturers of Medicinal Products composed, however, mostly of buyers of medicinal products manufactured from the by-products of the coal-tar industry, has asked for a better protection on these manufactured medicinal products; certainly not in order to increase the cost of these medicinals which they must buy, but evidently because they believe that American domestic production of these products, promoted by proper and fair tariff rates, must bring about a reduction in cost to them.

The following is Congressman Hill's opinion expressed several months ago:

"The practical famine of dyestuffs which exists in the United States and in the whole world, is proof of the supreme folly which is now shown in allowing one nation in the world to control all others in any industry.

"When it comes to the point that American manufacturers are compelled to scour China for the leavings of German dyes in order to continue their manufacturing operations in America, it would seem as though it was high time to put this nation on a self-reliant and independent basis, and the report of the chemical society is the clearest and most intelligent presentation of the situation which has yet been made of this whole subject by men who are thoroughly familiar with the industry and know whereof they are speaking."

Why is it that this otherwise so valuable document reported by the committee, makes no reference whatever to medicinals and flavors?

We should be interested in the development and perpetuation

of an independent domestic production of these essential products, the coal-tar medicinals, so that there may be domestic competition with foreign producers after the war.

It is to the interest of the dye industry to encourage the development of the manufacture of medicinals and synthetic flavors produced from intermediates, as it assures a ready market for some by-products obtained in the manufacture of dyes.

Let us now see what other nations are doing to protect their chemical industries.

We have heard of recent agreements among German dyestuff manufacturers who, as already stated, are also the greatest manufacturers of medicinal and fine chemicals.

The German dyestuff manufacturers have taken steps that are likely to be of far-reaching industrial importance. According to a report of the U. S. Consul at Frankfurt on the Main, the two important groups among the large important dyestuff and chemical industries of Germany have combined in a defensive alliance. Arrangement is being made for a mutual exchange of information as to factory methods and other matters tending to reduce the cost of manufacture and otherwise strengthen the industry as a whole. The total profits are to be divided at the end of the year, according to an agreed scale.

The concerns named as included in the new arrangement are the following:

	Capital Stock in Marks
Badische Anilin- und Sodafabrik.....	54,000,000
Farbwerke von Meister, Lucius & Brüning.....	54,000,000
Leopold Cassella & Co.....	30,000,000
Farbenfabriken Friedrich Bayer & Co.....	54,000,000
Aktiengesellschaft für Anilin-Fabrikation.....	19,800,000
Chemische Fabriken vorm. Weiler ter Meer.....	8,000,000
Kalle & Co.....	6,000,000

These firms combined represent a capital of 225,800,000 marks, or about \$55,000,000.

England is also preparing an alliance, Brunner Mond Co. with Castner-Kellner Alkali Co. A strong association of the manufacturing interests is in process of formation; the object will be to foster the trade of the empire under the new conditions which will arise after the war. The membership already represents capital to the amount of over 80,000,000 pounds sterling, or roughly about \$400,000,000.

Prospects point to the possibility that a severe international contest will be witnessed after the war.

Japan, in her quiet manner, with the full coöperation and support of the government, is pushing ahead in the production of chemicals. According to articles which recently appeared in the Japanese press, the following products are now being produced in Japan: acetanilide, antipyrine, aspirin, carbolic acid, phenacetin, salicylic acid, salol, sodium salicylates, caffeine, bismuth subnitrate, bromine, bromides, ether, formalin, glycerine, iodoform, lactic acid, menthol, morphine, naphthalene, benzol, etc., tannic acid, picric acid, magnesium salts, etc., and many others.

We find all nations actively engaged in building up industrial combinations, and it is important that we look ahead in view of the great industrial strife which will follow the war.

The organic branch of the chemical industry in the United States is still in its infancy. The whole country, however, realizes to-day more than ever, the importance of the chemical industry, and while heretofore many of our legislators were satisfied that dyes, medicinals, etc., such as we require, should be manufactured for us in Germany, to-day there is a growing belief that we should develop independent domestic production.

The firm with which I am connected has, since the war started, undertaken the manufacture of several intermediates and other finished products. We are manufacturing phthalic anhydride, parphenetidin, phenol, aniline, acetanilide, coumarin, products enabling us to a certain extent to continue the production of pharmaceutical products which we were manufacturing before the war.

To continue the manufacture of chemicals in the face of the impending trade war, will require the united efforts of all, legis-



lative bodies, manufacturers, those indirectly interested in the growth of American chemical manufacture, and last, but not least, we require the aggressive support of the Chemical Society individually and collectively to act as a connecting link between the various chemical manufacturing branches.

The most productive field, it would appear, in which to direct the united efforts of all is to assist in providing for fair and proper tariff legislation.

### CAPITALIZATION OF TRAINING AS A BASIS FOR COMPENSATION

By E. O. HEINRICH

Received October 28, 1916

During the several years that I have been engaged in independent practice I have received numerous applications for work from chemists in various stages of professional development. In nearly every case the applicant had no definite ideas regarding the value of his services either to himself or to me and stated his case with considerable detriment to himself.

Even among the mature chemical workers of my acquaintance the fundamental propositions of business do not seem to be included in all instances in their valuation of services rendered or sought. On the contrary the view seems to prevail that the cost of living is synonymous with the cost of production of service and if this is covered, all is well.

What I have to suggest here is neither new nor novel. My whole purpose is to make a comparison which may be of service in affording a slightly different angle of view on the question of pay; to suggest a test for comparing service with compensation; and to intimate that the cost of living is not completely synonymous with the cost of service production.

No matter what may be the stage of his career, the chemist's essential capital consists of 1400 g. of gray matter, supposedly keen. His progress in a large measure depends on how he values and markets what he can extract from it and convert into service. Under our competitive conditions he must regard himself as a salesman and sell his services under the same principles which govern the sale of commodities.

These principles may be stated thus:

- (1) Service rendered must produce a profit to the recipient, thereby fixing its maximum value.
- (2) Service rendered must yield a profit to the producer, thereby fixing its minimum value.

All too often is the chemist inclined to overlook that jobs and lines of business follow these common rules. He sees only the leaves and thinks not of the root.

The acorn of business is capital, by which is meant accumulations of productive wealth. Like a living thing the growth of business requires constant intensive cultivation, with constant comparative reference to the original acorn and the tap root which sprang from it.

In a like manner the job, by which is meant that which produces income through service, has somewhere in it a tangible acorn from which it sprang and a tap root to keep it steady. This acorn is nothing else than the cost of preparation, computed as fairly as possible, with suitable credits and debits from time to time for appreciation and depreciation with changing environment.

From this point of view it becomes apparent that the charge for rendering service legitimately includes other things besides mere cost of living. As a matter of fact a certain investment has been made in training and equipment in order to produce a minimum earning capacity and the cost of living merely enters as the acid test to determine the sufficiency of the investment.

The real factors to be taken into consideration are (1) equipment and overhead charges; (2) capacity for work, or, the time element. These are all elements which can be determined with a fair approximation to accuracy for each individual case. Moreover, the increment to the principal can also be worked out

since it is true that intensive cultivation of a job is largely a matter of ability and effort to convert daily experiences into working knowledge, for reserve equipment in the handling of new problems.

The growing, rising chemist should always want to know. He will progress measurably as he reaches out for information in varying directions and organizes it for his practical use. When he sells his service this constructive reorganization of previous experiences is the big value that the chemist has to cultivate and offer. Few can rise without it; and if one has it, or will adopt it deliberately, his name will not be a frequent visitor on the waiting job list of his *Alma Mater*. It will take him from the minor to the major stages of responsibility for it comes pretty near being the whole thing in personal values.

Granted then that every chemist is willing continually to study and reorganize his accumulating experiences, all that remains is to see that the initial pay is as fair as possible. To what he may be entitled by way of compensation can be most easily determined by comparison with distinctly different types of investment. To illustrate let us compute an average investment for a man at the end of a normal college course and establish his initial salary.

Under normal conditions the student pays during his college career not only the cost of living and attendance, but surrenders his earning capacity during that time. An 18-year-old high school graduate can readily earn \$600.00 per year; at 20, \$720.00 per year; and at 21, \$780.00 per year. By surrendering these earnings he invests in this way during the 4 years \$2700.00. He also invests 4 years' sustenance at \$600.00 per year, or \$2400.00. In addition, the State has invested in him as a high school graduate 8 grades at \$40.00 per year and 4 grades at \$100.00 per year, amounting to \$720.00.

The total investment now amounts to \$5820.00. Deducting the usual 15 per cent knocked off of first cost for the first year in nearly all lines of business, leaves \$4940.00, and most graduates have enough books and chemical apparatus by way of equipment legitimately to make the round sum for the first year out of college, \$5000.

Here then comes the issue. Is the man with \$5000 invested in training entitled to the same return as the man with \$5000 invested in a personally conducted business? I think he is. The only obscure point arising is what the other fellow realizes from his investment in the average case.

My own observations lead me to believe that the average merchant turns his stock twice a year with a 40 per cent gross margin, or 80 per cent increment for the year. Out of this come his operating costs, except salary, averaging 75 per cent of the gross earnings. The employee has no operating cost. Eliminating it we arrive at the proper point for comparison—the net return as salary on equivalent capital. Extracting the operating charge leaves 25 per cent of 80 per cent as the net return or 20 per cent on the original investment, equal to \$1000 per year as the amount which his investment should bring.

Cultivated with constructive curiosity the principal should increase according to  $P = be^{rt}/100$ , the compound interest law, where "be" equals  $P_0$ , the principal at the time "t" equals zero," or graduation from college, and "r" is legitimately chosen from a consideration of new experiences.

In this way income can be tested from time to time. In doing this many contingencies may arise in each individual case. Yet with a base established along the foregoing lines a legitimate conclusion can be reached with fair-minded treatment of the factors arising, and a more equitable relation established between buyer and seller of services.

The investment in training when capitalized must be sufficient to provide the cost of living, with a surplus for contingencies, for depreciation and wear, and for individual growth.

## FIFTH ANNUAL SAFETY CONGRESS

Papers read before the Chemical Section of the National Safety Council at Detroit, October 16 to 20, 1916

### CHAIRMAN'S ADDRESS

By J. R. DE LA TORRE BUENO

To your presiding officer falls a high honor, a great opportunity. My pleasant yet sober task is to sound the clear note of effort crowned by achievement that shall characterize this, the second annual meeting of the Chemical Section, National Safety Council.

You will hear how a few of us organized this section as we sat modestly by a wall in a great chamber where a railroad sectional meeting was in enthusiastic progress.

Briefly I shall tell you what we have done and what we have tried to do. At first the smallness of the section made it impossible to do more than name committee chairmen, and indeed, as you know, in most instances those committee chairmen were officers. They will presently report to you, except the Membership Committee, whose report is contained in this. The Program Committee report, as you will hear, is the carefully arranged schedule under which we will work to-day.

At the second meeting of the Section there were present about 20 members, and the last report from the Secretary of the Council gives a membership of 150 companies and individuals including company representatives; of all these only 26 are chemical manufacturers.

The chair need not dwell on the terrific pressure under which the chemical industry has lived and moved in the past two years. It is known to all. For this reason your Executive Committee has done little beyond rearing a skeleton organization, laying down the general principles to rule the Section. It has also prepared the preliminary series of bulletins you have already received. The willingness and enthusiasm of the chemical members in safety work are known to all. Because of the acuteness of their many present problems, your officers have not pressed them to enter more fully into the sectional work.

But the time is now here when all should coöperate in advancing the section. The most pressing problem is to draw in the chemical industry by a well-considered and energetic membership campaign. I suggest that every member here present pledge himself to enlist at least *one* new member in the course of the year. If this be done by all, instead of having only 150 on our roll, we shall number 300 enthusiasts in industrial safety when the next annual meeting comes around. You are also urged to coöperate with the Standardization and Causes Committee in their fundamental survey work of the hazards of the industry. The Bulletin Committee likewise needs and indeed must have your strong support.

Gentlemen, the Section is what you make it. Your officers are only too pleased and ready to do all they can to promote its success, but no general can win battles without a loyal army at his back. In the year coming, give your officers not alone your generous appreciation but your enthusiastic labor likewise.

Our great, progressive, scientific industry should lead in safety as it does in research. In the year to come let us labor wholeheartedly then to make and keep the Chemical Section of the National Safety Council the foremost in high enthusiasm, in intense work and in splendid achievement.

### HEALTH PROBLEMS IN THE CHEMICAL INDUSTRIES

By GEORGE M. PRICE

Director Joint Board of Sanitary Control; Formerly Director of Investigations, New York State Factory Commission

Of all industries the chemical is the most hazardous to the workers. Other industries may and do contain one or more of the industrial hazards. The chemical has them all.

The chemical industry is full of perils to health, limb and life. To the dangers of motive-driven machinery are added those due to vats, pans and caldrons. Extremes of temperature, excessive humidity and other unhygienic conditions prevail in many establishments. Abundant dust, suffocating fumes and poisonous gases are the rule, not the exception. Moreover, there is hardly an establishment in the chemical industry where various virulent poisons do not present a menace to the health and life of the workers.

In proportion to the extent of motive power, machinery and the number of workers, the chemical industry shows a far greater number of accidents than any other industry, while the extent of occupational diseases, either suddenly terminating the lives of the workers or slowly and gradually undermining their health, has never as yet been determined.

In spite of the undoubted enormous industrial menace to the health and lives of the workers, there is no industry, so far as I know, in which the human element is so woefully neglected as in the chemical.

This was my impression, based upon an extensive investigation of several hundred chemical establishments in New York State and a large number outside of the state. After two years' investigation, during which I was assisted by eminent members of the chemical profession, we were reluctantly compelled to come to the above conclusion.

The evident neglect of the human factor in the chemical industry may be rationally explained even if not justified. The industry was comparatively young; it was largely based upon brilliant discoveries and inventions; its methods were revolutionized every few years; the industry was undergoing constant changes and transformations; it was scattered among a large number of employers; it was often housed in temporary ramshackle structures; most of the work was performed by unskilled labor, by foreigners, by recent ignorant immigrants.

Under such conditions it is apparent why little or no attention was paid by the captains of the industry to the sanitary conditions of the establishments and the hygienic control of the workers.

Within the last years the chemical industry has fortunately been revolutionized. It has been concentrated and its control is in fewer hands. The industry is getting stabilized; the ramshackle temporary structures are giving place to splendid permanent concrete buildings; steady employment gives place to shifting work; and the demand for increased efficiency has changed the attitude of the employers to their workers. The character of the labor element is also changing; it tends to become more permanent and is recruited less and less from the unskilled and immigrant class. A more efficient and strict state supervision has compelled the installation of many safeguards and the introduction of many sanitary improvements, while the compensation laws, enacted in most of the progressive states of the Union, have compelled the industry to think seriously of the solution of the problems of accident prevention and industrial hygiene.

The industry collectively and the manufacturers individually are at last being convinced of the necessity of a just recognition of the human element in the industry and have ceased to regard the labor element as a commodity subject to the inexorable laws of demand and supply.

There is as yet much to be accomplished by chemical manufacturers as well as by the chemical industry as a whole. The safety of the workers' limbs and lives must be assured. In order to accomplish this result the character of the buildings in the industry must be improved: more light, better ventilation,



improved construction of floors are absolute requisites; elevators, hoistways, ladders, etc., must be provided with proper safeguards; all machinery must be made safe and fool-proof; all vats, pans, caldrons and all chemical containers must be properly protected. The general sanitary conditions of the factory must be improved in so far as they relate to dressing-rooms, washing, bathing and lunch facilities, etc.

Add to these fundamental improvements the proper provisions for medical supervision and educational work and there would be no reason why the chemical industries should not become comparatively safe and hygienic.

By medical supervision I mean complete medical supervision of the whole plant—its physical conditions, its sanitary features, the various industrial processes—and of all the employees, not only while they are within the shop but also while they are outside of the establishment. A medical supervision should consist of the following: (a) supervision of the sanitation of the establishment; (b) supervision of the industrial processes in so far as they are liable to harm the workers; (c) preliminary examination of all new applicants for work; (d) first aid and care for accidents and diseases of the workers; (e) periodical examination of workers; (f) supervision of the home surroundings of the workers; and (g) medical care of the workers outside of the establishment.

The educational activities which must be combined with the medical supervision are essentially those which tend to acquaint the workers with the dangers of their calling, with the perils of the various gases, fumes and toxic agents which they must necessarily handle, and education of the workers in the proper means of safeguarding themselves from the ill effects of the various perils of which the industry is so full.

With the above program for the individual employers in the chemical industry, the industry as a whole should not be content.

The organization of the Chemical Section of the National Safety Council proves that the whole industry has great common interests. In Germany the chemical industry is organized in a powerful association (*Berufsgenossenschaft*). There, owing to the sickness insurance laws, the industry as a whole is strongly organized and looks out for the common interests. The association exercises general supervision over all its components. It legislates for the industry; it has evolved a uniform and standardized method of safety, accident prevention and medical supervision; it appoints its own inspectors to investigate the sanitary, safety and health conditions in the establishments of its members; it punishes delinquent members by raising the rate of their insurance and it exercises general control of their safety, sanitation and health of the industry.

What has been done in Germany and elsewhere may easily be accomplished here. There is need of a greater uniformity and better methods of standardization of the safety, sanitation and health control in the chemical industry. With all their desire, individual manufacturers cannot do as much as a whole industry. Many accidents and a large number of occupational diseases are still due either to negligence or to ignorance of employers and their operatives, and to the faulty and often incompetent medical supervision in the various establishments.

Only a general control by the industry as a whole, combined in a National Association or section of the National Safety Council, may be able to standardize the industry, to improve the conditions of safety and health in the industry and to remove from the industry the stigma of the extreme menace to the health and life of its workers. Individual efforts, no matter how worthy or earnest, must give way to a general, joint, combined, uniform and standardized health supervision of industry.

Great as has been the prosperity of the chemical industry in the field of economic production, vast as have been its achieve-

ments within the last few years, enormous as has been its progress in all the various fields of its endeavor, greater progress yet awaits the industry when, by a complete and thorough safeguarding of its establishments and a complete hygienic control of the health of its workers, the industry will proudly proclaim to the world that it no more is the most dangerous of all trades, but that it has become the most humane of all the industries.

31 UNION SQUARE, WEST  
NEW YORK CITY

## THE GOGGLE PROBLEM IN THE CHEMICAL INDUSTRY

By J. R. DE LA TORRE BUENO

Editor, General Chemical Bulletin, General Chemical Company

The chemical protective goggle and its use presents every one of the difficulties of the goggle problem, only in a vastly more acute degree. The goggle need not be stout to resist violent impact, but it must be of a material unacted on by acids or other chemicals. It must also prevent liquids from striking or flowing into the eye; and finally, it must be ventilated to prevent blurring.

Some form of goggles must be worn in all work which demands protection of the eyes. Everywhere, the use of goggles presents a problem both material and psychological. The problem is material, in that the type of goggle must be carefully adapted to the work and its inherent hazard to afford perfect protection; it should also afford a maximum range of vision and be comfortable to wear. It is psychological, because we men are vain, far vainer than women, and so loth to wear anything disfiguring or that may expose us to ridicule; further, many men *will* take a chance. All industries have to contend with these adverse conditions and experiment and education are gradually overcoming them, by devising suitable and comfortable goggles, and by training the men in safety principles by constant instruction and reiteration.

Many goggles have been made for chemical plants; some are still used. One type consists of a frame of soft rubber with a broad piece going across the nose and other pieces projecting beyond the temples. Another has hard rubber cups fitted with pneumatic cushions along the edges to be inflated, when worn, by means of two little rubber tubes with stopcocks. Both have the defect of heat. The soft rubber ones have eyelets let in for ventilation, but in such a way that there is always danger of corrosive liquids flowing in. The hard rubber contrivance is impractical. Besides, the pneumatic binding readily gets out of order. The goggle most in vogue consists of a close-fitting, flexible rubber half mask or visor which adheres so closely to the face that liquids cannot seep under it and flow into the eye. This has a very great disadvantage, besides being unsightly—it is the extreme discomfort it produces in the wearer by reason of the heat and perspiration it induces over the entire surface of the face with which it is in close contact.

None of these types has efficiently solved the goggle problem in the chemical industry.

Let me draw the ideal goggle. First, it has only one object, to protect perfectly the eye—that organ, at once so delicate and so important to the worker. It is meant neither for comfort nor for beauty, but for safety. But in attaining its prime object, none of the collateral points should be ignored. These, then, are the objects to be attained, the marks of the ideal goggle, in the order of their importance.

- (1) Perfect protection to the eye
- (2) Large field of vision
- (3) Comfort
- (4) Sightliness

PERFECT PROTECTION can be secured only by making the goggle of a material unaffected by chemicals and by making it fit so closely that neither above nor below nor at the sides may the least drop of a corrosive liquid penetrate to the eye, either by

dashing against the goggle or by seeping under it. It must be therefore flexible in order to conform closely to the contour of the face.

LARGE FIELD OF VISION is a solved problem; it works against a deep eye-cup, which tends increasingly to limit the angle of sight with increasing depth.

COMFORT depends on two elements: the weight of the goggle, and its ventilation to prevent excessive perspiration. In the nature of things, as the chemical goggle is practically a half mask, its weight can be but little reduced, except by making it of aluminum and of light construction, two possible points of improvement. Excessive heat is overcome by ventilation and by reducing the surface in contact with the face.

SIGHTLINESS is immaterial, given the necessity for perfect protection with a maximum of comfort.

To meet the conditions set forth, the goggle frame or mask should be of flexible wire netting; shaped to the face but dished sufficiently to keep it from contact except along the edges which should be bound with a soft, resilient rubber tubing. The edges should be made flexible, so that they may be bent to conform with the facial contours to avoid undue pressure at one spot or being too far away at another. The rubber setting for the large glasses should afford a wide range of vision and be perforated near the lenses to allow the escape of heated air, thus preventing condensation of moisture and clouding. The openings should be on the slant of the frame so that in case acid flows down the face to the glass-settings, it will not readily leak into them; but if it does, they must be so close to the glass that any acid would flow down the inside of the lenses. The mask should be coated with a flexible acid-proof varnish to make it impermeable and at the same time to preserve it from the corrosive action of the fumes about a chemical plant.

This goggle would overcome three of the difficulties—it would give effective protection with maximum sight, together with a large degree of comfort. This is offered as an approximate solution of the goggle problem in the chemical industry.

25 BROAD STREET, NEW YORK CITY

## CARE OF WORKMEN EMPLOYED IN THE MANUFACTURE OF ANILINE AND BENZOL PRODUCTS

By A. B. MITCHELL

Benzol Products Company

On account of the effects on the men employed in the manufacture of Nitrobenzol, Aniline and their kindred substances through coming in contact with the compound being produced either by inhaling the gases evolved or absorption through the skin, the following safeguards have been adopted and facts noted in the operation of the plant of the Benzol Products Company.

THE PLANT is of modern construction, brick and steel, and is designed throughout on the gravity system. The maximum amount of air possible is obtained by means of large windows, sliding doors and shutters, and all buildings are fitted with monitors the entire length of the roof. Electrical power is used wherever practical. A locker room is attached to the entrance gate and is provided with steel lockers, showers, toilets and lunch room.

EMPLOYEES—The workmen employed on the processes are all American with the exception of the Aniline House where most of the labor is Polish who from experience have been found to stand this work well. An applicant is inspected by a doctor and examined by him for lungs and heart. Blood pressure is taken and physical defects noted on a card which with the Doctor's recommendation is returned to the office. If the man is employed he is examined monthly—any defective development being reported on the cards.

### SAFETY RULES

The following rules are issued to foremen and workmen—the foremen being required to sign a receipt that they have carefully read the instructions. The instructions are printed in English, Polish and Russian and posted around the works, and are as follows:

#### BENZOL DEPARTMENT

- 1—Benzol is very inflammable and floats on water. It explodes when mixed with air and lighted.
  - 2—Never use an extension light—use an electric Bull's Eye.
  - 3—If you smell Benzol, open doors and windows before going into shop.
  - 4—Remember Benzol vapor is heavier than air.
  - 5—Never enter any tank, pit or well which has contained Benzol without first blowing it out with air, then ask foreman.
  - 6—If you spill Benzol on your clothes go outside into the fresh air until it blows off.
  - 7—If you feel any effect such as sleepy feeling or light head go into the fresh air at once and send for foreman of shop.
- REMEMBER—Fresh Air—Keep Clean—and Benzol will do you no harm.

#### NITRO SHOP

- 1—If you spill Nitro on your hands wipe it off at once.
- 2—Never work over hot Nitro—allow it to cool first.
- 3—Wash before eating.
- 4—Never enter a nitrator until it has been washed out and air blown in and you have leave to do so by your foreman.
- 5—If you feel sick, report at once to foreman of shop.

#### ANILINE

(Also printed in Polish and Russian.)

*Keep Clean*

*Keep Clean*

*Safety First*

- 1—Leaks, spills or trouble are to be reported to the foreman of the Aniline House.
- 2—If you spill Aniline on your clothes, change them.
- 3—If you get Aniline Oil on your hands, wash it off at once.
- 4—You must wear clogs.
- 5—Do not wear gloves soaked with Aniline.
- 6—Wash your face and hands before eating.
- 7—If you are feeling bad, tell your foreman at once.
- 8—Aniline and "Booze" are bad, keep them as far apart as possible.

*Keep Clean*

FOREMAN

*Keep Clean*

*Safety First*

- 1—Look after your men.
- 2—Keep them away from Aniline gas as much as possible.
- 3—See that they have clogs on.
- 4—Never let them work over spilled Aniline—especially if it is hot.
- 5—See that they get all the fresh air that is possible.
- 6—If they look "blue" send them out into the air and keep an eye on them.
- 7—Work them slowly on hot days.
- 8—Make them change their clothes if Aniline is spilled on them.
- 9—Don't let them wear gloves (cotton) with Aniline on them.
- 10—Order them to wear mouth protectors if you are in doubt.
- 11—See that the sponges in the protectors are cleaned every day.
- 12—In any case of doubt send for the General Foreman—he will help you night or day.
- 13—If a man gets sick, report it at once to the "First Aid" Department.
- 14—KEEP YOUR MEN CLEAN.



## (Form A-1 Safety First)

**FIRST AID**—The plant is equipped with a Sick Bay containing a lung motor, oxygen, etc., which is under the charge of the Laboratory one chemist being detailed for this work. He makes out daily report sheets every morning if the patient has returned to work so that the case may be followed up by the works physician if deemed necessary.

**NOTES**—No cases of Benzol or Nitrobenzol poisoning have come under the writer's experience of twenty years and with healthy men and a properly designed plant there is no danger.

**NITROS**—These are some of the most trying to manufacture. Great care must be taken of the workmen as they readily absorb it through the skin and by inhaling the fumes and at once show signs of blueness on their lips. Young men seem most susceptible, though men vary in their susceptibility. The answer is proper ventilation and change your men every day. Make them wear clogs while working in the shop and provide respirators for them and have plenty of water handy for them to wash in. On the first sign of blueness send them into the fresh air. Treat same as Aniline.

**ANILINE**—The quantity of Aniline produced is between five and six thousand tons per year. In the cool months no trouble has been experienced with the men employed, but in the hot weather great care is necessary as the Aniline is readily absorbed through the pores on the skin and through the feet.

The Polish labor has been found very satisfactory. They are encouraged to keep in condition by doses of Salts which are kept on tap for them. They are watched carefully and on showing any signs of blueness are sent away from the Aniline shop to the Sick Bay. Here they are made to take a shower and if they smell of Aniline are sponged off with weak Acetic Acid and given a dose of Salts. New men are more susceptible than those who have worked for some months; in fact, two men (Poles) who have been employed on this work for years have never been reported sick and their medical examinations show no deterioration.

Oxygen is not given except in a bad case.

The worst case here—that of a pipe fitter who got his clothes saturated with Aniline Oil and took no notice of it—was back at work in six days. As a rule the men report for work the following morning.

MARCUS HOOK, PENNSYLVANIA

## FUME POISONING FROM NITRIC AND MIXED ACID

By L. A. DeBLOIS

Engineering Department, Safety Division, E. I. du Pont de Nemours & Co.

Most of us are probably familiar with the "strong nitric acid" of the laboratory or trade which, though containing perhaps 30 per cent of water, is known as an extremely active and corrosive reagent, but it is those whose business is concerned with the nitration of organic materials by "mixed acid" (nitric and sulfuric) in which the nitric reaches 100 per cent strength who are brought to full and perhaps sudden realization of what dangers can arise in the manufacture or use of a strong acid.

An acid "spill," the contact of acid with water, etc., the ignition or rapid decomposition of the material being nitrated, or even the exposure of small quantities of acid to the atmosphere may set free greater or less amounts of fumes. While the reddish gas, nitric peroxide, which may be formed abundantly under such circumstances is generally credited with being the chief cause of acid fume poisoning—or, as I would prefer to call it, "fume sickness"—it is probably not the only poisonous constituent of such fumes which are undoubtedly made up of

poisonous gases and finely atomized acid carried in suspension. As the composition of these fumes varies greatly it is sufficient to include all under the term "nitrous fumes," and, as far as I am aware, their effect on the human system varies only in degree.

The inhalation of dense nitrous fumes for a short time or weaker fumes for a more prolonged period may bring on a feeling of suffocation attended by coughing and local soreness in the upper air passages. The susceptibility to these effects and to the more serious attacks varies in individuals and we encounter many who claim immunity through continual exposure. Moreover, a certain pride is taken in their boasted immunity which they attribute to their long experience or excellent constitution, thereby increasing the danger of a prolonged exposure with possibly fatal results. The primary effects may perhaps be entirely relieved by going into the open air—in some cases such symptoms may be entirely absent and in either event there may be no indication that a dangerous dose has been received. In fact, in most cases fume sickness develops no further and the man returns to his work suffering no ill effects, but if the inhalation has been too great, after a period varying from an hour to a few days, the victim may become weak and short of breath perhaps to such an extent that he can get sufficient air to support life only by lying perfectly quiet propped up in a sitting position; sometimes a cough and abdominal cramps appear.

In fatal cases, the shortness of breath increases, with coughing and expectoration of a frothy, straw-colored sticky fluid, the blood is darkened and the veins engorged, and the man dies from suffocation which sometimes ends in a convulsion. The duration of the attack may be only 6 or 8 hours.

The above conditions are the result of edema (dropsy) of the lungs. Much as a "water-blister" is formed on the skin by a burn, a fluid is secreted within the lungs which fills the air-sacs so that air cannot enter them until the victim practically drowns in his own fluids, but if even a small part of the lung escapes the action of the fumes, it may be sufficient to tide him over the critical period until the fluid is partly coughed up and partly absorbed and the lung returns to the normal—hence, the practice among more experienced "acid men" of taking only shallow breaths when compelled to enter an atmosphere of dense fumes without proper protective appliances.

Sometimes, if not enough fumes have been inhaled to cause edema, pneumonia may be set up, but such pneumonia is not as a rule particularly severe unless the patient is already afflicted with some other complicating disease. In this connection it is to be noted that because of their apparent susceptibility to fatal fume sickness the du Pont Company has considered it best to avoid the employment of negroes in fume-laden atmospheres.

When the edema has once set in, little can be done to arrest its progress, though if a small portion of the lungs have escaped, the administration of oxygen is of course indicated, but in all cases of fume sickness it is our custom to administer chloroform at once. Fifteen drops should be added to a tablespoonful of aromatic spirits of ammonia and this shaken up in three-quarters of a glass of water and drunk in several portions, the entire amount being taken in from a half-hour to an hour. Careful investigation has not indicated that this is effective in preventing the development of the edema, but it undoubtedly gives some relief—probably its chief effect is on the abdominal cramps that sometimes appear. If the vapors from this medicine are deeply inhaled they also appear to afford some relief, but it seems unwise to suggest the inhalation of stronger alkaline vapors such as ammonia, which in itself is capable of setting up edema. Where first-aid or hospital attention is not at once available, it is customary to keep chloroform at hand in individual doses (glass ampoules) with the necessary materials for

mixing and administering the doses, though as a general rule all such cases should be immediately reported for proper medical surveillance.

Herein lies what is perhaps the most important of the preventive measures—the promulgation among the men of a full knowledge of the dangers of nitrous fumes, the symptoms of fume sickness and the importance of immediate medical attention. So sudden is the development of the secondary stage of the sickness and so unexpected, that the danger is an extremely insidious one and apt to be forgotten.

While we depend on our foremen and supervisors for continual vigilance in safeguarding their men against these attacks, we also issue small booklets to the men, giving full information in a simple manner and in the necessary foreign languages. More complete information is contained in a booklet for foremen, chemists, etc., while additional information is given to works physicians and doctors practicing in the vicinity of our works. In our larger plants where by the nature of things personal supervision over the men, especially after working hours, is more difficult, occasional or periodic safety meetings and short talks to men employed in the area probably help to keep the matter before them. However, acid work does not, in our experience, attract the more intelligent grade of Americans, even with good wages, as much as the uneducated and often perverse foreigner. Such men are prone to come and go and are difficult to instruct, and with a constant fluctuation of labor the campaign of education is beset with difficulties. Furthermore, among the better educated and more experienced men, we have to meet the spirit of independence as well as their convictions of complete immunity. Thus, it is evident why most of our fatal cases have occurred in men who have gone home without previous notice to the hospital and have then collapsed.

Respirators as a protection against nitrous fumes are not too dependable. Manufacturers frequently make broad claims, but I have observed one in particular very thoroughly overcome (at his own risk) in a practical trial and exceedingly glad to take his chloroform and withdraw his claims. Lately we have had considerable success with an aluminum respirator, having an exhaust valve and inflated rubber face-cushion, by substituting for the sponge a disc of "Filtros,"  $2\frac{1}{2}$  in. in diameter by  $\frac{1}{4}$  in. thick, fitted with rubber gaskets and moistened with a teaspoonful of 20 per cent solution of caustic potash. These discs appear to be practically indestructible and may be washed and recharged until the pores are filled with lint or other dirt, when they can be replaced at a cost of about 25 cents. Respirators, however, do not appeal to all workmen on account of some slight obstruction to breathing and to the pressure of the rubber cushion against the face. The latter induces perspiration which collects acid, and this in turn may cause sores.

The correct solution of the fume sickness problem is, of course, proper ventilation, but this, as many can vouch for, is not always easily accomplished, especially in the type of building used for acid work. I think I can say without reservation that the du Pont Company has tried almost every known system and combination of systems and that the excellent results that have been lately obtained were reached only after much careful and expensive experimentation on full scale. This system is, briefly, the handling of the fumes by large exhaust fans with the draft conducted downward from the source of the fumes with such vertical enclosures as may be practicable. In the case of cotton nitrated in earthenware pots, the latter are placed in partial enclosures and over slatted openings through which the fumes are drawn. Where the fumes were formerly rather heavy, the air in these rooms is now changed at the rate of fifty times an hour, the velocity through the slats being about 830 ft. per minute with full opening and in some cases 2500 ft. per minute

close to the top of the pot. General ventilation is obtained through ample windows and monitor roofs. Extreme conditions such as the above are of course not necessary throughout the process and no fixed rules can be prescribed that will meet all situations. Atmospheric conditions are also an important factor, the heavy damp air of early morning being especially troublesome.

While systems like the above may handle the fumes produced in normal operation, they may be incapable of dealing with those thrown off in vast quantities if the product should "fire." In such emergencies the operators readily escape to the outside galleries or to the ground through emergency doors but are generally impatient to return and resume operations. Where these conditions were the worst we have met them by installing powerful aeroplane propellers direct-connected to electric motors which can be switched into operation from the outside. Where formerly ten to fifteen minutes would have been required to clear the building of fumes, they are now swept out through the open doors and windows in from one to three minutes with much increase to the safety of the operators and shortening of the periods of inoperation.

Considerable experimental work has been done in the neutralization of nitrous fumes by aqua ammonia or ammonium carbonate solution sprayed directly into the air by compressed air atomizers. These proved remarkably effective and not as expensive to maintain as would first appear, but were abandoned as better results were obtained when suitable exhaust systems were developed—proper regulation being one of the principal difficulties. Each atomizer consumed about  $2\frac{1}{2}$  cu. in. of 30° Bé. aqua ammonia per hr. at an air pressure of 25 lbs., neutralizing rather dense fumes over an area of approximately 252 sq. ft. of floor surface.

Another source of danger is the enforced entry into acid tanks or other receptacles for repairs, cleaning, etc. Tanks are washed carefully and, if necessary, neutralized. Whether they can then be entered is determined by some one in authority and, if necessary, oxygen helmets and life-lines are worn. We have adopted oxygen helmets of the "half-hour" type which are installed in pairs in special boxes together with extra supplies, the rubber mouthpiece being kept in boric acid solution. On our principal acid plant they are inspected daily, all oxygen cylinders which have been attached being brought in for recharging whether their contents have been entirely or only partially used. Their use and upkeep has given us little trouble save as regards the destruction of the breathing bag by acid fumes. Their misuse is considered sufficient excuse for immediate discharge.

Investigations to prevent fume sickness were begun by the du Pont Company a number of years ago though fatal cases were of very rare occurrence. Little or no information could be gleaned from outside sources either in this country or abroad and much that we know to-day about this rare and insidious malady has come from the able work of Dr. W. G. Hudson. Lately, as our field of operations has broadened and many new men have been employed, the danger again assumed serious proportions. New methods were being introduced with which protective measures could not keep step. Thus at our principal acid works in the most dangerous process employing 540 men in three shifts, under conditions which would have formerly been considered excellent, there were about 740 cases of fume sickness reported in the months of March and April, 6 of which were fatal. Though we still have much to learn and may yet anticipate further regrettable accidents, great improvements have been made, and it is gratifying to note that in the past six months the number of reported cases of fume sickness has been greatly reduced and not one fatality has occurred.



## CURRENT INDUSTRIAL NEWS

### SIBERIAN IRON ORE

Recent surveys of the iron deposits of the basin of the Telbeso and the Tamir Tau district in Siberia result in aggregate estimates of 20,000,000 tons of iron ore. A large proportion of the deposits yield 55 per cent of iron.—A. McMILLAN.

### RUSSIAN WAX SCARCITY

In a general notice on honey and wax in a Russian contemporary, it is observed that the demand for beeswax, although the past year was a good bee year, cannot be satisfied. As Germany used to be the principal source of supply, candlemakers found themselves in a difficult position shortly after the outbreak of war. The production of candles at home was so limited that the diocesan authorities were obliged to remove candles from the churches that had run out of them. The price has risen from 60 to 80 kopecks per funt before the war to 2 and 3 roubles per funt now.—M.

### ELECTRIC POCKET-LAMPS

According to the *Electrician*, a new form of electric portable lamp, the light from which is adjustable is being brought out in Germany. A small spiral resistance in series with the lamp and switch is mounted above the battery. The resistance can be readily varied by the motion of a small knob at the side of the case, the brightness of the lamp being thus altered within the limits of maximum intensity and a dull red glow. This enables the current to be economized when only a small light is needed, prolonging the life of battery and lamp. The resistance is also useful in preventing the tendency to overrun the lamp unduly when a new battery is substituted for an old one.—M.

### PETROLEUM PRODUCTION IN ARGENTINE

According to a report in the *British Board of Trade Journal*, the Argentine Minister of Finance has been authorized to hand over 746,607 pesos (\$326,500) to the Comodoro Rivadavia Petroleum Exploitation Committee for the purchase of additional machinery and materials for the working of deposits.—M.

### VALUE OF LICHENS AS FOOD AND FODDER

A paper in *J. prakt. Chem.*, 93 (1916), 254, discusses the possibility of using native lichens as substitutes for foodstuffs and states that Iceland moss gelatin, in the form of jellies flavored with chocolate or other flavors cannot be distinguished from those made with sago or with agar agar. *Cetraria nivalis* is also recommended as a cheap and pleasant flavored article of food. *Cetraria islandica*, in the air-dry condition, contains 80 per cent of carbohydrates and from 13 to 14 per cent water. The bitter taste is removed by preliminary treatment with cold 1:100 potassium carbonate solution.—M.

### BRITISH OIL SUPPLIES

Speaking at the Royal Society of Arts, London, on the subject of British oil supplies, Dr. Forbes-Leslie declared that investigation had revealed the presence in Norfolk, England, of an oil-shale series of very considerable importance. On a test from a ton of the shale, 40 gallons of oil have been obtained, also 66 lbs. of sulfate of ammonia and 25,000 cu. ft. of a dry gas of high illuminating properties. There was little doubt that a large oil-shale bed existed in Norfolk, and England did not seem, in his opinion, to be so entirely destitute of oil resources as many people supposed. In the near future, the oil-fields of the Kimmeridge outcrop might be supplying much of the oil and petrol consumed in the country.—M.

### OIL TEST

Mr. H. W. Petty, in a recent paper on lubrication, read before the Association of Engineers, London, recommended the following simple test for oil which had undergone oxidation and become resinous: Place a small quantity of the oil in a glass beaker and put in a nearly equal amount of nitric acid. Should the oil have no tendency to gum, the acid and oil will combine and get very thick, while should there be any objectionable characteristic, the oil will remain thin.—M.

### PETROL SUBSTITUTE

A patent has recently been taken out by Mr. H. K. Tompkins, London, for a new petrol substitute, the constituents of which are cheap and easily obtainable. The fuel consists essentially of a solution of ethane and its higher gaseous homologues or isologues in paraffin oil, or other liquid hydrocarbon under pressure. Coal gas produced by low temperature distillation of coal is washed with paraffin oil or other liquid hydrocarbon under pressure and the solution of hydrocarbon gases so obtained is delivered under pressure into drums. For use, the solution of gases is drawn off from the bottom of the drum and is delivered into the carbureter through a small orifice without wire-drawing so as to obtain the full atomizing effect of the dissolved gases. The paraffin oil is partly or entirely volatilized in the carbureter according to the proportion of the dissolved gases.—M.

### SPANISH MINERAL INDUSTRY

The Council of Mines has just published complete statistics for 1915, of mining and metallurgical industries of Spain. The following table gives the various figures of interest to the chemical world:

	PRODUCTION (TONS)	VALUE AT MINE \$
Asbestos.....	39	1,560
Antimony.....	300	10,500
Bitumen.....	4,521	11,074
Sulfur.....	28,937	41,237
Baryta.....	4,218	15,096
Bismuth.....	16.8	4,716
Zinc.....	81,921	1,225,541
Copper-pyrites.....	2,001	32,191
Copper-ferro-pyrites.....	1,464,349	4,520,355
Fluorspar.....	370	1,702
Iron-pyrites.....	730,368	1,654,578
Iron ores.....	5,617,839	7,120,286
Magnesia.....	1,400	1,036
Manganese ore.....	14,328	54,968
Platinum.....	210.4	21,991
Lead ores.....	285,265	13,371
Argentiferous lead.....	2,934	42,795
Salt.....	305,035	348,041
Soda sulfate.....	191	800
Aluminous earths.....	314	2,198
Wolfram.....	511.3	43,664

—M.

### DIESEL ENGINES IN INDIA

In the early stages of the development of the Diesel engine, says the *Times Engineering Supplement*, India was one of the most promising fields for its application for stationary work, but manufacturers do not seem to have devoted sufficient attention to the possibilities of the country. As a result, while heavy oil-engines of the Diesel type are to be found in fairly large numbers throughout India, there are still great opportunities for their further utilization, the relative prices of oil fuel and coal being such as to give the oil-engine a distinct advantage over steam. There is an excellent prospect for Diesel engine manufacturers in India after the war. Practically none of the manufacturers—British or Continental—has European representatives in India and, in the opinion of the above journal, a really capable agent thoroughly trained in internal combustion engines would have no difficulty in doing good business in India.—M.

## MINING IN ROUMANIA

The mineral resources of Roumania, says *Mining World*, 91 (1916), 409, comprise antimony, coal, copper, hematite, petroleum, rock salt and stone. Beds of anthracite and bituminous coal (lignite) crop out in various parts of the country, and anthracite is mined at Schela in the province of Gorj. Lignite beds exist which are 20 ft. thick. Coal is mined in the following provinces: Mehedinți, Muscel, Dambovitza, Prahova and Bacau, the mines in Dambovitza being worked in concession by the state. The principal petroleum centers are Prahova, Dambovitza, Buzen and Bacau, but nearly 90 per cent comes from the Prahova district. It is obtained partly from shallow dug hand wells and partly from bore-holes: 900,000 metric tons are exported annually. Roumania possesses rich deposits of salt which extend for a distance of about 100 miles along the Carpathians. One bed of pure rock salt is said to be from 800 to 1000 feet thick and two beds, viz., those at Oencle-Nari and Targul-Ocnei are estimated to contain 600,000,000 tons of salt. The industry is a government monopoly and the quantity produced annually is about 126,000 metric tons, valued at \$1,750,000. Ample supplies of stone and building material, including granite and marble, are found in the country, the largest number of quarries being worked by the government.—M.

## CARBO-TEREDO TIMBER PROCESS

*Engineering* reports that Mr. J. G. Cunningham, of Sydney, New South Wales, demonstrated his carbo-teredo process in the presence of representatives from nearly all the main-line railways of England. Sections from treated and untreated hardwood and Oregon pine timbers employed in five tests conducted by the Commissioners of Sydney Harbour Trust were shown and a photograph showing the result of the white ant test. In view of the fierceness of attack both by teredo and termites, the evidence appeared to be convincing. The process consists, broadly speaking, of impregnation by a hydrocarbon followed by burning with a high pressure gas flame. It is applied to piles before and after they are slung to the frame of the driver so that there is assurance that the protecting stratum is intact when it passes into the water. Though the process was primarily directed against the operations of borers, it has been ascertained that it protects timber from weathering and decay. It has been suggested that the treatment would not be suitable for railway sleepers because the exterior surface is likely to become abraded. The inventor, however, claims that the necessary protection is maintained by the calcined undercrust which, in fact, is a hardening of the surface of soft wood. The process is said to be used by several Australian Governments for wharfs, railway and road bridges and river embankments.—M.

## CREAM OF TARTAR EXTRACTION

According to an article in the *Giornale Vini. Ital.*, the Cambiaggi method for the extraction of cream of tartar from grape marcs depends on its solubility in a cold solution of commercial soda. Cream of tartar, as is known, is almost insoluble in pure water but dissolves readily in water containing soda with the formation of the double tartrate of sodium and potassium. The mass of grape marcs is acted on by an upward moving solution of soda which passed on through four other masses in a similar manner. On treating the liquid with hydrochloric acid, the acid tartrate of potassium crystallizes out. The mother liquors are then treated with lime, and calcium tartrate is precipitated. The marcs are treated by a mechanical arrangement which permits each layer to be uniformly and completely washed. The liquors generally take about a day to exhaust the contents of a recipient. The process also provides for the scientific utilization of the residue and one of its advantages is that it gives a pure cream of tartar instead of a crude one.—M.

## SUPPLY AND DEMAND OF RUBBER

A writer in the *London and China Telegraph* says that in 3 1/2 to 4 1/2 yrs. the available supply of rubber may not be sufficient to meet the world's demands. The world's output increased in 1915 by 31.8 per cent and the gain for the current year is estimated at 27.3 per cent. This rate is, however, not likely to be maintained as no very considerable areas have been planted since 1911. The additional 214,000 acres brought into bearing this year is the largest increase there will be for many years to come. It is estimated that between now and 1920, the total increase in the areas in bearing will be only 377,000 acres. The average yield per acre now stands at 336 lbs. and, in 1920, it may have reached 400 to 450 lbs. This would give a world's output of from 300,000 to 330,000 tons provided the receipts of wild rubber were maintained. The question of consumption is more difficult. The average increase in the United States during the past six years was 24 per cent and, if that rate were maintained, in 1920, there would be a serious rubber shortage. If the world's demand increased by 20 per cent per annum, 373,000 tons would be required in 1920.—M.

## SWEDISH PRODUCTION OF IRON ORE

A report on the production of iron ore in Sweden for last year has been published by the Swedish Department for Commerce. It would seem that, notwithstanding the difficulties arising from the war, the Swedish iron industry had quite a successful year on the whole during 1915; the production of iron ore including concentrates amounted to 6,883,308 tons as against 6,586,630 tons for 1914, an increase of 4.5 per cent. The returns from all the iron ore mines show an increase with the exception of the Upsala and Norbotten districts; in the latter the diminution was no less than 467,520 tons and was chiefly due to the manner in which shipments, via Narvik, have been impeded. The report does not include the Gellivara ore used for concentrates at Högabörs, West Sweden, in the total for 1915. The total value of iron ore produced in Sweden during last year amounted to \$581,490. The production of pig iron showed an increase of 120,983 tons and the value in the year's production is the highest on record amounting to about \$787,524, giving a much higher average per ton than for the preceding year.—M.

## TIN MINING IN QUEENSLAND

In the annual report of the Queensland Mine Department for 1915, an interesting note is given regarding the mining for tin in the Herberton field where the outstanding feature is the large number of mines owned and worked by parties of miners and the diminishing number of mines under the control of companies. The result of this is the production of a higher-grade tin than that mined by the larger combinations. Vulcan mine in Herberton district had 9,396 tons of ore to its credit in 1915, which yielded 397 tons of tin concentrates valued at \$137,065. Stannary Hills district, however, was far from flourishing during 1915, and work on the tin dredges in the Stanhope district was irregular.—M.

## DETECTION OF STEARIC ACID IN BEESWAX

According to a paper in *Annales chim. Analyst*, 21 (1916), 179, the presence of stearin or stearic acid as an adulterant of beeswax may be readily detected in the following manner: A small quantity of the sample is heated with a little of an aqueous solution of a copper salt or of copper potassium hydroxide reagent. If the beeswax is pure it either retains its yellow tint or shows at the most a pale green color. If, however, stearic acid is present, a light green color will be produced. This reaction is the cause of the green color seen in the grease of certain candles when used in copper or brass candlesticks.—M.



## BRITISH PIG IRON EXPORTS

The exports of pig and puddled iron from the United Kingdom in August were 95,925 tons as compared with 73,450 tons in August 1915, and 28,401 tons in August 1914, and, in these totals, pig of all kinds figured for 95,655, 73,283 and 28,342 tons, respectively. The aggregate exports for the first eight months of this year were 675,221 tons as against 319,721 tons for the corresponding period of 1915 and 615,297 tons for the same period in 1914. The largest export of pig iron to any one country has been made this year to France which took 390,584 tons to August 31, as compared with 45,571 tons in the first eight months of 1914. The great increase in French demands is, of course, due to the occupation of the northern French metallurgical districts by German troops. Italy imported 91,276 tons from Britain as compared with 47,610 and 64,672 tons for eight months of the years 1915 and 1914, respectively, while the United States took 56,647 tons to August 31 as compared with 42,354 and 57,689 tons for 1915 and 1914.—M.

## NUTRIENT VALUE OF EDIBLE OILS

At a recent meeting of the French Academy of Medicine, M. E. Maurel, of Toulouse, speaking of the shortage of home-produced fats in France (which he estimated at 60,000 metric tons), recommended that colonial oils such as groundnut, coconut, sesamum and cottonseed should be used as substitutes. Owing to the high price of butter, the first two of these are already in use to some extent, but a certain part of the population considers that these oils are not suitable as articles of food. The difficulty is to get the general public to believe that these fatty substances have just as much nutrient value as ordinary fats and butter. Mr. Maurel showed that the calorific value of groundnut oil is practically the same as that of olive oil or nut oil and that coconut oil has about the same calorific value as animal fats, lard or butter.—M.

## OZONE GENERATOR

On behalf of a new laboratory apparatus brought out by Messrs. Ozonair, Ltd., London, says the *Times Engineering Supplement*, the claim is made that it will produce ozone of a strength hitherto unobtainable in a commercial appliance. It is stated that by its use 16 g. of ozone per cu. m. of air (8,000 parts per 1,000,000 by volume) are readily obtained, or in other words, about 6 per cent of the oxygen of the air can be ozonized. The apparatus is fitted with a large cooling surface for the dissipation of the heat produced during the process and is enclosed in a lead-lined tank cooled by water for low concentrations and preferably by a freezing mixture for the higher ones. Its capacity at the highest concentrations is about 2½ liters of ozonized air a minute, but a much larger volume is available at lower concentrations. The efficiency is about 25 g. of ozone per kw. at the high concentrations. If desired for the purpose of accurate estimation a special test meter can be furnished to measure the volume of air passed. Its large dial is marked for a total of 10 liters, divided into tenths of a liter and there are three smaller dials registering a total of 10,000 liters. Dials graduated in cubic feet can also be obtained.—M.

## DUTCH TAR AND DYESTUFFS INDUSTRIES

The *Gas World* states that in Holland there are two small tar distilleries and three coal-tar dye works which depended on Germany for supplies of material. When war broke out, the German Government permitted the export of dyestuff material into Holland up to 50 per cent of the normal amount and, after October 1915, up to 75 per cent. In January last, however, owing to the rate of exchange and the method of payment, there was a considerable rise in the price and it was resolved to organize a Dutch coal-tar dye industry. A company has been formed to coöperate with the Naarden chemical works and a beginning has been made, confined so far to the manufacture of aniline oil. There is a difficulty in obtaining chemists trained in the industry. Meanwhile, Holland has prohibited the export of tar and tar residues and also materials containing phosphoric acid.—M.

## SPELTER OUTPUT

According to statistics, the output of spelter in Great Britain is small, being only one-fifth of that annually produced in Germany, the largest European producer. The annual production for the last ten years has remained steadily between 50,000 and 60,000 tons. In 1913, Great Britain produced 58,200 tons or 6 per cent of the world's output compared with 56,300 tons in 1912. Germany is the largest producer of zinc, the output for 1913 being about 280,000 tons, while Belgium produced 200,000 tons.—M.

## BRITISH BOARD OF TRADE

During the month of October, the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles. Firms which may be able to supply information regarding these things are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall St., London, E. C.

Aniline dyes, suitable for copying ink  
Barrels for oil  
Brushes, quill for artists and marking  
Butlers, metal or celluloid, with flag designs

CHEMICALS:  
Arsenite of soda  
Fluoride of aluminum, chemically pure with small water content  
Fluoride of calcium  
Nitrobenzol  
Nitrophenol  
Aluminum phosphate, chemically pure and free from lime  
Thiazol  
Cellulose acetate, 2nd quality  
Phosphorus, red  
Resorcin  
Potassium permanganate  
Lead sulfate

China-pots for ointments  
Combs, hair, horn or substitute thereof  
Cutlery  
Flint-glass bottles  
X-ray plates  
Leather cloth

MACHINERY AND PLANT:  
Automatic bottle machinery  
Grinding machines for razors and pocket-knife blades  
Automatic machines for casting lead and lead alloys  
Collapsible tube-making machinery  
"Cone-paper" manufacturing machinery  
Pencil (chalk and slate) making machinery  
Marbles, porcelain  
Mineral teeth  
Mouthpieces, vulcanite for tobacco pipes  
Milk-powder  
Oils:  
Edible refined rape oil  
Linseed oil  
Pharmaceutical castor oil  
Sweet refined castor oil  
Paints, bronze blue dry color for printing inks  
Razors, safety  
Pins, safety  
Steel-spring for taking machines  
Steel, rustless for cutlery  
Stoves, oil, with 8 in. and 10 in. wicks  
Vacuum pans and pumps for making coffee extract

—M.

## SCIENTIFIC SOCIETIES

## THE DECENNIAL INDEX TO CHEMICAL ABSTRACTS

In view of the fact that the price of the Decennial Index to Chemical Abstracts to members of the American Chemical Society is to be \$12 per copy instead of \$10 to those who have not subscribed up to the end of the current year, it seems desirable once more to call attention to this index and especially to the increase in price that is soon to be made. In addition to the fact that a saving is to be accomplished by subscribing

before January 1, 1917, it is also to be noted that the decision as to the number of copies to be issued must be made early in 1917 and that this decision must be made on the basis of the number of subscriptions at hand. To delay will be to run a risk of not getting a copy. In the December 10th number of *Chemical Abstracts* there will be published a complete list of subscribers to date. If your name is not on that list and you want a copy of the index it would be well to send your order

at once to *Chemical Abstracts*, Ohio State University, Columbus, Ohio.

The above prices apply to copies bound in paper. Subscribers will be given an opportunity later to secure specially bound volumes (there will be four volumes) by paying enough extra to cover cost. Specific information regarding this will be sent to subscribers when available.

The following information regarding the nature of the index is taken from a "Preliminary Statement with Reference to the Decennial Index to *Chemical Abstracts*," which was made in a dummy that was prepared for the American Chemical Society's booth at the Second National Exposition of Chemical Industries.

"Although the collective author index will closely resemble the annual author indexes to *Chemical Abstracts*, the collective subject index has been greatly changed. The innovations have been made with the purpose of adding to the usefulness of the index and to its time-saving qualities. Special attention is called to the following features of the subject index:

(1) "It is to be a subject index in the strictest sense of the word, not an index of 'words' or of 'titles.' Subjects are being indexed from the body of abstracts as well as from their titles and the selection of subjects to be indexed (this is checked by a second and sometimes a third person, along with other checking) is made on the basis of the meaning and not of the words which happen to be used in expressing it, as is very often the case in indexing. Special efforts are being made to insure consistency and to avoid the scattering of like subjects due to the fact that the idea is differently expressed.

(2) "The entries under a given heading are to be printed in entry-a-line form with the idea considered to be the most important brought to the front of the modifying phrase; these phrases are to be alphabetized. This will result in the intimate grouping of similar subjects and will bring the most important parts of the entries into a vertical line, which should be a great help in examining a subject, especially if a particular phase of it only is being sought.

(3) "The references are to be not only to the volume and page but also to the fraction of a page (ninths) in which the subject being indexed is first considered. For example, if the reference reads 3 : 3208<sup>7</sup>, the subject is to be found in the 7th ninth of page 3208 of Volume 3. By placing the fore or the middle finger one-third of the distance from the top of the printed matter on the page and the thumb one-third of the distance from the bottom, a procedure very easily carried out, it is possible readily to estimate ninths of a page with considerable accuracy. In the above example, then, the subject indexed would be found on or just below the line opposite the thumb. This scheme is going to save a great deal of time, especially in cases in which the subject indexed has been selected from the body of an abstract and therefore cannot be located without reading down the page to the point of occurrence.

(4) "All new compounds and those for which new data are given are to be entered in the index. In order to facilitate the location of organic compounds these are to be indexed on the basis of parent compounds with a systematic order of radicals. This means that dinitrophenol and trinitrophenol, for example, will both appear in the same part of the index under the headings 'Phenol, dinitro-' and 'Phenol, trinitro-' respectively, rather than one being under 'D' and the other under 'T.' The many difficulties of such a method and the need of great care in carrying it out are thoroughly realized. The indexing of the organic section of *Chemical Abstracts* is in the hands of Dr. Austin M. Patterson, who is preëminently fitted to take care of this work and to produce a result which will be a great improvement over the ordinary type of organic subject index.

"It may be said in general of the collective index that although not all of the imperfections of the old or other known systems of indexing will be removed, the new features, which will ensure thoroughness and convenience in use, the precautions which are being taken for the sake of consistency and accuracy, and the fact that *Chemical Abstracts* itself has covered the field of chemistry with a near approach to completeness, will make it an unusually valuable compilation.

"The index will be published as soon as possible. It is desirable, however, to call attention to the fact that it is going to take a very great amount of time carefully to index, according to the scheme outlined above, the 190,000 abstracts which will have appeared at the end of 1916. In consideration of consistency, so important in indexing, and of certain other features

of indexing, the best accomplishment of which is dependent on long experience, it is considered unwise to permit certain time-consuming features of the work to be done by anyone other than the few available workers of long experience in the office of *Chemical Abstracts*, so that we desire to ask for patience as regards the appearance of the index."

OHIO STATE UNIVERSITY  
COLUMBUS, November 1, 1916

E. J. CRANE  
Editor *Chemical Abstracts*

#### ADJOURNED MEETING AMERICAN CHEMICAL SOCIETY WITH THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE, NEW YORK CITY, DECEMBER 26 TO 30, 1916

At the New York Meeting of the American Chemical Society it was voted to adjourn the meeting then being held to meet with the American Association for the Advancement of Science during Convocation Week, the week following Christmas, 1916. It was voted that the meeting be held with Section C of the American Association for the Advancement of Science in New York City. The main part of the program of the adjourned meeting will be a symposium on "Atomic Structure," in which it is hoped that Section B (Physics) will also take part. The meeting will be under the direction of the officers of Section C, of which Prof. Julius Stieglitz is chairman and Dr. John Johnston, secretary. All papers and all correspondence with reference to the meeting should be sent to Dr. John Johnston, Geophysical Laboratory, Washington, D. C.

#### RESULTS OF FURTHER COÖPERATIVE WORK ON THE DETERMINATION OF SULFUR IN PYRITES<sup>1</sup>

By H. C. MOORE

Received October 20, 1916

In the summer of 1914, after reaching the conclusion that a reasonable agreement in results of sulfur analysis reported by different laboratories, even when working on portions of the same ground sample, was quite unusual, the writer decided to investigate the cause of such discrepancies. The condition had become quite persistent and casual investigations had thrown but little light on the matter. It usually appeared that all laboratories claimed to have followed apparently practically the same details of analysis. The matter became serious, and arguments and disputes over the results of analysis submitted by the referee chemists for pyrites shipments were numerous. Allen and Johnston,<sup>2</sup> Folin,<sup>3</sup> and others had previously pointed out certain precautions which must be observed when following any modification of the Lunge Method in order that even in the hands of the same analyst, concordant results might be obtained. It was apparent, therefore, that either these precautions were not generally heeded or else other causes were also contributing to errors in analysis. The best plan to follow seemed to be that of coöperative work on carefully prepared samples. Accordingly, two samples, ground to pass 80-mesh, were carefully prepared, separately, thoroughly mixed, and sealed portions sent to a number of laboratories who expressed a desire to participate in the work. Results were received from 17 laboratories, and a complete report was presented before the Fertilizer Division at the meeting of The American Chemical Society at New Orleans, in 1915.<sup>4</sup>

Formerly, the Lunge Method, with many modifications, had been used almost without exception for the determination of sulfur in pyrites, and the same method was used by most of the laboratories participating in the aforementioned work, the results of which disclosed many sources of error, mostly

<sup>1</sup> Presented at the 53rd Meeting of the American Chemical Society, New York City, September 25 to 30, 1916.

<sup>2</sup> *J. Am. Chem. Soc.*, May 1910, June 1911; *THIS JOURNAL*, **2** (1910), 196.

<sup>3</sup> *J. Biol. Chem.*, **1** (1906), No. 273.

<sup>4</sup> *THIS JOURNAL*, **7** (1915), 643.



those pointed out by former investigators, but many of these errors were not receiving proper attention. Shortly after this work was begun, Allen and Bishop had proposed<sup>1</sup> what they claimed to be an exact method for the determination of sulfur in pyrites, and one free from the errors and defects of the Lunge Method. The results of many trials with this method by the writer and his assistants convinced us of the truth of the authors' claim. The agreement between the laboratories who used this method in the coöperative work referred to was much better than in the case of the Lunge Method.

In conversation and correspondence with quite a number of chemists there has been some criticism of this method on account of the amount of sample called for and the amount of resulting solutions to be handled, size of apparatus, etc. A modification of this method, using a smaller sample and correspondingly smaller solutions, has simplified the method and overcome the former objections until now quite a number who have adopted this method, or some similar modification, prefer it to the Lunge Method as being not only more accurate but more conveniently handled.

Following the report mentioned, the writer was appointed by the Committee on Research and Methods of Analysis (Fertilizer Division, A. C. S.) to recommend a tentative standard method for the determination of sulfur in pyrites, and report to this Committee. Before making any definite recommendations as to the details of analysis it seemed advisable to carry on further coöperative work to familiarize more of the laboratories with the Allen and Bishop Method and to bring out any defects or errors inherent in this method. It was decided to invite chemists outside the fertilizer field to participate in this work. Accordingly a letter was prepared, explaining the purpose of the further work and inviting participation. This letter was addressed to 45 laboratories, 39 of which signified their desire to participate in this work. Results have been received from 25 laboratories (not listed in the same order as results in Table I) as follows:

N. P. Pratt Laboratory,	.....	Atlanta, Ga.
International Agricultural Corp.,	C. A. Butt	Atlanta, Ga.
Virginia-Carolina Chemical Co.,	R. E. Ingham	Richmond, Va.
Selby Lead & Smelter Co.,	J. R. Marston	Selby, Calif.
F. S. Royster Guano Co.,	M. H. Coblenz	Macon, Ga.
General Chemical Co.,	W. S. Allen	Laurel Hill, N. Y.
Swift & Co.,	W. D. Richardson	Chicago, Ill.
The Hegeler Zinc Co.,	.....	Danville, Ill.
Cascayne & Co.,	.....	Baltimore, Md.
Tennessee Chemical Co.,	F. K. Wanner	Nashville, Tenn.
Planters Fertil. & Chem. Co.,	R. D. Caldwell	New Orleans, La.
Standard Oil Co.,	Harry Johnson	Bayonne, N. J.
E. I. du Pont de Nemours & Co.,	.....	Wilmington, Del.
The Grasselli Chemical Co.,	(7 laboratories)	Cleveland, Ohio
Pennsylvania Salt Mfg. Co.,	Harold Diorup	Philadelphia, Pa.
Armour & Company,	W. J. Imig	Chicago, Ill.
Armour Fertilizer Works,	V. A. Moore	Chrome, N. J.
	R. Neu	Jacksonville, Fla.
	H. M. Hutson, J. O.	Atlanta, Ga.
	Holbrook, H. C. Moore }	

Coöperation has been, therefore, quite generous. The results reported appear in Table I. The instructions accompanying the samples, which were sent out, follow:

#### INSTRUCTIONS FOR COLLABORATORS IN COÖPERATIVE WORK ON THE DETERMINATION OF SULFUR IN PYRITES

The samples for this work are marked Nos. 1, 2 and 3. Each sample represents a different kind of ore. Samples have been ground to pass an 80-mesh screen and require no further preparation.

**MOISTURE**—Determine by drying 5 g. in an oven at 100° C. for 5 hours. Sample 1 is slightly hygroscopic and if weighings are made at different times for this sample the moisture should be frequently checked.

#### SULFUR

**METHOD I (Modified Allen and Bishop Method)**—Transfer 0.5495 g. to tall form beaker (E. H. Sargent No. 581), 300 to 400 cc. capacity. Add 6 to 8 cc. of a mixture of 2 parts by volume of liquid bromine and 3 parts carbon tetrachloride. Cover beaker, and after allowing to stand for 15 minutes at room temperature, with oc-

casional shaking, add 10 cc. concentrated nitric acid. Let stand at room temperature, with occasional shaking, for 15 minutes longer. Heat below 100° C. (placing beaker on piece of asbestos on top of steam plate, if convenient), until all action has ceased and most of the bromine has been volatilized. Now place beaker on the steam plate and evaporate to dryness (evaporation is greatly hastened by raising the cover glass with one or more bent glass rods). Add 10 cc. concentrated hydrochloric acid, shake beaker carefully to mix thoroughly, and again evaporate to dryness, keeping beaker covered as before. Dehydrate silica by leaving beaker on a steam plate for 1/2 to 1 hour or in an air bath at 100° C. Moisture contents of beaker with 1 cc. concentrated hydrochloric acid followed by 50 cc. hot water and rinse down cover, riders and sides of beaker. Heat until solution is complete and after allowing to cool from 3 to 5 minutes add 0.1 gram of powdered aluminum<sup>1</sup> and shake beaker to mix thoroughly with the liquid. When reduction to ferrous iron is complete, as indicated by the color of the solution, and the latter has cooled sufficiently so that no "misting" is noted in the beaker, rinse down cover glass and sides of beaker, filter through a 11 cm. or 12 1/2 cm. filter paper (B & A grade "A," S & S No. 590, or Munktell No. 0) into an 800 cc. beaker and wash residue 9 times with hot water. Subsequent filtration is facilitated by having the excess of aluminum small. Add to filtrate 2.5 cc. concentrated hydrochloric acid and sufficient cold water to make the volume 650 cc. and stir to mix thoroughly. Precipitate sulfate by adding 50 cc. of cold 5 per cent barium chloride solution slowly and without stirring. The barium chloride solution may be conveniently added by means of a special precipitating cup designed by Allen and Bishop (made by Eimer & Amend, or Emil Greiner, both of New York) or by means of a capillary tube connected to a burette so that the solution is added in single drops at the rate of about 5 cc. per minute. After the barium chloride has been added, mix solution by stirring and let settle for 2 hrs. or preferably over night. Filter by suction through a No. 4 Gooch crucible (35 cc. capacity) having fixed perforated bottom and packed with a thick layer of asbestos. After the clear liquid has run through the filter, transfer precipitate by a stream of cold water from the wash bottle, rub inside of beaker thoroughly with a rubber policeman and after all precipitate has been transferred wash 6 times in crucible with cold water. Dry precipitate in the oven, finally heating in a moderate flame for a minute or two, then igniting to constant weight over the full flame of a Fletcher, Méker or similar burner, or in an electric furnace at about 1600° F. The weight of barium sulfate divided by 4 and multiplied by 100 gives per cent of sulfur.

**METHOD II (Modified Smoot Method)**<sup>2</sup>—Proceed as in Method I until the silica has been dehydrated. Treat residue with 25 cc. of hot water and stir until it is disintegrated, complete solution being unnecessary. By means of the wash bottle transfer solution and residue to the mercury-cathode electrolytic precipitation beaker,<sup>3</sup> and dilute to about 75 cc. with water. Connect to suitable source of current, from 0.8 to 1.0 ampere, using platinum anode and mercury cathode; cover beaker with a funnel and leave for 5 or 6 hours. A weaker current may be allowed to act over night. Iron and all other metals pass into the mercury. After the electrolytic separation is complete, wash down funnel and side of beaker and decant into a 300 cc. beaker. Pour off the liquid as closely as possible (a siphon may be used if desired). Wash beaker and mercury with 25 cc. of cold water, decant into main solution and repeat this operation 4 times. Pour the mercury into a small beaker from the "off side" of the electrolytic beaker and wash beaker out thoroughly with a stream of water from a wash bottle and add to main solution. Filter the solution into an 800 cc. beaker, rinsing beaker and washing paper and residue thoroughly with hot water. Dilute to 650 cc. with cold water, add 2.5 cc. concentrated hydrochloric acid and precipitate as in Method I.

**METHOD III**—Follow your usual method and describe briefly the details used.

In reporting results by the above methods report individual results as well as averages. To avoid confusion please report moisture, sulfur (wet basis) and sulfur (dry basis).

*Run a Blank Test to Determine the Amount of Sulfur, if Any, Present in the Reagents Used.*

#### NOTES

(1) For packing Gooch crucible, long fibered Italian asbestos which has been prepared by scraping up into lint digested with strong hydrochloric acid to remove all impurities, is especially

<sup>1</sup> Sufficient aluminum powder should be added for complete reduction but any considerable excess is to be avoided.

<sup>2</sup> For use where suitable electric current is available.

<sup>3</sup> Fig. 1, *Engineering & Mining Journal*, 94, No. 9, 412.

<sup>1</sup> 8th Intern. Congr. of Appl. Chem., 1, 33.

TABLE I—SULFUR IN PYRITES (DRY BASIS)

Anal- yst	SAMPLE 1 ALLEN & BISHOP					(a)	SAMPLE 2 ALLEN & BISHOP					(a)	SAMPLE 3 ALLEN & BISHOP					(a)
	Method	Method	Orig.	Mod.	Mod. Lunge		Method	Method	Orig.	Mod.	Mod. Lunge		Method	Method	Orig.	Mod.	Mod. Lunge	
1	53.41	II			52.91		I	II			39.25		I	II			47.60	
2	53.36				52.79		39.74				39.07		47.41				46.57	
3A	52.87				52.73		39.51				39.29		47.27				47.00	
B	52.98						39.53						47.28					
4	52.91	52.83	52.94				39.18	39.16	39.13									
5	53.00	52.94			52.95		39.76				39.67		47.42				47.30	
6	53.10				53.26		38.93x				39.71		47.60				47.49	
7	52.60								39.64									
8A	52.91	52.86	53.14				39.58	39.49					47.19	47.25	47.17			
II	53.11	52.81	53.04				39.82	39.38	39.55				47.31	47.26	47.25			
9	53.12				53.42b		39.53				39.69b		47.59				47.71b	
10					51.82							38.55					47.16	
11					52.83c						39.49c						47.41c	
12	52.74	53.57		53.34d			39.45	39.92			38.89d		46.91	47.90			47.36d	
13	52.97			53.02d			39.64				39.86d		47.32				47.39d	
14	53.27			53.16d			39.66				39.67d		47.33				47.34d	
15	52.99			52.89d			39.50				39.50d		47.13				47.12d	
16	53.32			53.09d			39.82				39.52d		47.16				47.24d	
17	53.17			53.45d			39.63				39.98d		47.65				47.69d	
18	53.02			53.06d			39.63				39.74d		47.24				47.35d	
19	53.15	52.76		52.91e			39.85	40.01			39.66e		47.21	47.11			47.48e	
20	53.14						39.54						47.89f					
21	53.14			53.10f			39.53				39.53f		47.24				47.21f	
22	52.63			52.24			39.29				38.68		47.34				46.71	
23A	53.22						39.71						47.45					
B	53.21						39.74						47.25					
24A	52.97						39.42						47.27					
B	53.04						39.54						47.27					
C	52.96						39.44						47.18					
25	53.09			53.01g							39.31g						47.31g	
No. of Anal.	28	6	4	9	10	1	25	5	4	9	10	1	24	4	3	9	10	1
Max.	53.41	53.57	53.14	53.45	53.42		39.87	40.01	39.64	39.98	39.71		47.65	47.90	47.26	47.69	47.71	
Min.	52.32	52.76	52.71	52.89	52.24		39.18	39.16	39.13	39.50	38.68		46.91	47.11	47.17	47.12	46.71	
Av.	53.01	52.96	52.96	53.11	52.87	51.82	39.60	39.59	39.46	39.67	39.31	38.55	47.32	47.38	47.23	47.35	47.14	47.16

(a) No reference made to method used.

(b) Modified Lunge Method, adding 0.3 per cent for every 50 per cent S found.

(c) Modified Lunge Method: Solution effected by adding Br water (saturated) with  $\text{HNO}_3\text{-KClO}_4$  solution, finally evaporating with  $\text{HCl}$ . Two separations of iron by adding  $\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$ , finally precipitating in a solution acid with  $\text{HCl}$ , hot with hot 7/4 per cent  $\text{BaCl}_2\cdot\text{H}_2\text{O}$  solution, boil and let settle. Filter and ignite precipitate.

(d) Usual Method. Original Allen and Bishop Method slightly modified.

(e) Modified Allen and Bishop Method: Essentially same as Method I

recommended. This asbestos is more expensive than the ordinary grade but it is far superior for preparing Gooch crucibles. It may be obtained from E. H. Sargent &amp; Co.

(2) The bromine and carbon tetrachloride should be tested and found to be free from sulfur compounds before being used. Some lots of both these reagents, marked C. P., have been found to contain considerable amounts of sulfur compounds, sufficient in the case of one lot to affect the results by several per cent. Baker and Adamson's bromine and carbon tetrachloride, both pure, and specified to be free from sulfur compounds, have been found satisfactory. A blank determination should be run in order to make the necessary corrections to results.

(3) The method of Allen and Bishop in its original details may be found among the original communications—*8th Intern. Congr. Appl. Chem.*, 1, 33 to 51, and the Method of Smoot in *The Engineering & Mining Journal*, 94, No. 9, 412.

(4) In the ignition of the precipitated barium sulfate it is advisable to observe the precaution proposed by Folin (*J. Biol. Chem.*, 1, Nos. 2 and 3, 149). To avoid mechanical loss the crucible should be provided with covers and bottoms. If porcelain Gooch crucibles are used, the cover for a platinum crucible may serve as a bottom, the crucible resting on the platinum lid supported by a triangle. The flame is applied to the platinum lid. Folin states that unless these precautions are observed, mechanical losses of barium sulfate follow.

## REMARKS

Please supplement your report on this work with your comments on the methods used and any additional pertinent remarks of interest.

It is realized that comparatively few laboratories are equipped with suitable electrolytic apparatus to carry out the details of Method II; however, it is desired that as many as possible make determinations by this method.

As no small amount of time and work is required to arrange and classify a large number of results and prepare in readable form, you are requested to make your report within 30 days.

It is noted from a study of Table I that while the results by Method I are more concordant than those by the Lunge Method, yet the agreement leaves much to be desired. The agreement of the few results reported by the original Allen and Bishop Method is very good. The agreement between results reported by miscellaneous modifications of this method are also quite good.

except after  $\text{BaSO}_4$  has been precipitated and settled is allowed to digest just before boiling for a half hour. Filtered and washed with hot water.

(f) Original Allen and Bishop Method, using half amount of sample, etc.

(g) Lunge Method, drying  $\text{BaSO}_4$  on a hot plate.(h) Lunge Method, igniting  $\text{BaSO}_4$ .

(i) Omitted from average. Evaporation made on high pressure steam plate.

(j) Omitted from average. Reported later that large blank was found on reagents used in testing this sample.

Many of those who participated in this work had had no previous experience with the Allen and Bishop Method, and it was noted from a careful study of the results in connection with the correspondence with the various collaborators with reference to their usual method and the Allen and Bishop Method that the agreement between those laboratories hitherto familiar with this method was much better. The tabulation of these results appear in Table II, and it is noted that while the average remains about the same

TABLE II—SUMMARY OF RESULTS REPORTED BY LABORATORIES HITHERTO THOROUGHLY FAMILIAR WITH THE ALLEN AND BISHOP METHOD, EITHER IN ITS ORIGINAL OR MODIFIED FORM

Anal- yst	SAMPLE No. 1			SAMPLE No. 2			SAMPLE No. 3		
	Method	Orig.	Mod.	Method	Orig.	Mod.	Method	Orig.	Mod.
	I	A & B	A & B	I	A & B	A & B	I	A & B	A & B
4	52.91	52.94		39.18	39.13				
7A	52.60	52.71			39.64				47.17
B	52.91	53.14		39.58	39.53		47.19	47.26	
12	53.11	53.04		39.82	39.55		47.31	47.25	
13	52.74		53.34	39.45		39.89	46.91		47.36
14	52.97		53.02	39.64		39.58	47.32		47.39
15	53.27		53.16	39.66		39.67	47.33		47.34
20	52.99		52.89	39.50		39.50	47.13		47.12
21	53.14			39.54					
21A	53.14		53.10	39.53		39.53	47.24		47.21
B	52.97			39.42			47.27		
C	53.04			39.54			47.27		
25	52.96			39.44			47.18		
Analyses	13	4	12	10	3	5	12	3	5
Maximum	53.27	53.14	53.34	39.82	39.64	39.89	47.33	47.26	47.39
Minimum	52.60	52.71	52.89	39.18	39.13	39.50	46.91	47.17	47.12
Average	52.98	52.96	53.11	39.53	39.46	39.63	47.22	47.23	47.28

the agreement is much closer. From further study of these results it was noted that in the case of each of the three samples, if the maximum and minimum results by Method I in Table II were discarded, that the agreement was very satisfactory indeed, and is equally as good as that by the original Allen & Bishop Method as shown below:

METHOD I—INCLUDING ONLY LABORATORIES FAMILIAR WITH ALLEN AND BISHOP METHOD AND OMITTING THE MAXIMUM AND MINIMUM RESULT IN CASE OF EACH SAMPLE

	SAMPLE 1	SAMPLE 2	SAMPLE 3
No. of Analyses	11	10	8
Maximum	53.14	39.66	47.32
Minimum	52.74	39.42	47.18
Average	52.99	39.53	47.24



Omitting the extreme results leaves the average practically unchanged. This indicates that after a little experience with the method, results by Method I should be practically identical with those found by the original method. The only modification is in the amount of sample and solutions to be handled. Table III shows the average by all methods and also compares the average of the results reported in the former work when samples Nos. 15095 and 15096 were the same as Nos. 2 and 3 in this work.

TABLE III. SULFUR IN PYRITES (DRY BASIS)

Average of all Methods (Results from Laboratory No. 10 omitted)				
METHOD	SAMPLE NO. 1	SAMPLE NO. 2	SAMPLE NO. 3	
I.....	53.01	39.60	47.32	
II.....	52.96	39.59	47.38	
Allen and Bishop, Original.....	52.96	39.46	47.23	
Miscellaneous Modifications.....	53.11	39.67	47.35	
LESSER MODIFIED.....	52.87	39.31	47.14	
Maximum.....	53.11	39.67	47.38	
Minimum(a).....	52.87	39.31	47.14	
AVERAGE.....	52.98	39.53	47.28	

(a) It is interesting to note that in each case the minimum is the average of results obtained by the Lunge Method.

SUMMARY OF RESULTS REPORTED IN COÖPERATIVE WORK, 1914-1915  
Samples No. 2 and No. 3 are the same as No. 15095 and No. 15096, respectively, as used in this former work.

For complete report see *This Journal*, 7 (1915), 643

RESULTS ON DRY BASIS	Allen & Bishop Sample 2	Method Sample 3	Modifications of Lunge Method. Sample 2	Sample 3
No. of Analyses.....	6	6	19	18
Max. per cent sulfur.....	39.59	47.87	40.00	47.88
Min. per cent sulfur.....	39.15	47.31	38.60	46.60
Average per cent sulfur.....	39.47	47.49	39.18	47.28

Under the details of analysis for Method I, one careless reference seems to have been made, where it states that the evaporation is to be made on a steam plate. Several misinterpreted this detail and understood that a steam plate carrying steam at high pressure should be used. This should have read "a steam bath," or "water bath," in which the temperature was not to exceed 100° C. Several who had used a steam plate reported results that were low, but all except one determination so affected was repeated and better results obtained.

The results of this work are encouraging, and with further practice it is believed that the Allen and Bishop Method, either as the original or as Method I, will yield very satisfactory results and be much closer to the truth than those by any other method. Method II also seems to be an excellent one, but there is no ad-

vantage of this method over that of Allen and Bishop, and it requires apparatus which many laboratories do not possess.

Causes for some of the extreme results by Method I have not been suggested except that evaporation at temperatures much above 100° C. causes loss of sulfur as sulfuric acid and also that some have found difficulty in getting bromine and especially carbon tetrachloride free from sulfur. Several have mentioned the latter difficulty and quite a number have substituted glacial acetic acid for the carbon tetrachloride since it serves the same purpose and can easily be obtained free from sulfur.

Some additional suggestions as to the details of analysis have been made. One collaborator recommends that the time of oxidation with bromine be increased from 15 minutes to 30 minutes. Several prefer to use in place of Gooch crucibles for filtering the barium sulfate the Shimer filter tube containing a perforated hard rubber dish packed with filter paper (Black Ribbon) pulp. The pad and precipitate are transferred, pad up, to a platinum crucible and finally ignited. It was also recommended that the time for drying the moisture sample be made one hour instead of five.

#### CONCLUSIONS

The following conclusions may be summarized from the work:  
I—The disagreement by the Lunge Method is about in line with past experience.

II—The agreement by the Allen and Bishop Method, either the original or modified, is much better and in the hands of analysts experienced with the method, yields results in close agreement, closer in fact than in the case of most analytical determinations.

III—The Allen and Bishop Method is recommended to all chemists as an accurate method for determination of sulfur in pyrites and apparently merits the claims of its authors that it is an accurate method.

The writer wishes to thank all those who have participated in this work and for the valuable suggestions received. He recommends that the work be continued for another year when one representative sample of commercial ore, or mixture of ores, be selected and sent out for further coöperative work.

ARMOUR FERTILIZER WORKS  
ATLANTA, GEORGIA

## NOTES AND CORRESPONDENCE

### REVISION OF OUR CHEMICAL STATISTICS

*Editor of the Journal of Industrial and Engineering Chemistry:*

I listened with much interest to the very practical suggestions made by Dr. Hesse at Rumford Hall on Friday last (Oct. 13th), relative to obtaining, through the coöperation of associations of chemists, an extension of the classifications of imports of articles concerning which the chemical industries desire more detailed information than is supplied in the tables now issued by the Department of Commerce. Admirable as Dr. Hesse's plan appears, it seemed to me that it might be worth while to point out that the preparation of a list of statistical designations satisfactory to the practical chemists, while an extremely useful contribution, would be only the first step towards any material increase in the number of titles in the official statistics of chemical imports.

Bureau chiefs in Washington will almost always welcome with enthusiasm the coöperation of technical and commercial organizations when this coöperation is intended to improve the practical value of the reports issued by their respective offices and will carry into effect any suggestions as far as may be practicable. Usually, however, these suggestions imply a material increase of service, and this means more clerks—and more appropriations.

Appropriation committees of Congress are accustomed to the ardor shown by each bureau or division chief for the development of his particular branch of the government service, and they

pare his estimates ruthlessly, unless these estimates are supported by something more than his own arguments for the usefulness of his work. Some stronger influence from outside the Department must be felt, especially when it is a question of spending money for such apparently academic work as statistics, the practical value of which is so often doubted by the public.

There must be strong assurances from some influential section that these statistics are worth while and will have a value that justifies Congress in appropriating for whatever additional clerks may be needed in the Bureau of Foreign and Domestic Commerce and the statistical divisions of the Customs branches of the Treasury Department. The statement recently printed in the trade journals that a glance at Dr. Norton's census (in proof) of dye imports was worth a million dollars to an American manufacturer of colors, would impress a committee of Congress much more than pages of recommendation from those in charge of such work in Washington. If it can be shown that new industries, or increased profits to our commerce will result from spending more money on statistics, there will be a likelihood that the appropriations will in time be forthcoming. And the place to present these arguments is before the committees of Congress rather than the Executive Departments. The latter will usually do all that is possible when the necessary resources are at hand. The time to present such arguments is also important. This is when these matters are actually under con-

sideration, as much of the effect is lost if weeks or months intervene between the filing of recommendations and the meetings of committees. It must be the duty of some one to watch for the right opportunity, with his material prepared in such form that it will carry conviction, not only from the force of the arguments presented, but also from the number and character of the individuals, firms, and associations, or societies represented.

So, too, in the event of a revision of the tariff, much can be accomplished by proper argument before a ways and means committee as to suitable and practical designations. Once a title is imbedded in a tariff law it will appear automatically in the official statistics, and this quite apart from the question of the import duty that may be fixed, or omitted, with respect to the article in question.

A. H. BALDWIN, *Former Chief*

NEW YORK CITY      Bureau of Foreign and Domestic Commerce  
October, 17, 1916

## REVISION OF OUR CHEMICAL STATISTICS

*Editor of the Journal of Industrial and Engineering Chemistry:*

The widespread interest and discussion evoked by the preliminary studies of the Committee appointed at the Seattle Meeting of the American Chemical Society, to devise practical schemes of revising the current methods of classifying and publishing the statistics of our international trade in chemicals, show that the Society has undertaken a work of pressing and far-reaching importance. The admirable studies in this connection by Dr. Bernhard C. Hesse, the Chairman of the Committee in question, are most illuminating and suggestive.

The question naturally arises whether it might not be desirable to attack the subject promptly and vigorously, along the line of least resistance. It is easily feasible to prepare in a short time, and at slight expense, a complete portrayal, in full detail, of the annual importation of chemical products into this country, under normal conditions, for a fiscal year, such as 1913-14.

During the past year the Bureau of Foreign and Domestic Commerce, Department of Commerce, recognized the imperative need of a detailed "census" of the multitude of synthetic dyestuffs imported into this country. With the cordial cooperation of the Treasury Department, such a census was taken. Its character and the method of collecting and collating the data are described, with some fullness, in *THIS JOURNAL*, 8 (1916), 1039.

The data in question covered 5,675 separate color designations, and included, in each case, the name of the foreign manufacturer, the total weight of the importation for the fiscal year 1913-14, and the invoice value of the importation.

The machinery for collecting and handling such information has been completely organized, and the period of apprenticeship with its inevitable errors and losses of time—the accomplishments of any effort in an unexplored field—belongs to the past.

Could not the same mechanism be utilized to furnish the manufacturing chemists of our country with exact data regarding the dependence of the United States upon foreign sources for the remaining chemicals, not included in the category of artificial colors?

The total number of items would certainly be less than in the case of synthetic dyestuffs. While the names of manufacturing firms are indispensable for accurate knowledge in the case of most coal-tar colors, there is rarely the same necessity in connection with other chemical products.

No mention was made of American importing firms, or consumers, in the census of dyestuffs. Such mention is equally unnecessary regarding chemicals in general.

Brief geographical indications of the countries of origin are all that the case requires.

By utilizing the existing and perfected method for ascertaining

and tabulating the facts, and at an expense of a few hundred dollars, the chemical interests of the United States can have at their service a complete exhibit of the importations, during a normal year, of all finished chemicals, and all raw or semi-manufactured material required in their production—quantity, invoice value, and country of origin being indicated.

Current appropriations are not available for the comparatively small amount needed for competent clerical assistance.

It might be desirable for the American Chemical Society, or for a group of leading manufacturers, to consider whether it would not be practicable to cooperate with the Department of Commerce in this connection, as is now done in another field, by the lumber interests of the country. The one can contribute the mechanism, and the experience; the other, the very limited amount requisite to carry out the work. The results could be printed in *THIS JOURNAL*.

Such a clear, comprehensive portrayal of conditions existing immediately prior to the European war would furnish exactly the needed data for intelligent and prompt action by American capital and chemical enterprise. It would furthermore supply the necessary statistical basis for recommendations by the Committee, to Governmental agencies connected with the publication of information regarding our foreign trade.

Such work might advantageously be extended later to a survey of our exports of chemicals for the year immediately prior to the war.

Data bearing upon the trade movement, under existing conditions, possess a relatively subordinate interest. The essential thing is to pave the way for exact, helpful, comprehensive statistics, revealing the nature of our foreign trade in chemicals, as soon as normal international exchanges are resumed.

WASHINGTON, D. C.  
November 11, 1916

THOMAS H. NORTON

## PHENOL CONDENSATION PRODUCTS

*Editor of the Journal of Industrial and Engineering Chemistry:*

In the May and June, 1916, numbers of *THIS JOURNAL* there is an interchange of letters between Dr. L. V. Redman and associates and Dr. L. H. Baekeland, bearing on the art of phenol condensation products. We have no desire to take sides in that controversy, but as Dr. Redman in initiating his correspondence gives as his reason the necessity "to preserve an accurate record of the scientific and industrial development of synthetic phenol resins," mention should be made of the achievements of the late J. W. Aylsworth to whom was granted, for inventions in this field, some 47 United States and many foreign patents, more than those of any other inventor.

Dr. Redman reviewed the work of Dr. Baekeland with relation to that of those who preceded him, pointing out in many particulars how Dr. Baekeland's work differed sometimes but little, or again unimportantly from that of others. Without going into the merits of these contentions, we would like to record our appreciation of the work that Dr. Baekeland has done as a whole in the field of phenolic condensation products. Whatever the numerous earlier inventors who have worked on the phenol-methylene reaction did, there was certainly one thing that all of them together did not do, and that was to reduce any of their inventions to a commercial possibility. Dr. Baekeland was the first to do this, and it does not detract from the value of his work that it should have been done almost simultaneously with the like advent of the work of J. W. Aylsworth.

In one instance Dr. Redman has clearly implied that he and not Dr. Baekeland was the first in the field. This reference is to the use of hexamethylenetetramine in the production of an infusible and insoluble final product and reads as follows: "but this second date of application (Dr. Baekeland's) is subse-



quent to the work which the writer did in the University of Kansas on hexamethylenetetramine, and the patent itself is granted subsequent to many of the patents issued to J. W. Aylsworth on the hardening of phenol resins with hexamethylenetetramine." On reading this, one might infer that Redman was the first, Aylsworth the second and Dr. Baekeland among the "also rans," but in order, as Dr. Redman says, "to preserve an accurate record of the scientific and industrial development" we would point out that Aylsworth's main patent involving the use of hexamethylenetetramine No. 1,202,593 was applied for February 11, 1910, whereas Dr. Redman did not conceive his invention (according to Dr. Baekeland, who was his opponent in interference) until April 29, 1910. The difference between the two dates of conception is, of course, much greater.

The only patent so far granted to Dr. Redman is No. 1,188,014 of June 20, 1916, on an application filed February 24, 1914. The only patents of Dr. Baekeland on reaction products and processes involving hexa are also later than Mr. Aylsworth's (Nos. 1,187,230 and 1,187,231 of June 13, 1916, on applications filed December 13, 1910, and December 11, 1912, respectively).

The Redman or "dry" process apparently involves reaction of hexa and phenol, which evolves ammonia, but no water. In the Redman patent No. 1,180,014, referred to above, a fusible anhydrous phenol resin is made, using hexa in place of formaldehyde, and this is later hardened by addition of more hexa (together with formalin, or alcohol and water, etc.). This process is only a variation of that described and claimed in the earlier and more inclusive Aylsworth patents No. 1,029,737 of June 18, 1912, and No. 1,020,593 of March 19, 1912, referred to above.

The Baekeland patent No. 1,187,230, referred to, describes a reaction between hexa and phenol and in proportions to produce the infusible product, under heat and pressure, a portion only of the ammonia being expelled. This seems to be a variation of the earlier Baekeland process, involving formaldehyde instead of hexa, and the chief object seems to be to produce a yellow, amber-like mass (which Aylsworth had earlier produced). The main Redman process, on which no patent has apparently been issued to date, would seem to be similar, but, according to Dr. Redman, is an entirely "dry" process. The other Baekeland patent, No. 1,187,231, is a modification, substituting a salt of hexa for the hexa, with the object of causing part of the ammonia evolved to combine with the HCl or other acid entering into the constitution of the salt of the hexa. This is a modification of the earlier Aylsworth method of rendering the ammonia harmless. (Patent No. 1,046,420, December 3, 1912, and No. 1,046,137, December 3, 1912, reissued as No. 1,353,1, February 11, 1913.)

The Aylsworth process involving the use of hexa is, as stated, earlier than those of the others, is broadly protected, and, we believe, has important advantages. According to the main Aylsworth process, a phenol resin is first prepared, in which the proportion of methylene is such that the resin is permanently fusible (unchanged when heated to 420° F. or higher). Therefore it can be heated to a high temperature for complete dehydration. It was found by Mr. Aylsworth that about 400° F. of heat is required to remove all the water, free and combined. Such dehydration of a *partial* condensation product, of the type which becomes infusible on further heating, would of course be impossible, because the mass would be hardened long before the desired temperature was attained.

To form the final fusible product, this dehydrated, fusible resin is combined with the necessary percentage of hexa (or with paraform, Aylsworth patent No. 1,102,630). One advantage of using hexa is that the reaction is anhydrous, ammonia being evolved but no water, formaldehyde or other gaseous products. No other counteracting pressure is needed; the

ammonia evolved is rendered harmless by an added substance which combines therewith (such, for example, as an organic acid anhydride, which also fixes any traces of moisture and remains as a desirable solid solvent in the final product).

Aylsworth was thus the first to form an entirely anhydrous commercial final product. This is of great advantage where high dielectric results are desired. Excellent results are obtained from the anhydrous Aylsworth condensate, on dielectric tests, while the presence of minute quantities of water, either free or combined, registers a fall in dielectric strength. The above are very practical results.

As to the question of the equivalence of formaldehyde and ammonia to hexa, it need only be said that hexa is a condensation product of formaldehyde and ammonia with the formation of water. In the Aylsworth process, the use of hexa is advantageous (in comparison with formaldehyde or a polymer thereof, plus ammonia used as a condensing agent) in that it has no tendency to cause foaming of the mass, even if an excess is used. Paraform or formaldehyde tends to escape as gas if an excess be used above the combining amount, or if the final reaction be carried on too quickly, or at too high a heat. The hexa is only decomposed as it combines with the phenol resin, the methylene radical going to the resin in exchange for some of the hydrogen of the latter, which unites with the nitrogen of the hexa to form ammonia. Likewise there is no water evolved to cause bubbling and porosity, which is the case if formaldehyde is used (unless counteracting pressure is employed, which keeps the water occluded within the mass).

In the above process, the ammonia radical is retained in the mass in unstable combination, and is not readily removed, except from thin films, unless the mass be pulverized and heated. Therefore, for many uses, the ammonia may advantageously be "fixed" as stated above, by adding substances which combine with it to form permanent constituents of the product, which are harmless, and indeed are advantageous.

As to the prior art alluded to by Dr. Redman and Dr. Baekeland, we need only say (1) that Dr. Baekeland has not claimed novelty in any of his patents, broadly, for the use of ammonia as an agent for producing infusible phenolic condensation products, but has only claimed the use of a "base serving as a condensing agent, the proportion of base in the product being less than one-fifth of the equimolecular proportion of the phenolic body used" (patent No. 942,809); (2) as to the Wetter British patent 28,009 of 1907, the patentee refers to hexa as a substitute for formaldehyde, and states that it "yields formaldehyde." It does not yield formaldehyde in the Aylsworth process, in which no acid or other condensing agent is used; here the methylene radical combines with the fusible resin, without formation of formaldehyde or evolution of water. Wetter thought of hexa only as being a yielder of formaldehyde, and did not foresee any of the advantages of hexa over formaldehyde in an anhydrous process, as first pointed out by Aylsworth.

The above is not, of course, intended as a complete presentation of the Aylsworth process involving hexa, but merely to indicate the position of Mr. Aylsworth in the art, in connection with the matters discussed by your previous correspondents. The Aylsworth patents, particularly referred to above, may be consulted for a fuller discussion for the matter in hand.

Mr. Aylsworth could never be induced to speak or write about his achievements. So strong was his dislike for publicity of that sort, that he could never be induced to read papers before the societies of which he was a member, or write "*Letters to the Editor*." He felt, and rightly so, that the record of his achievements as shown in the hundreds of valuable patents granted to him by the United States and other countries, spoke to better purpose and with better grace.

CONDENSITE COMPANY OF AMERICA  
BLOOMFIELD, NEW JERSEY  
October 26, 1916

KIRK BROWN

## ACTIVE AND LATENT SOIL ACIDITY *vs.* IMMEDIATE AND CONTINUED LIME REQUIREMENT

*Editor of the Journal of Industrial and Engineering Chemistry:*

In THIS JOURNAL, 8 (1916), 756, there appeared a letter from Mr. E. Truog, of the University of Wisconsin, in answer to a previous letter addressed to you by the undersigned. Force of circumstances has prevented an earlier reply to the letter of Mr. Truog.

The writer had no desire to institute a controversy, nor did he wish to engender any personal feeling. He did wish, however, to cite what appeared to him to be several inconsistencies in the article by Mr. Truog, in the April number of THIS JOURNAL, 8 (1916), 341. The reply by Mr. Truog attributes to the writer efforts so divergent from his real intention that, in justice to himself, it seems essential that the writer state his own position.

In Mr. Truog's reply there appeared two supplementary citations: one from Mr. F. P. Veitch, and the other from a recent article by Mr. Truog himself. Since the cited article of Veitch had not been mentioned in the previous article by Mr. Truog and since the article by Truog had not appeared in print at the time when the undersigned forwarded his communication to THIS JOURNAL, it is obvious that these two articles are not germane to the discussion and hence will be so considered.

The gist of Mr. Truog's letter is that the undersigned desired recognition or adoption by Mr. Truog of the terms *immediate* and *continued lime requirement*. This conception may have been due to the phraseology of the caption of the letter by the undersigned, or to the use of quotation marks in designating the respective terms used by the writer and Mr. Truog. The writer did not expect Mr. Truog to adopt his terminology, since such a course would be inconsistent with the belief of Mr. Truog in the permanent occurrence of true acids in the soil. Mr. Truog considered the lime requirement method of the writer in a paragraph embodying a discussion of "soil acidity determinations." But, the writer does not believe that true acids occur in soils, save for the limited occurrence of organic acids during a brief transitory stage, subsequent to such conditions as the incorporation of green manure. While wishing to have an open mind upon this question, he has not been able to find proof of the occurrence of true soil acids. In his work, cited by Mr. Truog, the writer has shown that pure  $\text{SiO}_2$  and numerous ignited siliceous substances were able to effect the decomposition of earthy carbonates, which phenomenon is assumed by Mr. Truog to be a function of true acidity only. Such a reaction must be due either to physical absorption of the basic ion with liberation of  $\text{CO}_2$ , or else it must be assumed that the exceedingly weak  $\text{SiO}_2$  and  $\text{TiO}_2$  radicals are capable of effecting decomposition of the carbonate under the influence of their mass.

In using the respective terms care was taken that the terminology should indicate, without possibility of confusion, the divergent view-points held by Mr. Truog and the writer. While we have no final tribunal to pass upon terminology, the term "*lime requirement*" is given official recognition by the Association of Official Agricultural Chemists, two referees being assigned to its study, while the term "*soil acidity*" and the supposed method for its determination have been discarded. It was intended, however, that the terminology should be considered as incident and entirely secondary to the observations, in discussing the article by Mr. Truog.

The writer had the opportunity of studying the lime-treated plats of the Pennsylvania Station in 1911 and he observed at that time an extensive and continued absorption of lime by the alkaline soil of those plats. During several years' study of lime absorption under laboratory control at the Tennessee Station he has been able to confirm the observation. In other words, the absorption of earthy carbonates continues long after alkaline reaction is attained as a result of application of calcium carbonate in excess of that required to give an alkaline reaction.

The writer believes that he was the first to chronicle such an observation. He also believes that the absorption of bases noted by Mr. Truog is the same phenomenon, though different in degree. For, as might be expected, the absorption of K ions from a strongly dissociated solution would be different from the absorption of Ca and Mg ions from the relatively insoluble carbonate.

Mr. Truog further expresses himself as being unable to understand the writer's differentiation between "*immediate*" and "*continued lime requirement*" and intimates that the latter, if existent, should be a definite and determinable quantity. The writer endeavored to emphasize the fact that one, the immediate, was quantitative under certain conditions, while the other, the continued, was progressive and indefinite in extent. In his original article giving the method for the determination of immediate lime requirement, the writer stated—"The studies further lead to the conclusion that there is a considerable difference between a soil's immediate ability to decompose  $\text{CaCO}_3$  and its propensity to continue the decomposition, when soil and an excess of  $\text{CaCO}_3$  continue in moist contact. . . . In offering the method, the differentiation is therefore made between *immediate* and *continued lime requirements* of soils." Recognizing thus the differences between the two types of absorption, the writer endeavored to develop the procedure which would effect the decomposition of maximum amount of  $\text{CaCO}_3$  under laboratory conditions, at the same time noting the fact that further long-continued contact between soil and basic carbonates would result in additional absorption of the basic ions.

Further reference to the work of the writer and his associates was made by Mr. Truog in the April number of THIS JOURNAL, as establishing the correctness of Mr. Truog's thesis as to the presence in the soil of acids of varying "avidity." The viewpoint thus advanced seemed inconsistent to the writer, and he wished to record his belief. After offering a table of data showing an apparent approximation in equivalence of basic ions absorbed from barium, calcium and sodium hydrates as demonstrating "the intervention of true chemical reactions," Mr. Truog states that the excessive absorption of magnesium reported by the writer and associates is explained by the deferred activities of a large amount of "latent acidity." He failed to note, however, that in the case of equivalent applications of  $\text{CaCO}_3$  made simultaneously, only a small fraction had been absorbed, even after nine months of contact. This marked disparity between the amounts of the two bases absorbed results from a phenomenon diametrically opposite to the one indicated by the hydrate absorption studies offered by Mr. Truog. Previously published work of the writer, together with Messrs. Willis and Hardy, has shown that soils long in contact with an excess of  $\text{CaCO}_3$  were still able to decompose a considerable amount of  $\text{MgCO}_3$ . It would seem that a year's contact between a sterile soil and an excess of  $\text{CaCO}_3$  would definitely preclude the presence of any true acidity, and that subsequent decomposition of further applications of carbonate should be attributed only to absorption.

KNOXVILLE, TENNESSEE  
November 16, 1916

W. H. MACINTIRE

## INDUSTRIAL CONFERENCES AND CHEMICAL SHOW—CORRECTIONS

In our report on pages 955 and 956, Dr. Matthewson is printed for H. W. Matheson.

On pages 961 and 962, Walter H. Dixon should read Walter H. Dickerson.

On page 967, Dr. Salisbury is printed for A. C. Stalknecht, Dr. Conrad for Dr. Conradson, Dr. Baker for C. V. Bacon; American League should read American Legion.

On page 970, Barber Asphalt Paving Company should read The Barrett Company. Also, description of the Barber Asphalt Paving Company's exhibit was entirely omitted.



### THE EXPLOSIVE CHARACTER OF MERCURY OXYCYANIDE

A fatal explosion which wrecked the interior of the building in which it occurred, took place at the plant of Powers-Weightman-Rosengarten Co., on the morning of November 21, while an employee was preparing to transfer a batch of Powdered Mercury Oxycyanide from a factory container into storage bottles.

As there were no open flames in the room and as the only

surviving witness of the explosion has stated emphatically that there was no smoking, etc., the cause of the explosion is not clear to us but we desire to publish the occurrence so that others dealing with the same article may take warning.

We might add that we never had the slightest indication of the explosive character of the material even though we have at times powdered it with a pestle in open mortars.

POWERS-WEIGHTMAN-ROSENGARTEN CO.

PHILADELPHIA, PA.

## PERSONAL NOTES

The Annual Meeting of the American Paper and Pulp Association and the Technical Association of the Pulp and Paper Industry will be held in New York, February 6 to 8, 1917, with headquarters at the Hotel Waldorf-Astoria.

The new ceramic engineering building of the University of Illinois was formally dedicated on November 20 and 21. In connection therewith an industrial conference was held, in which topics of current interest to the ceramic engineer, the clay-worker and the manufacturer will be discussed by well-known experts.

Dr. Amos W. Peters has been appointed assistant professor of bio-chemistry in the laboratories of the University of Nebraska College of Medicine, Omaha.

The eighth annual convention of the Independent Oil Men's Association was held at the Hotel La Salle, Chicago, October 18 to 20. President F. E. Van Tilburg was unanimously re-elected for the ensuing year.

The new acid phosphate plant of the Davison Chemical Company, at Baltimore, which began active operations October 14, is now working up to its normal capacity of 1000 tons of acid per day.

Mr. M. G. Kopf has opened a consulting engineering office at 602 Chemical Building, Chicago. Mr. Kopf has been chief engineer for the McCormick Laboratories at Dayton, O., chief engineer of the technical laboratories of the Automatic Electric Company and electrical engineer for the National Cash Register Company.

The Carborundum Company of Niagara Falls, N. Y., will construct a new administration building on the Niagara River front, and it is proposed to tender the use of the present offices to the Massachusetts Institute of Technology, which has decided to establish a station at Niagara Falls with the Carborundum Company.

In response to the request of the General Supply Committee of the executive departments of the Federal Government in the District of Columbia for specifications to govern the purchase of gasoline in the District, the Bureau of Mines has prepared tentative specifications and has sent copies of them to the refiners, automobile engineers, jobbers and other men prominent in the industry, for criticism, in order that the final specifications will be fair to both refiner and consumer.

Of interest to the naval stores industry is an appropriation by Congress to the U. S. Department of Agriculture of \$10,000 for "investigating the grading, weighing, handling, and transportation of naval stores, the preparation of definite type samples thereof, and for the demonstration of improved methods or processes of preparing naval stores, in cooperation with individuals and companies." With this appropriation the Bureau of Chemistry will be able to continue its investigations and undertake additional field work. A canvass of the producing area will be made and such helpful advice as the department is able to secure will be placed at the service of those interested.

Dr. Edward Hart has retired as active head of the chemical department of Lafayette College. He will, however, remain connected with the department as professor of chemical engineering and as librarian of the Henry W. Oliver Chemical Library.

Dr. Eugene C. Bingham has resigned the professorship of chemistry at Richmond College to become professor of chemistry and director of the Gayley Chemical Laboratory at Lafayette College. During last year Dr. Bingham was on leave of absence from Richmond College in order to carry out special investigations at the Bureau of Standards on the subjects of fluidity and plasticity. Dr. Eugene P. Wightman has been appointed professor of chemistry at Richmond College to succeed Professor Bingham.

Dr. J. Hunt Wilson has resigned his position at Lehigh University in order to become assistant professor of chemistry at Lafayette College.

Dr. Garnett Ryland, who was acting professor of chemistry at Richmond College last year, has returned to Georgetown College, Georgetown, Ky., after a year's leave of absence.

Dr. J. Ernest Carman, of the University of Cincinnati, has succeeded the late Prof. Charles S. Prosser, to the chair of geology at Ohio State University.

The doctorate of laws was conferred upon Thomas A. Edison over the telephone by Dr. John H. Finley, president of the University of the State of New York, on October 20. Mr. Edison was in his laboratory at Orange, N. J.; Dr. Finley was in the New York Education Building.

Walter D. Harris has resigned his position with the Bureau of Chemistry to take an active interest in the Valhalla Company, Chicago, manufacturers of electrochemical machinery.

A meeting to plan a memorial to Sir William Ramsay was held in London on October 31, after which Prof. J. Norman Collie, director of the University College Chemical Laboratories, delivered a memorial lecture on "The Scientific Work of Sir William Ramsay."

William Cooper Cuntz, general manager and director of the Goldschmidt Thermit Company, and also a director of the Goldschmidt Detinning Company, died at Auburndale, Mass., on November 2.

The new plant of the Isco Chemical Company, Niagara Falls, N. Y., completed at a cost of \$450,000, has commenced operations.

The Grace Nitrate Company has been incorporated with \$4,000,000 capital stock at Dover, Del., by L. B. Phillips, M. M. Hirona and J. B. Bailey, "to explore for caliche or nitrate and put the same on the market."

The fertilizer plant of the I. P. Thomas & Son Company, at Mantau Point, N. J., was burned recently, with a heavy loss.

The University of Chicago has received a fund to create the Edith Barnard Memorial Fellowship in Chemistry. Miss Barnard was instructor in the department of chemistry when she died and had been connected with it for ten years.

The Bayway Chemical Company, plant at Bayway, Elizabeth, N. J., has moved from 120 Broadway into its new sales office in the U. S. Express Company Building, 2 Rector Street, New York.

William Francis Hillebrand, Ph.D., chief chemist of the Bureau of Standards, Washington, D. C., gave the Chandler lecture at Columbia University, on Monday, November 27 1916, his subject being: "Analytical Chemistry and Its Possible Future." The Chandler Lecture Fund was established by former students of the University in memory of Charles Frederick Chandler, Sc.D., Mitchell Professor Emeritus of Chemistry.

Herman & Herman, Inc., Chemicals, are extending their foreign service. On November 4 one of the vice-presidents, Mr. T. Ono, sailed for Japan to open offices in that country and also to take charge of Herman & Herman's business in the Far East. His headquarters will be in Osaka. On the same day Mr. George W. Fiske, another officer of the company, sailed for South American ports. He will establish branches in Rio de Janeiro, Sao Paulo, Buenos Aires and Santiago.

The L. E. Knott Apparatus Company, of Cambridge, Mass.,

held an Exhibition of Laboratory Apparatus during Thanksgiving week, when they opened their new building. This company have discontinued handling European lines and replaced them with American-made goods; among the new lines of manufacture they have secured is the agency for Hoskins electric furnaces, hot-plates, and pyrometers for laboratory use.

L. M. Tolman and David Klein have been elected president and secretary, respectively, of Section B of the American Association of Dairy, Drug and Food Officials.

R. J. Quinn has been appointed chief chemist of Morris & Company to succeed A. Lowenstein. Mr. S. Drucker has severed his connection with the company.

R. C. Shuey has finished his work on an Armour Fellowship at the Mellon Institute, and is now on the permanent force at the Armour glue works.

The Fourth Annual Welfare and Efficiency Conference of the Commonwealth of Pennsylvania was held in the hall of the House of Representatives at Harrisburg, on November 21 to 23.

## GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

**NOTICE**—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

### DEPARTMENT OF AGRICULTURE

**Comparison of the Bacterial Count of Milk with the Sediment or Dirt Test.** H. C. CAMPBELL. Contribution from the Bureau of Animal Industry. Department Bulletin 361. 7 pp. Paper, 5 cents. Published June 29, 1916.

**Fish Meal: Its Use as a Stock and Poultry Food.** F. C. WEBER. Contributions from the Bureau of Chemistry and the Bureau of Animal Industry. Professional Paper. Department Bulletin 378. 21 pp. Paper, 5 cents. Published August 22, 1916. The object of this publication is to set forth the value of fish meal as a feed for domestic animals, in order to stimulate its more general use as a supplementary stock feed and to encourage its manufacture for that purpose.

**Present Status of Pasteurization of Milk.** S. HENRY AYERS. Department Bulletin 361. 16 pp. Reprint with slight changes. Paper, 5 cents.

The Journal of Agricultural Research, Vol. 6, includes the following three articles of chemical interest:

(1) **A Respiration Calorimeter, Partly Automatic, for the Study of Metabolic Activity of Small Magnitude.** C. F. LANGWORTHY AND R. D. MILNER. Pages 703-720.

(2) **Use of the Moisture Equivalent for the Indirect Determination of the Hygroscopic Coefficient.** FREDERICK J. ALWAY AND JOUETTE C. RUSSEL. Pages 833 to 846.

(3) **Effect on Plant Growth of Sodium Salts in the Soil.** FRANK B. HEADLEY, E. W. CURTIS AND C. S. SCOFIELD. Pages 857 to 869.

**Osage Orange Waste as Substitute for Fustic Dyewood.** F. W. KRESSMAN. Agricultural Yearbook (1915). Separate 670. 4 pp. Paper, 5 cents.

**The Preservative Treatment of Farm Timbers.** GEORGE H.

**HUNT.** Farmers' Bulletin 744. 32 pp. This bulletin is of value to all who are interested in prolonging the life of building timbers, poles, and posts, especially on farms at a distance from preservative works.

**Industrial Alcohol.** Farmers' Bulletin 420. Paper, 5 cents. This bulletin furnishes concise information regarding the source and process of manufacture of denatured alcohol.

**Composition of Food Materials.** C. F. LANGWORTHY. Revised Edition of 15 charts, each about 24 in. by 18 in., published by A. Hoen and Company, lithographers. These are for sale by the Superintendent of Documents for \$1.00 per set. The charts are as follows: (1) Milk and milk products; (2) eggs and cheese; (3) meat, fresh and cured; (4) fish, fish products, and oysters; (5) butter and other fat-yielding foods; (6) cereal grains; (7) bread and other cereal foods; (8) sugar and similar foods; (9) roots and succulent vegetables; (10) legumes and corn; (11) fresh and dried fruit; (12) fruit and fruit products; (13) nuts and nut products; (14) composition, functions, and uses of food; (15) dietary standards.

### BUREAU OF STANDARDS

**Methods of Making Electrolysis Surveys.** BURTON MCCOLLUM AND G. H. AHLBORN. Technologic Paper 28. 84 pp. This paper deals with the methods of procedure to be followed in examining underground pipes and cables, and the return systems of electric railways, in order to determine the liability of the pipes and cables to damage from stray electric currents from the railways. The various classes of electrical measurements are described and methods of procedure are outlined in some detail. The selection of instruments for making such tests is treated, and some of the more important considerations involved in the interpretation of the results of electrolysis surveys are discussed.

**Influence of Frequency of Alternating or Infrequently Reversed Current on Electrolytic Corrosion.** BURTON MCCOLLUM AND G. H. AHLBORN. Technologic Paper 72. 29 pp. The importance of the results given in this paper lies in the fact that there are large areas in practically every city in which the polarity of the underground pipes reverses with periods ranging from a few seconds to an hour or more, due to the shifting of railway loads. The investigation shows that the corrosion under such conditions is much less than has generally been supposed.



**Data on Electric Railway Track Leakage.** G. H. AHLBORN. Technologic Paper 78. 20 pp. This report is a part of the general investigation of electrolysis carried on by the Bureau of Standards, and its object is to show the leakage of electric current which may occur from street railway tracks under operating conditions. The report emphasizes the importance of maintaining as high resistance to ground as is feasible, but especially of having a high standard of rail bonding and cross bonding on all lines.

**Summary of Experiments on the Silver Voltameter at the Bureau of Standards, and Proposed Specifications.** E. B. ROSA AND G. W. VINAL. Scientific Paper 285. 36 pp.

**Calculation of Planck's Constant  $C_2$ .** J. H. DELLINGER. Scientific Paper 287. 11 pp. "The constant  $C_2$  of Planck's radiation equation has heretofore been obtained from radiation data by processes involving the use of a graph. It may be determined very simply and directly from two observations at any wave lengths and temperatures. The formula for the case of constant temperature is only slightly different from the familiar equation for equal ordinates. The method eliminates all graphical difficulties, and is less limited by experimental conditions, such as absorption bands in the air and the prism.

**Wheatstone Bridges and Some Accessory Apparatus for Resistance Thermometry.** E. F. MUELLER. Scientific Paper 288. 15 pp. "A type of Wheatstone bridge suitable for use in resistance thermometry is described, in which plugs or dial switches are used and the circuits so arranged that the errors due to contact resistances are no greater than with the mercury contact bridges heretofore used. The application of these bridges to the measurement of resistances with potential terminals is described. A convenient interchanger by means of which several thermometers may be successively measured with one bridge is also described."

**The Damping of Waves and Other Disturbances in Mercury.** M. H. STILLMAN. Scientific Paper 289. 6 pp.

**International System of Electric and Magnetic Units.** J. H. DELLINGER. Scientific Paper 292. 32 pp. This report discusses the advantages of different systems of units and the practical significance, the symbols for, and the interrelations of the units in different systems. (See also the following abstract.)

**Electrical Units and Standards.** ANONYMOUS. Circular 60. 66 pp. In this circular the systems of units are described in detail. Definitions for each, the historical significance of the units and standards, the interrelations and values of the units, and the methods of establishing standards are given elaborately.

**The Saccharimetric Normal Weight and Specific Rotation of Dextrose.** RICHARD F. JACKSON. Scientific Paper 293. 21 pp. "The purpose in view in studying dextrose was threefold. First, the purified substance was added to the list of standard samples<sup>1</sup> of this Bureau as a standard reducing sugar, in order to assist in standardizing reducing sugar analysis. It was therefore necessary that the purification and the properties of the substance should receive as thorough a study as is the case with the other standard samples. Second, the normal weight required to be determined in order that the quartz-wedge saccharimeter might become available in analyzing the substance. Third, its rotation of monochromatic light required further study."

**Freezing Point of Mercury.** R. M. WILHELM. Scientific Paper 294. 7 pp. The result of all measurements gives  $-38.873^\circ$  for the freezing temperature. The maximum deviation of any determination from the mean is  $0.005^\circ$ .

**Density and Thermal Expansion of American Petroleum Oils.** H. W. BEARCE AND E. L. PEPPER. Technologic Paper 77. 24 pp. "The work presented in this paper was undertaken for the purpose of securing data from which to calculate standard density and volumetric tables for American petroleum oils.

The data have been secured and the tables prepared and published as *Circ. 57* of this Bureau. These tables are intended to be applicable to all petroleum oils, both crude and refined, produced in the United States. They cover a density range of 0.620 to 0.950, and a temperature range of  $30^\circ$  F. to  $120^\circ$  F. In addition to these, a special table for heavy lubricating and fuel oils has been prepared with a temperature range up to  $210^\circ$  F."

This Technologic Paper describes the experimental methods and results from which these tables have been prepared.

**Properties of Some European Plastic Fire Clays.** A. V. BLEININGER AND H. G. SCHURECHT. Technologic Paper 79. 32 pp. "In the manufacture of glass pots, tank blocks, glass furnace accessories, graphite crucibles and similar refractories, a certain amount of plastic clay is required for the purpose of bonding together the grains of calcined material, ground potsherds, and previously burned fire clay, which constitute from 50 to 60 per cent of the mixture used.

"The requirements of such clays are very exacting and may be summarized as follows:

"First, they must possess sufficient refractoriness to withstand the high heat of the furnaces under the pressure of the liquid charge, without showing deformation; second, great plasticity and bonding power, making possible the cementing together of the grains of calcined material to a satisfactory compact mass; third, considerable mechanical strength and toughness, especially in the dried state; fourth, the quality of becoming dense at comparatively low temperatures in order to produce a structure impervious to the liquid glass or metal and resisting their corroding influence; fifth, the property of retaining a sound structure, free from vesicular development upon long-continued heating; sixth, the quality of resisting sudden temperature changes without checking or spalling; seventh, the property of drying and firing safely without cracking."

An investigation of these characteristics of clays is reported on and a tentative specification for such clays is recommended.

**Liquid-Measuring Pumps.** F. J. SCHLINK. Technologic Paper 81. 25 pp. This paper relates primarily to gasoline measuring pumps.

**Determination of Aluminum as Oxide.** WILLIAM BLUM. Scientific Paper No. 286. 20 pp. Paper, 10 cents. "This paper gives the results of a research to define the conditions for the determination of aluminum. From observations made with a hydrogen electrode and with suitable indicators, the conditions for the quantitative precipitation of aluminum hydroxide by ammonium hydroxide were determined. In practice the completion of precipitation may be defined by means of methyl red or of rosolic acid. The effect of various factors upon the precipitation, washing, and ignition of the precipitate was determined. The procedure for obtaining accurate results is also described."

#### BUREAU OF FOREIGN AND DOMESTIC COMMERCE

**Development of an American Linen Industry.** W. A. GRAHAM CLARK. Special Agents Series 122. 23 pp. Paper, 5 cents. This publication is a report on the investigation of the American linen industry discussing conditions of flax growing and manufacturing as affected by the problems involved in the development of the industry.

**Edible Oils in the Mediterranean District.** Special Agents Series 75. Paper, 5 cents. This report considers the edible oil industry with special reference to the cottonseed-oil industry in the United States. It also describes the markets for sale of American crushing machinery abroad.

#### FEDERAL TRADE COMMISSION

**Report on Fertilizer Industry.** Unnumbered publication. 269 pp. Paper, 50 cents. This report gives the results of an exhaustive investigation into the conditions affecting the production and sale of the principal materials which enter into the composition of fertilizers.

<sup>1</sup>Bureau of Standards, *Circ. 25*.

## BUREAU OF MINES

**Melting Aluminum Chips.** H. W. GILLET AND G. M. JAMES. Bulletin 108. 79 pp. Paper, 10 cents. "In its work on mineral wastes the Bureau of Mines is studying losses in the melting of nonferrous metals and alloys. The greatest of these losses is that of zinc through volatilization in brass melting, but another and considerable loss is that of aluminum and its alloys in the melting of finely divided material."

**The Use of Mud-Laden Fluid in Oil and Gas Wells.** JAMES O. LEWIS AND WILLIAM F. McMURRAY. Bulletin 134. 62 pp. Paper, 15 cents.

**Underground Wastes in Oil and Gas Fields and Methods of Prevention.** WILLIAM F. McMURRAY AND JAMES O. LEWIS. Technical Paper 130. 25 pp. Paper, 5 cents.

**The Nitration of Toluene.** E. J. HOFFMAN. Technical Paper 146. 24 pp. Paper, 5 cents. "This paper is the result of experiments made in the Bureau of Mines on the preparation of trinitrotoluene from toluene obtained in the manufacture of water gas. There seems to be a rather prevalent view that so-called water-gas toluene is unsuitable for the manufacture of trinitrotoluene, because of the toluene containing hydrocarbons of the aliphatic series whose removal cannot be effected by the usual methods of purification. It was in anticipation of such difficulty that the present investigation was undertaken.

"The investigation early showed that if the sample of water-gas toluene under investigation contained any aliphatic hydrocarbons they were present in negligible quantity so far as affecting nitration. Consequently, the investigation became a more general one, embracing the nitration of any good grade of toluene, and it was continued with a view not only of ascertaining the conditions under which the best yield of trinitrotoluene could be obtained from the sample in hand, but also of developing a method that might be capable of satisfactory industrial application to the nitration of any toluene of approximately the same degree of purity."

**A Method for Measuring the Viscosity of Blast-Furnace Slag at High Temperatures.** ALEXANDER L. FEILD. Technical Paper 157. 23 pp. Paper, 5 cents. "In this report is described a new method for determining the viscosity of blast-furnace slag at temperatures as high as 1600° C. The convenient application of this method has necessitated the development of a suitable electric furnace, which is described in detail. A number of viscosity measurements on slags are given for the purpose of illustrating the general application of the method."

## GEOLOGICAL SURVEY

**Lead in 1915.** General Report. C. E. SIEBENTHAL. Separate from Mineral Resources of the United States, 1915. Part I, pp. 187-205. Published September 23. The second paragraph under this heading in THIS JOURNAL, 8 (1916), 1081, should read as follows:

"The output of refined lead in the United States from domestic ores in 1915 was valued at \$47,660,000, at the average price of refined lead in New York, as compared with \$39,998,000 in 1914, a loss in quantity of 5,768 tons, about 1 per cent, and a gain in value of \$7,662,000, nearly 20 per cent."

**The Oil and Gas Geology of the Foraker Quadrangle, Osage County, Oklahoma.** K. C. HEALD. Bulletin 641-B, from Contributions to Economic Geology, 1916, Part II, pp. 17-47. Published August 21, 1916.

**Mineral Resources of Alaska. Report on Progress of Investigations in 1915.** ALFRED H. BROOKS AND OTHERS. Bulletin 642. 262 pp. and numerous plates. The statistics for Alaska's mineral production in 1914 and 1915 are given in the following table:

	QUANTITY	VALUE
Gold (fine ounces).....	807,966	\$16,702,144
Silver (fine ounces).....	1,071,782	543,393
Copper (lbs.).....	86,509,312	15,139,129
Tin (tons of metallic tin).....	102	78,846
Antimony (tons of crude ore).....	833	74,000
Lead (short tons).....	437	41,118
Coal (short tons).....	1,400	3,300
Marble, gypsum, petroleum, etc.....	.....	272,299
Total,		\$32,854,229

This bulletin includes the following five articles:

- (1) **The Alaskan Mining Industry in 1915.** A. H. BROOKS. 36 pp.
- (2) **Mining Developments in Southeastern Alaska.** THEODORE CHAPIN. 32 pp.
- (3) **Water-Power Investigations in Southeastern Alaska.** GEORGE H. CANFIELD. 23 pp.
- (4) **Mineral Resources of the Upper Chitina Valley.** F. H. MOFFIT. 8 pp.
- (5) **Mining on Prince William Sound.** B. L. JOHNSON. 9 pp.

**Bibliography of North American Geology for 1915, with Subject Index.** J. M. NICKLES. Bulletin 645. 144 pp.

**Salt, Bromine, and Calcium Chloride in 1915.** W. C. PHALEN. Separate from Mineral Resources of the United States, 1915, Part II, pp. 265-276. Published August 23. "The marketed production of salt in the United States in 1915, including Hawaii and Porto Rico, was 38,231,496 bbls.<sup>1</sup> or 5,352,409 short tons, valued at \$11,747,686, an increase of 3,426,813 bbls. or 479,753 short tons in quantity and of \$1,550,269 in value, as compared with 1914. Expressed in percentage the increase was 10 per cent in quantity and 15 per cent in value.

"The average price of salt in 1915 was \$0.31 per bbl. or \$2.19 per ton, as compared with \$0.29 per bbl. or \$2.09 per ton in 1914. During the last five years the price of salt, as well as the marketed production, has been slowly increasing.

"Bromine is made in connection with the manufacture of salt. In Michigan the bromine has been marketed in the form of fine chemicals, but the great increase in demand, brought on by the war in Europe, has caused a great deal of the bromine to be marketed as such. Along Ohio River, where there is cheap transportation by rail and water, and cheap coal and gas, and where salt and bromine occur naturally, bromine has been produced for export for many years to be made into fine chemicals. Here is an opportunity for the American chemist which should not be neglected.

"The price of bromine during the first five months of 1916 ranged from \$4.75 to \$6.50 per lb. in New York, the result in part at least of the unprecedented demand from abroad, where it is said to be used in asphyxiating gases. The comparatively low price per pound indicated in the averages is due to the fact that considerable bromine was sold at prices specified in contracts made before the demand increased and to the further fact that the figures indicate prices at the point of production, and hence do not include the cost of freight.

"These figures given in the table below do not include the output obtained in the manufacture of soda, as such calcium chloride is not an original constituent of the brine. Large quantities of calcium chloride formerly wasted in the manufacture of soda, the source of which is different from that considered in this report, are now being used in part, and it is to be hoped that new uses for what is still wasted may soon be found."

## "CALCIUM CHLORIDE SOLD IN THE UNITED STATES 1913-1915"

Year	Quantity (Short Tons)	Value
1913.....	19,611	\$130,030
1914.....	19,403	121,766
1915.....	20,535	130,830

<sup>1</sup> The barrel containing 280 lbs. and the short ton are the units of measure chiefly used in the salt industry.



**Sulfur, Pyrite, and Sulfuric Acid in 1916.** W. C. PHALEN. Separate from Mineral Resources of the United States, 1915. Part II, pp. 291-306. Published September 23. "Sulfur was produced in 1915 in Louisiana, Texas, Nevada, and Wyoming. The production in the two Western States was small, amounting to only slightly more than 1 per cent of the total output of the country. Thus more than 98 per cent came from the Union Sulphur Company, in Louisiana, and the Freeport Sulphur Company, in Texas. To avoid revealing confidential reports of output of these companies the figures for sulfur will not be tabulated, as they have been heretofore.

"Though 1915 was a prosperous year in the sulfur industry, the output was not so great as in 1914. During the early part of the year business was somewhat dull, but it improved gradually as the year advanced. Slack conditions in the paper trade account in part for the falling off. The export trade in sulfur was the lowest in some years.

"Though the imports of foreign pyrite were not so great in 1915 as in 1914, they amounted to 964,634 long tons. In spite of these large imports and of a domestic output of pyrite of 394,124 long tons (an increase as compared with 1914), there has been, especially late in 1915 and early in 1916, an increasing call for sulfur from which to make sulfuric acid, owing to the great expansion in certain branches of chemical industry, and to the fear that in some way foreign shipments of pyrite might be curtailed. The high price received for the acid has made the use of the comparatively high-priced sulfur possible, but the use of sulfur has also certain obvious advantages, owing to its purity and to the consequent fact that it leaves little or no residue. It is possible that in the manufacture of the highest grades of acid sulfur will continue to be used.

"The production of sulfuric acid in 1915, expressed in terms of 50° acid, was 3,868,152 short tons, valued at \$29,869,080, to which must be added 189,795 short tons of oleum, or fuming acid of different strengths, valued at \$2,787,971, a total of 4,057,947 short tons, valued at \$32,657,051. These figures include by-product acid; that is, acid produced at copper and zinc smelters. The production of acid from this source in 1915, expressed in terms of 50° acid, was 1,056,830 short tons, valued at \$7,042,126, together with 59,189 short tons of oleum of different strengths, valued at \$579,115."

**The Pliocene Citronelle Formation of the Gulf Coastal Plain and Its Flora.** GEORGE CHARLTON MATSON and EDWARD WILBER BERRY. Professional Paper 98-L, from Shorter Contributions to General Geology, 1916, pp. 167-208. Published September 11, 1916.

#### COMMERCE REPORTS, OCTOBER, 1916

Among important Philippine sources of **paper pulp** are bamboo (caña bojo), abaca waste, maguey waste, and numerous grasses. (P. 22.)

Two **wood-pulp** plants are to be operated on Vancouver Island. (P. 34.)

Mineral resources of Persia include **iron, lead, copper, coal, manganese, borax, salt, mercury, nickel, and cobalt.** Owing to lack of transportation none have been developed. (P. 41.)

Most of the **graphite** mined in Ceylon is now exported to the United States, at prices far above normal. (P. 42.)

A plant for the manufacture of **carbon electrodes** has been established at Sheffield, England. At present all the electrodes come from the United States. (P. 55.)

New discoveries of **gold** are reported from Tasmania. (P. 60.)

Steps toward the systematic **coking** of all coal to provide **dye stuff** materials, and the use of only coke and gas as fuels, are urged in England. A combination of all dye producers is suggested, to prevent overlapping and waste. (P. 88.)

Six **petroleum** companies are operating in Venezuela. Development has been hindered by the swampy nature of the oil fields. (P. 90.)

The British government has arranged to purchase annually 100,000 tons of **zinc concentrates** from Australia. (P. 97.)

The area of both Hevea and Ceara plantation **rubber** in India is increasing. The methods of cultivation and treatment are described. No coagulant is needed for the latex from the Ceara rubber. (P. 108.)

Production and export of **sugar** from Peru show a large increase. (P. 122.)

Galalith, a **celluloid substitute** made from casein and formaldehyde, is being manufactured extensively in Germany. (P. 123.)

Important discoveries of **petroleum** are reported in Chile near the Straits of Magellan. (P. 127.)

Two new **steel plants** are being erected in Norway, especially for the manufacture of ship plates. (P. 132.)

A company has been organized for extracting oil from **peats** containing **Kauri gums** in New Zealand. (P. 153.)

Large quantities of **sesame oil** are being extracted in Holland for use in margarine. (P. 157.)

Several varieties of **mangrove**, suitable for **tanning**, are found in Porto Rico. (P. 169.)

Additional large plants for smelting **iron and zinc ores** are being erected in Japan. (P. 212.)

The British Imperial Council of Commerce is strongly urging the adoption of the **metric system** in the British Empire. (P. 218.)

The United States Bureau of Mines and Bureau of Standards are coöperating in efforts to formulate **specifications for gasoline.** (P. 228.)

The exclusive use of the **metric system** is hereafter to be enforced in Peru. (P. 244.)

A new large **turpentine** plant has been opened in the Caucasus. (P. 255.)

Important deposits of **copper ore** (chalcopyrite), containing 29 per cent copper, have been discovered in Newfoundland. (P. 259.)

An outline of the **courses in chemistry** at the Bradford Technical College is given. (P. 275.)

Valuable deposits of **lignite** have been discovered in Sicily. (P. 321.)

Estimates place the quantity of **unmined iron ore** in Spain at 700,000,000 tons, carrying 30 per cent iron. (P. 346.)

Burmese myrabolans contain from 16 to 32 per cent **tannin**, but owing to their large content of non-tannins are inferior to the Indian myrabolans. (P. 353.)

A mill has been started in New Brunswick for the treatment of **tungsten ore.** (P. 382.)

#### SPECIAL SUPPLEMENT ISSUED IN OCTOBER

BRITISH WEST INDIES—22a and b	CHINA—52f and g
CUBA—25b	FRENCH INDO-CHINA—54a
DUTCH WEST INDIES—27a	BRITISH NORTH BORNEO—59a
ST. PIERRE—37b	AUSTRALIA—60b
BRAZIL—40d	BRITISH SOUTH AFRICA—66b
BRITISH GUIANA—44a	LIBYA—74a
BRITISH INDIA—50b	MOROCCO—75a

#### STATISTICS OF EXPORTS TO THE UNITED STATES

BRITISH WEST INDIES	DUTCH WEST INDIES—	CHINA—Sup. 52g
—Sup. 22a	Sup. 27a	Albumea
Hides	Aloes	Antimony
Asphalt	Castor beans	Bones
Balata gum	Bones	Cail nuts
Copra	Divi-divi	Hides
Divi-divi	Hides	Indigo
Gold	Mangrove	Bean oil
Mangrove bark	Fustic	Cottonseed oil
Tonca beans		Rapeseed oil
Petroleum	BRITISH GUIANA —	Soya bean oil
	Sup. 44a	Wood oil
CUBA—Sup. 25b	Balata	Vegetable tallow
Beeswax	Coconuts	BRITISH NORTH BOR-
Coconut oil	Gold	NEO—Sup. 59a
Copper ore	Sugar	Cutch (mangrove ex-
Guano		tract)
Hides	BRITISH INDIA—Sup.	Rubber
Iron ore	50b	MOROCCO—Sup. 75a
Manganese ore	Asafedita	Gum sandrac
Molasses	Bone meal	Hides
Sugar	Hides	

## BOOK REVIEWS

**The Flotation Process.** By H. A. MEGRAW. Pp. 250. McGraw-Hill Book Co., Inc., 1916. Price, \$2.50.

This is a valuable assemblage of published matter on this extremely important subject. It will be suggestive and helpful to the practical man in the mill in his efforts to meet the concrete problems of daily recovery. It is, however, a dangerous mentor from the patent point of view. Reading the book might well lead the metallurgical engineer to ignore or forget entirely numerous facts that in justice to his employer or client should receive very careful consideration.

The reader should carefully avoid what logicians call the "Fallacy of the Undistributed Middle" and distinguish between "Flotation," "Skin flotation," "Oil flotation," "Bulk oil flotation," "Frothed oil flotation" and "Air froth flotation." They are different things actually and may prove to be legally.

The Chapter II, "Patent Record of Flotation" reads like Hamlet with all reference to the "melancholy Dane" left out. Of the sixteen pages in this chapter, eight pages are devoted to the life history of Carrie Jane Billings Everson, and her U. S. Patent 348,157 of 1886 is quoted in full, with comments that imply that she originated air froth flotation. No mention whatever is made of the patents which may be decided to dominate the modern art of air froth flotation. These patents are now before the U. S. Supreme Court for adjudication after having been favorably considered by the highest courts of the British Empire and sustained in two Districts in the United States, but defeated in one Circuit, the decision of which is on appeal. Mrs. Everson was an American and a woman. But neither patriotism nor gallantry will satisfy the mine owners, should Mr. Megraw or one of his disciples lead them to install Mrs. Everson's "flotation," *i. e.*, "froth flotation," *i. e.*, "air froth flotation" with less than Mrs. Everson's minimum 6 per cent of oil; and should they find they have unwittingly trespassed on patent rights and are liable for heavy damages.

These rights are now in process of determination. If Mr. Megraw feels that Everson disclosed modern air froth flotation, he cannot be blamed for a certain shame that the metallurgists of this country should have had the patents of Everson before them for twenty years without utilizing them practically. But this is no excuse for ignoring the important legal questions pending. Personal bitterness or "an axe to grind" have been apparent in other publications, but this book pursues the policy of the ostrich and ignores the facts. The policy is clear throughout the book and clearly dangerous to its readers.

That the reviewer's caution is not ill founded may be made clear by a few brief quotations from the decisions so far handed down by the courts.

*House of Lords of Great Britain:* "Instead of relying upon the lesser specific gravity of oil in bulk they rely upon the production of a froth by means of an agitation which not only assists the process of the minute quantities of oil reaching the minute particles of metal, but forms a multitude of air cells, the buoyancy of which air cells, forming around single particles of the metal, floats them to the surface of the liquid."

*Privy Council of Great Britain:* "The real difficulty which their Lordships have to determine is whether the Respondents in the process of separation which they employ, entrap or coat and hold or carry the metallic particles in oil, using oil as the selective agent."

"Apart from any question of theory, the Respondents use oil in their process under conditions which make it almost impossible to entrap or coat and hold the metallic particles by the selective agency of oil."

"The resulting concentrate is practically free from oil and no mechanical contrivance to separate the oil from the metallic particles is required or used."

*Judge Bourquin, U. S. District Court, Montana:* "Detailed comment in respect to anticipation is little necessary, save to Froment."

"The differences hereinbefore set out between Froment's process and this in suit are so obvious, numerous, radical, and, in many respects, vital, it is clear they constitute different processes. They are different in ingredients, function of some thereof, combination, manipulation, principle and result. Their points of resemblance serve only to accentuate their difference."

"Upon all the evidence, the Court is of the opinion, the defense of lack of novelty and anticipation is not established."

"The patent is valid in respect to all claims in issue."

*Judge Bradford, U. S. District Court, Delaware:* "The first patent in suit is for what is known as an air flotation process, in which, owing to the use of a frothing agent in conjunction with such agitation of the ore pulp as will distribute the metallic particles of the ore throughout the mixture and produce bubbles of air and bring them in contact in the mixture with the metallic particles so distributed, the bubbles will become attached to such metallic particles, carrying them separate from the particles of gangue up through the surface of the mixture where they can readily be collected by skimming, overflow, or the use of other well known devices. In this process the frothing agent consists of an oil or other immiscible substance or material of an oily nature, and the bubbles and metallic particles become attached to each other through affinity between the bubbles and the metallic particles enhanced by the coating of the latter with an extremely thin film of oil."

"There was, I think, patentable invention in the discovery thus made in March, 1905. Prior to that time there had been no suggestion in the art that the proportion of 0.1 per cent of oil to ore or of any other fraction of 1 per cent of oil to ore would or might result in successful concentration."

"No one to-day understands how the use of only 0.1 per cent of oil operates to secure the mineral froth of the first patent in suit. This is testified to by the experts and is admitted on both sides. If the principle of operation of the discovery is insolvable to the human mind to-day it could not have been predicted or anticipated by the human mind in March, 1905."

"The reduction of the oil to this quantity effected a change, not merely in the degree, but in the 'type of oiling,' leading to results which cannot be accounted for on the assumption that a mere change in degree as distinguished from patentable discovery was involved."

"The defendant contends that since its abandonment of its original infringing process at Miami above referred to, it had not and does not infringe the first patent in suit, for the reason that it does not in its process produce the coherent and permanent froth of the process of that patent but both are mineral froths, and that of the defendant is sufficiently permanent to effect through air flotation an efficient separation of the metallic particles from the rest of the mixture."

"Coherency and permanency in a froth admit of degrees, and such a degree as insures by air flotation an efficient and final separation between the metal and the gangue, whatever may be the duration of the froth, comes within the process of the first patent in suit."

"There is no room for doubt that agitation of the mixture in the process of the defendant is sufficiently vigorous or brisk to insure efficient ore concentration by an air flotation process such as is accomplished by the complainant by agitation under the process of the first patent in suit."



"In order that the bubbles in the pulp mixture may come in contact with the metallic particles there must be such movement between them as cannot be wholly accounted for by selectivity as between them, and their movement so far as not accounted for by selectivity is the result of agitation; and whether such agitation results from the stirring or beating of the mixture or the forcing or admission of air into it is immaterial; for what this court is dealing with is not an apparatus patent but a process patent."

"There is no escape, I think, from the conclusion, not only that the defendant infringed the first patent in suit by carrying on the process of ore concentration in its first installation at Miami in apparatus in imitation of the plaintiff's standard machine, but also has infringed and is infringing the same patent by carrying on the process of ore concentration in its pneumatic flotation plant at the same place." [Callow cells.]

"The novelty of this invention is to be found, not in any restriction of the amount of the mineral frothing agent to any stated proportion, for there is none, but in the fact that a mineral frothing agent as the means of separating the metallic particles from the gangue is substituted for the oil, fatty acid or other oily substance essential to the process of the first patent in suit. Such substitution has produced successful results, and, I think, involved invention. Frothing agents had hitherto been used in ore concentration, but not in the absence of an oily ingredient. Even were the grounds on which the validity of the patent can be sustained less clear, it should have the benefit of the presumption of validity arising from the grant of letters. That the defendant has infringed the claims in suit of the second patent is established by the evidence."

For reasons not convincingly stated in the decision, the Circuit Court of Appeals in San Francisco reversed Judge Bourquin's decision, and the Supreme Court has seen fit to reconsider this reversal. Final decision rests with them but no conscientious writer on flotation can afford to ignore the existence of the patents.

W. M. GROSVENOR

**The American Petroleum Industry.** By RAYMOND FOSS BACON, Director of the Mellon Institute of Industrial Research of the University of Pittsburgh, and WILLIAM ALLEN HAMOR, Assistant to the Director of the Mellon Institute of Industrial Research. 2 vols. 963 pp. McGraw-Hill Book Co., New York, and Hill Publishing Co., Ltd., London. Price per set, \$10.00.

No important publication has appeared on the petroleum industry from the point of view of American practice since the comprehensive report by Peckham in 1884 to the Federal Government. Much is included in the large works of Boverton Redwood, and Engler and Hoefler. In the preparation of "Erdol" Dr. Engler was quite desirous that it should contain a thorough review of American methods. In view of the great expansion in oil territory within recent years, improvements in refining, and the larger use of motor fuel oils and lubricants, perhaps it is fortunate that a clear field is open for the reception of an inclusive treatment of this great industry from Nature's storehouse of the crude oil to the finished products. In recognition of this need the authors evidently intended to present a complete account of the technology of crude oil and the preparation from it of commercial products. As mentioned in the preface, the particular objects in view were to provide a basis for systematic instruction in petroleum engineering for which there has recently been an increasing demand, and practical information to prospectors, refiners, and others in any manner interested in the technological features of this industry.

With the thorough review by Redwood before us, and especially of all petroleum literature by Engler in "Erdol," the brief sum-

mary of the composition of petroleum and the theories of its formation in the first chapter seem to be all sufficient. As an assurance of reliability the chapter on the geology of petroleum and others on its technology were written by specialists and experts eminent in the petroleum industry. The large chapter on the physical and chemical properties of petroleum and its products includes what is known concerning specific gravity, viscosity, refractivity, coefficient of expansion, boiling points, specific heat, and calorific values. It contains also the most complete data that has ever been published on representative specimens of California, Mid-Continental and Appalachian oil territory, the results of an investigation by the Federal Bureau of Mines. Since this data has come into the literature, it should be mentioned that sulfur is more widely distributed in petroleum than these results indicate; it may be that part of the blanks in this column indicate that sulfur was not determined.

In Chapter V, illustrated with portraits of the pioneers of the American industry, cuts of the early fields and machinery of refining, transportation, statistics of production from the beginning to the year 1915, and data of the great corporations with their capitalization, readers of economic history will find much food for serious thought. It is a most impressive example of the great business expansion in this country during the last half century.

Large space is devoted to oil-well technology and refinery technology with minute details of operation, and profusely illustrated with cuts and drawings. The cracking processes for gasoline and kerosene receive adequate attention as well as special features of refining, such as the Edelenau sulfur dioxide process, the use of Fuller's earth, desulfurization, and the artificial production of asphalt. Probably the chief attraction in this work to the business man and the petroleum engineer is the 136 pages in Chapter XIV devoted to refinery engineering. Specifications and plans with measurements in detail are here presented for the construction of a refinery in Pennsylvania and another in Kansas as an illustration of Eastern and Western practice. There are full descriptive designs of crude and steam stills, agitators, condenser boxes, tanks, earth reservoirs, and of a complete paraffin plant.

Workers in the petroleum industry should acquaint themselves with the hygienic considerations, effects of petroleum and its products on the health, forms of attack and protection described in Chapter XV. With ordinary care and protection it appears that they are not readily affected under the usual conditions of operation. The chapter on the shale oil industry will be of interest to those who see opportunities for its expansion here. Its development in Scotland is fully described and illustrated with cuts of plant and appliances; the principal products are defined with cost of production and profits. Those who feel that research on petroleum has been altogether too superficial, and who appreciate the need of broader fundamental study on a comprehensive plan will appreciate the suggestions in the chapter on "Some Problems of the Petroleum Industry." The writer is convinced, as he has elsewhere often stated, that the most important problem in the petroleum industry is the ultimate composition of the numerous varieties which can be ascertained only by thoroughgoing research on a refinery magnitude. In all metallurgical processes the first step is to ascertain the precise composition of the ore, the essential and the non-essential constituents, and the impurities to be eliminated. But in the technology of petroleum no heed is given to its ultimate composition. Crude oils from entirely different sources are run together in the refinery without regard to the proportions of the different series of hydrocarbons of which they are composed. The work closes with 80 pages devoted to "A Glossary of Bituminology" which gives definitions and brief descriptions of the constituents of petroleum and its products.

In the general plan and scope of this work it seems difficult

to suggest an improvement. The evident care in its preparation, the statements supported by numerous citations from petroleum literature, and the coöperation of practical experts, are the best assurance of its accuracy. The searching criticism of the classroom and the use of the working plans in the refinery will reveal any errors of omission or commission. A companion work is much to be desired on motor fuel oils, lubricants and lubrication based upon thorough experimental study.

CHARLES F. MABERY

**Manuring for Higher Crop Production.** By E. J. RUSSELL, Director of the Rothamsted Experiment Station. Cambridge, England: University Press, 1916. New York Representative: C. P. Putnam's Sons. Price, \$0.90.

The author states in the preface that he has collected information about manures and soil management which he hopes will prove helpful to farmers in drawing up their schemes for cropping. Conditions are changing so quickly, and labor and transport difficulties react in such complex ways, that no general advice could hold good all round. All farmers ought to increase the produce of their land, and most of them are trying to do so. He has aimed at giving them facts from which they can draw conclusions suited to their own conditions and bearing on their own problems.

The book contains only 69 pages with 16 illustrations and is divided into five chapters. Chapter I is devoted to the improvement of the soil, including cultivation, liming and green manuring; Chapter II treats of farmyard manures, including methods of handling, time of application, composition and results of field tests; Chapter III is devoted to artificial manures, giving brief descriptions of different materials used and their uses; Chapter IV gives recommendations for manuring of arable land for different crops; and Chapter V deals wholly with manuring of grass lands.

The author's opportunities of observation at Rothamsted and his wide experience afford him unusual facilities for presenting reliable and accurate data concerning matters pertaining to the cultivation and fertilization of the soil, and for the system of farming practiced in England, this book will undoubtedly prove of considerable value to agriculturalists. The recommendations are made wholly from experience gained in the British Isles and are not altogether applicable in other localities, although the general principles laid down are of universal application.

F. B. CARPENTER

**Catalysis and Its Industrial Applications.** By E. JOBLING, A.R.C. Sc., B.Sc., F.C.S. 120 pp. P. Blakiston's Son & Company, Philadelphia. Price, \$1.00.

This publication, which is a compact volume of scarcely over a hundred pages of reading matter, provides a convenient review of the more important catalytic processes. The book is made up of eight chapters discussing the following subjects: sulfuric acid manufacture, chamber and contact process; industrial chlorine, salt cake and sulfur recovery; fixation of atmospheric nitrogen; surface combustion; hydrogenation; dehydrogenation and oxidation; dehydration and hydrolysis.

Chapter I is devoted to a general discussion of the phenomena of catalytic action, the effect of inhibiting bodies or catalyzer poisons, the specific activity of catalysts, etc. In the latter case it is noted that "no general method is available by which guidance is offered in the selection of a suitable catalyst for a given reaction." \* \* \* Occasionally the discovery of such a body is a matter of accident or good fortune, as in the case of the manufacture of artificial indigo, where the accidental breakage of a thermometer liberated the catalyst which rendered practicable the most obstinate reaction of the process."

The chapter on sulfuric acid manufacture gives in a very con-

cise form the conditions of operation of the contact process employing platinum as a contact material and useful curves of yield with temperature, etc., are included. The catalytic action of ferric oxide also is considered.

An interesting review of the subject of nitrogen fixation is provided. This treatment embraces the oxidation of air-nitrogen by the processes of Birkeland and Eyde, Schönherr and Pauling, Serpek's process, and the direct synthesis of ammonia from its elements. The oxidation of ammonia by air to nitric acid in the presence of a platinum catalyst is briefly but well treated.

The discussion of surface combustion embraces the more important features of this process, most of the data evidently being taken from the writings of Bone. Jobling is inclined to favor the work of the British inventors, Bone and McCourt, in this field. He states "The revolution in gaseous heating" effected by surface combustion, "is largely due to the investigations of Bone and McCourt." He adds "It is only fair, however, to record that the process and, indeed, several of the small forms of apparatus, had already been patented in the U. S. A. by Lucke; but the British inventors are undoubtedly answerable for the extension and development of the method and the design of apparatus capable of establishment on an engineering basis."

The effect of additions of ceria to thoria to increase luminosity is noted under "Incandescent Gas Mantles."

The subject of hydrogenation is very neatly considered and the various ramifications of this catalytic process are touched upon. In discussing the hydrogenation of fatty oils, Jobling refers to the various applications of hardened oils and states: "There is nowadays the possibility of their utilization as edible fats. As to the likeliness of this latter application, it is difficult to give any definite opinion, for experts are at present investigating the question of contamination with the finely-divided nickel employed." In view of the extensive use in this country for a considerable period, of hardened cottonseed oil as an edible fat, this remark by Jobling is perhaps somewhat misleading.

He refers to the application on the large scale of the hydrogenation process in England and Germany but does not mention the important developments which have taken place in this country in this connection.

The book makes no pretenses at completeness. Jobling states that "The outbreak of the war and the fact that the author accepted a commission in his Majesty's forces has made it impossible to add certain details as originally intended." To one who is unfamiliar with the elementary principles of catalysis and of the more important applications of catalytic agents, this volume is most useful. The treatment is simple and the style clear, especially adapting the book to the requirements of those who seek for an insight into technical methods of catalysis, without the necessity of extensive study.

CARLETON ELLIS

**An Introduction to the Physics and Chemistry of Colloids.**

By EMIL HATSCHEK. Second Edition. 107 pp. with 17 illustrations. P. Blakiston's Son & Co., Philadelphia. Price, \$1.00.

The first edition of this book was reviewed in the *Journal of the American Chemical Society*, 35 (1913), 841. The main change which has been made in the new edition is the addition of a chapter on experimental technique. As a whole the book retains its character as one of the most readable and satisfactory introductions to the subject of colloids. For a small book, the amount of ground covered is surprising, practically all the important questions in colloidal chemistry and physics being touched upon, although naturally a complete treatment is impossible.

K. G. FALK



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## INORGANIC CHEMICALS

Acetate of Lime.....	100 Lbs.	3.40	@	3.50
Alum, lump ammonia.....	100 Lbs.	4.00	@	4.25
Aluminum Sulfate, high-grade.....	Ton	70.00	@	90.00
Ammonium Carbonate, domestic.....	Lb.	10	@	10 1/4
Ammonium Chloride, gray.....	Lb.	9 1/2	@	10
Aqua Ammonium, 26°, drums.....	Lb	5 1/2	@	6
Arsenic, white.....	Lb.	6	@	6 1/4
Barium Chloride.....	Ton	95.00	@	100.00
Barium Nitrate.....	Lb.	11	@	12
Barytes, prime white, foreign.....	Ton	—	@	—
Bleaching Powder, 35 per cent.....	100 Lbs.	4 1/4	@	4 1/2
Blue Vitriol.....	Lb.	11 1/2	@	12 1/4
Borax, crystals, in bags.....	Lb.	8	@	8 1/4
Boric Acid, powdered crystals.....	Lb.	12	@	12 1/2
Brimstone, crude, domestic.....	Long Ton	35.00		
Bromine, technical, bulk.....	Lb.	1.40	@	1.50
Calcium Chloride, lump, 70 to 75% fused.....	Ton	26.00	@	28.00
Calcium Chloride, granulated.....	Ton	40.00	@	—
Caustic Soda, 76 per cent.....	Lb.	4 1/4	@	4 3/4
Chalk, light precipitated.....	Lb.	4 1/2	@	—
China Clay, imported.....	Ton	18.00	@	30.00
Feldspar.....	Ton	8.00	@	15.00
Fuller's Earth, foreign, powdered.....	Ton	\$35.00		
Glauber's Salt, in bbls.....	100 Lbs.	55	@	60
Green Vitriol, bulk.....	100 Lbs.	1.00	@	1.05
Hydrochloric Acid, commercial, 18°.....	Lb.	1 1/4	@	1 1/2
Hydrochloric Acid, C. P., conc., 22°.....	100 Lbs.	1 1/2	@	1 3/4
Iodine, resublimed.....	Lb.	4.25	@	4.30
Lead Acetate, white crystals.....	Lb.	13	@	13 1/2
Lead Nitrate.....	Lb.	15 1/2	@	16
Litharge, American.....	Lb.	9 1/4	@	9 1/2
Lithium Carbonate.....	Lb.	1.02	@	1.05
Magnesium Carbonate.....	Lb.	21	@	22
Magnesite, "Calcined".....	Ton	—	@	—
Nitric Acid, 36°.....	Lb.	4 1/8	@	4 1/4
Nitric Acid 42°.....	Lb.	5 1/2	@	6
Phosphoric Acid, sp. gr. 1.750.....	Lb.	38	@	39
Phosphorus yellow.....	Lb.	95	@	1.10
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, casks.....	Lb.	39	@	40
Potassium Bromide (granular).....	100 Lbs.	1.30	@	1.35
Potassium Carbonate, calcined, 80 @ 85%.....	Lb.	50	@	55
Potassium Chlorate, crystals, spot.....	Lb.	62	@	64
Potassium Cyanide, bulk, 98-99 per cent.....	Mixture	80	@	85
Potassium Hydroxide.....	Lb.	80	@	85
Potassium Iodide, bulk.....	Lb.	3.45	@	—
Potassium Nitrate.....	Lb.	29	@	30
Potassium Permanganate, bulk.....	Lb.	2.65	@	2.80
Quicksilver, flask, 75 lbs.....	Lb.	\$80.00		
Red Lead, American, dry.....	Lb.	9 1/2	@	9 1/4
Salt Cake, glass makers'.....	Ton	13.00	@	14.00
Silver Nitrate.....	Oz.	44 1/8	@	—
Soapstone in bags.....	Ton	8.00	@	12.00
Soda Ash, 58°.....	100 Lbs.	3.00	@	3.05
Sodium Acetate.....	Lb.	11	@	12
Sodium Bicarbonate, domestic.....	100 Lbs.	1.65	@	—
Sodium Bicarbonate, English.....	Lb.	3 1/2	@	3 1/4
Sodium Bichromate.....	Lb.	20	@	21
Sodium Chlorate.....	Lb.	25	@	27
Sodium Fluoride, commercial.....	Lb.	—	@	—
Sodium Hyposulfite.....	100 Lbs.	1.25	@	1.30
Sodium Nitrate, 95 per cent, spot.....	100 Lbs.	2.95	@	3.00
Sodium Silicate, liquid.....	100 Lbs.	1.50	@	3.40
Sodium Sulfide, 30%, crystals, in bbls.....	Lb.	2	@	2 1/4
Sodium Bisulfide, powdered.....	Lb.	5 1/2	@	5 1/4
Strontium Nitrate.....	Lb.	30	@	32
Sulfur, flowers, sublimed.....	100 Lbs.	2.30	@	2.70
Sulfur, roll.....	100 Lbs.	2.00	@	2.25
Sulfuric Acid, chamber, 66° Be.....	Ton	23.00	@	25.00
Sulfuric Acid, oleum (fuming).....	Ton	35.00	@	40.00
Talc, American white.....	Ton	9.00	@	12.00
Terra Alba, American, No. 1.....	100 Lbs.	75	@	80
Tin Bichloride, 50°.....	Lb.	13 1/2	@	14
Tin Oxide.....	Lb.	46	@	49
White Lead, American, dry.....	Lb.	8 3/4	@	—
Zinc Carbonate.....	Lb.	24	@	26
Zinc Chloride, commercial.....	Lb.	13 1/4	@	15
Zinc Oxide, American process XX.....	Lb.	9 1/2	@	9 1/4
Zinc Sulfate.....	Lb.	6 1/4	@	7 1/4

## ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.....	Lb.	48	@	50
Acetic Acid, 56 per cent, in bbls.....	Lb.	6	@	6 1/2
Acetic Acid, glacial, 99 1/4%, in carboys.....	Lb.	15	@	17
Acetone, drums.....	Lb.	21	@	22
Alcohol, denatured, 180 proof.....	Gal.	62	@	65
Alcohol, grain, 188 proof.....	Gal.	2.70	@	2.72

Alcohol, wood, 95 per cent, refined.....	Gal.	80	@	85
Amyl Acetate.....	Gal.	4.00	@	4.25
Aniline Oil.....	Lb.	22	@	25
Benzoic Acid, ex-toluol.....	Lb.	9.50	@	10.50
Benzol, 90 per cent.....	Gal.	57 1/2	@	60
Camphor, refined in bulk, bbls.....	Lb.	80	@	81
Carbolic Acid, U. S. P., crystals, drums.....	Lb.	53	@	55
Carbou Bisulfide.....	Lb.	6 1/2	@	7
Carbon Tetrachloride, drums, 100 gals.....	Lb.	16	@	17
Chloroform.....	Lb.	50	@	51
Citric Acid, domestic, crystals.....	Lb.	67	@	68
Cresol, U. S. P.....	Gal.	1.25	@	1.30
Dextrine, corn (carloads, bags).....	100 Lbs.	3.95	@	4.00
Dextrine, imported potato.....	Lb.	11 1/2	@	12
Ether, U. S. P., 1900.....	Lb.	15	@	20
Formaldehyde, 40 per cent.....	Lb.	10 1/4	@	11
Glycerine, dynamite, drums included.....	Lb.	50	@	51
Oxalic Acid, in casks.....	Lb.	55	@	57
Pyrogallie Acid, resublimed bulk.....	Lb.	3.25	@	—
Salicylic Acid.....	Lb.	1.20	@	1.25
Starch, cassava.....	Lb.	—	@	—
Starch, corn (carloads, bags) pearl.....	100 Lbs.	2.85	@	—
Starch, potato.....	Lb.	7 1/2	@	8 1/2
Starch, rice.....	Lb.	8 1/2	@	9 1/2
Flour, sago.....	Lb.	4 1/4	@	5
Starch, wheat.....	Lb.	7 1/2	@	8 1/4
Tannic Acid, commercial.....	Lb.	65	@	75
Tartaric Acid, crystals.....	Lb.	67	@	69

## OILS, WAXES, ETC.

Beeswax, pure, white.....	Lb.	40	@	45
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2	@	—
Castor Oil, No. 3.....	Lb.	13 1/2	@	—
Ceresin, yellow.....	Lb.	10	@	12
Corn Oil, crude.....	100 Lbs.	\$12.25		
Cottonseed Oil, crude, f. o. b. mill.....	Gal.	86	@	90
Cottonseed Oil, p. s. y.....	Lb.	12 3/4	@	14
Creosote, beechwood.....	Lb.	2.20	@	2.25
Cylinder Oil, light, filtered.....	Gal.	21	@	26
Fusel Oil, crude.....	Gal.	3.75	@	4.00
Japan Wax.....	Lb.	14 1/2	@	15
Lard Oil, prime winter.....	Gal.	1.30	@	1.32
Linseed Oil, raw (car lots).....	Gal.	97	@	98
Menhaden Oil, crude (southern).....	Gal.	64	@	65
Neat's-foot Oil, 20°.....	Gal.	1.20	@	1.25
Paraffine, crude, 120 m. p.....	Lb.	5 1/4	@	5 1/2
Paraffine Oil, high viscosity.....	Gal.	29 1/2	@	30
Rosin, "F" Grade, 280 lbs.....	Bbl.	6.80	@	—
Rosin Oil, first run.....	Gal.	38	@	—
Shellac, T. N.....	Lb.	34	@	34 1/2
Spermaceti, cake.....	Lb.	25	@	30
Sperm Oil, bleached winter, 38°.....	Gal.	80	@	82
Spindle Oil, No. 200.....	Gal.	24	@	25
Stearic Acid, double-pressed.....	Lb.	14 1/2	@	14 3/4
Tallow, acidless.....	Gal.	1.05	@	1.06
Tar Oil, distilled.....	Gal.	35	@	40
Turpentine, spirits of.....	Gal.	49 1/2	@	—

## METALS

Aluminum, No. 1, ingots.....	Lb.	65	@	66
Antimony, ordinary.....	Lb.	13	@	13 1/4
Bismuth, N. Y.....	Lb.	3.05	@	3.10
Copper, electrolytic.....	Lb.	33	@	—
Copper, lake.....	Lb.	33	@	—
Lead, N. Y.....	100 Lbs.	7.03	@	7.05
Nickel, electrolytic.....	Lb.	45	@	—
Platinum, refined.....	Oz.	105.00	@	—
Silver.....	Oz.	71 1/4	@	—
Tin.....	Lb.	44 1/2	@	—
Tungsten (WO <sub>3</sub> ).....	Per Unit	17.00	@	18.00
Zinc, N. Y.....	100 Lbs.	11.25	@	11.50

## FERTILIZER MATERIALS

Ammonium Sulfate.....	100 Lbs.	4.20	@	4.25
Blood, dried F O B Chicago.....	Unit	3.50	@	—
Bone, 4 1/4 and 50, ground, raw.....	Ton	35.00	@	—
Calcium Cyanamid.....	Unit of Ammonia	2.75	@	—
Calcium Nitrate, Norwegian.....	100 Lbs.	—	@	—
Castor Meal.....	Unit	—	@	—
Fish Scrap, domestic, dried, f. o. b. works.....	Unit	4.25	@	10
Phosphate, acid 16%.....	Ton	11.25	@	11.80
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	2.75	@	3.00
Tennessee, 78-80 per cent.....	Ton	5.00	@	5.50
Potassium "muriate," basis 80 per cent.....	Ton	450.00	@	475.00
Pyrites, furnace size, imported.....	Unit	16	@	—
Tankage, high grade; f. o. b. Chicago.....	Unit	3.75	@	13



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